Review

Low-Temperature-Solid Combustion Technology of Biomass for Pollution Reduction: Potentials and Necessary Fundamentals

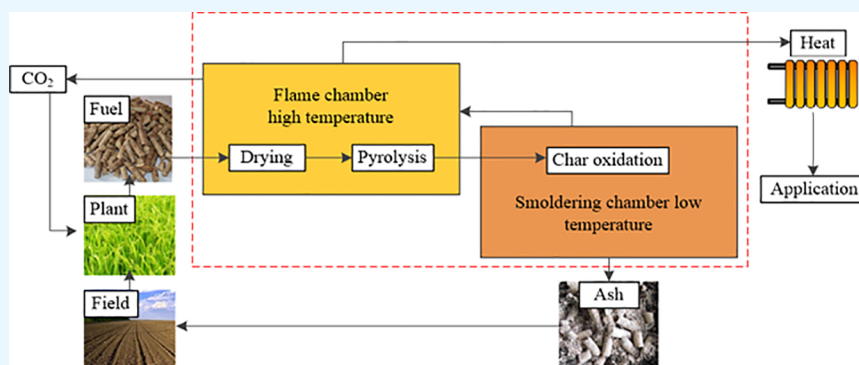Xiuhua Li, Xiaowei Wang,* Hailiang Wang, and Fang He

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ABSTRACT: The high temperature of solid combustion in modern combustors leads to serious pollution in the combustion of biomass and solid wastes. The broad demands of relatively small-scale combustion of solid fuels and the imposition of increasingly strict emission limits require more economical methods for pollution reduction. Based on literature and our own work, low-temperature-solid combustion technology, which applies low temperature for solids but normal temperature for gas during combustion, was introduced in this paper. The potential of this technology in pollution reduction was analyzed, and necessary fundamentals for equipment design/operation were discussed. It showed that, for straws, more than 60% of deposit and particle emission can be reduced and 100% of ash can be recycled when the solid temperature is <600 °C. Fundamentals on rates of inorganic release, char oxidation, phase transformation in the condensed phase, and NOx/SOx release are necessary for better application of the technology.

1. INTRODUCTION

Combustion of biomass[1,2] and solid wastes[3,4] is of increasing importance nowadays. The combustion systems are relatively small compared to those of power plants due to the high transportation/storage fee for a large amount of fuel (such as biomass),[5,6] the limited yield of waste from one or several factories, and/or the small capacity requirement of application.[7] The small-scale apparatus using solid fuels also applies broadly in industrial processes.

In many solid fuels,[8,9] besides the main elements (C, H, and O), there are nonmetal elements (N, Cl, and S), ash-forming elements (Al, Ca, Fe, K, Mg, Na, P, Si, and Ti), volatile minor elements (As, Cd, Hg, Pb, and Zn), and nonvolatile minor elements (Ba, Co, Cr, Cu, Mo, Mn, and V). During combustion, the possible pollution includes emissions (smoke and unburned hydrocarbons, NOx, SOx, Cl compounds, metal aerosols, Hg, As, and Se)[10,11] in flue gas, fouling (on the inner wall or heat exchanger surface) in the combustor,[12] and discharge of solid waste (fly ash and bottom ash).[13]

Pollution control technology in combustion systems appeared with the imposition of environmental protection laws (1955 in USA and 1964 in Germany)[14] and has greatly improved in the last several decades to comply with increasingly stringent regulations. Of the three control techniques for solid fuels, namely, precombustion, combustion, and postcombustion, most emphasis has been placed on postcombustion control. These techniques consist of gas treatments (gas cleaning to remove fly ashes, wet/dry neutralization of acid gases, selective catalytic reduction of NOx, filtration of small particles, adsorption of mercury/volatile organic compounds/dioxins, etc.[14]), fouling treatments (soot blowing, steam consumption, etc.),[15] and ash disposal
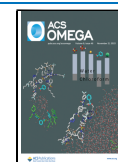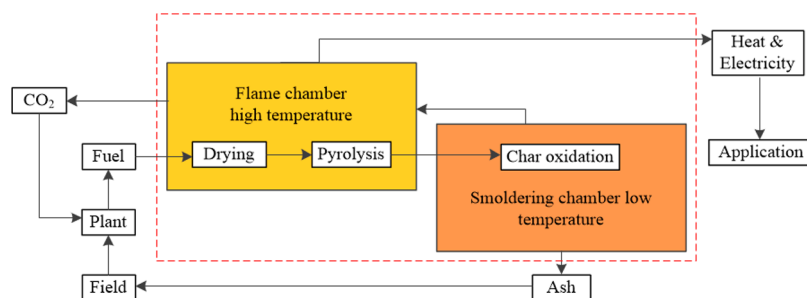
Figure 1. Low-temperature solid combustion technology of biomass with its input and output.
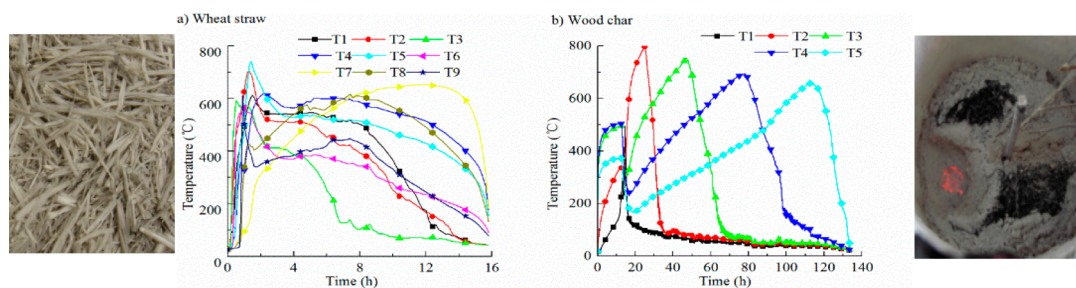

Figure 2. Smoldering experiments of agrostalks and wood char. Adapted from ref 46. Copyright Elsevier 2011. Adapted from ref . Copyright Elseview 2014. Adapted from ref 48. Copyright 2007 ETA Florence Renewable Energies.

(landfilling, cement utilization, etc.[16]). Some investigations have also been performed on precombustion control techniques,[17] such as water washing of material,[18,19] torrefaction,[20] and the addition of zeolite/Kaolin/peat.[21,22] Compared with this, only a few studies have been done on combustion control techniques,[23,24] such as stage combustion[25,26] and firebed cooling.[27]

The investment and operation expenses of most post- and precombustion controls are very high, which is not economical for small- or medium-scale utilization. More economical solutions are urgently needed because of increasingly stringent pollution regulation concerns for small-scale application,[28] similar to other scales.

In fact, the high temperature of the solid in modern combustion technology is the main reason for some of the above pollutions. The temperature is often more than 1000 °C[29,30] for a pulverized coal combustor or grate furnace and about 800−950 °C for a fluidized reactor.[31] This high temperature leads to high release of K and Na[32,33] to the gaseous phase in the combustor,[34] high NOx and SOx production,[35,36] and serious sintering[22,37] of bottom ash. The problem is severe for herbaceous biomass due to its high K and Cl content, and this is one of the challenges in the combustion utilization of biomass.[22,24] Based on research results in lthe iterature and our own previous work, it is found that controlling the solid phase at low temperature during the whole combustion process can significantly alleviate many of the mentioned problems.[33,34] Therefore, this low-temperature-solid combustion technology should be an efficient and economical method for pollution reduction and is beneficial for promoting the utilization of biomass combustion.

The temperature of the gas phase should be kept high to avoid incomplete combustion of volatiles in low-temperature-solid combustion technology. Compared to conventional combustion, the advantages of low-temperature-solid combustion technology include the following: (1) the operation is ease according to the slowness of combustion process, (2) heat demand and heat supply are well matched, and (3) the fertilizer property of ash is retained.

The objective of the present work is to introduce the idea of this low-temperature-solid combustion technology for biomass and other solid fuels. The potential of the technology in the pollution reduction of straws is calculated according to data from the literature and our own work. Necessary fundamentals for the equipment design and operation optimization are discussed.

2. LOW-TEMPERATURE-SOLID COMBUSTION TECHNOLOGY

2.1. Schematic of the Low-Temperature-Solid Combustion Technology. In fact, combustion of solid fuels includes drying, pyrolysis, and char oxidation. The temperature of the solid phase is normally <600 °C at the drying and pyrolysis stages regardless of the temperature of the environment. If the char oxidation stage is controlled independently at low temperature, as shown in Figure 1, we call it low-temperature-solid combustion technology.

A low-temperature-solid combustor differs from other combustors in its two combustion chambers: a high-temperature flame chamber and a low-temperature smoldering chamber. The raw fuel is fed into a flame chamber, dried, and pyrolyzed there. About 70% of mass is devolatilized, and the gas is burned at the freeboard of a high-temperature flame chamber, similar to the process in modern combustors. After drying and pyrolysis, char is immediately transported to a smoldering chamber, where it is oxidized. Measures of air limiting and cooling are taken to ensure the low temperature of char oxidation. Combustible gas of char oxidation from the smoldering chamber is blown into the flame chamber and burned there. Ash (2−15% of original fuel) from char oxidation can be returned to fields as fertilizer after simple treatment, and most of the nutrients will be absorbed by plants in their growth.
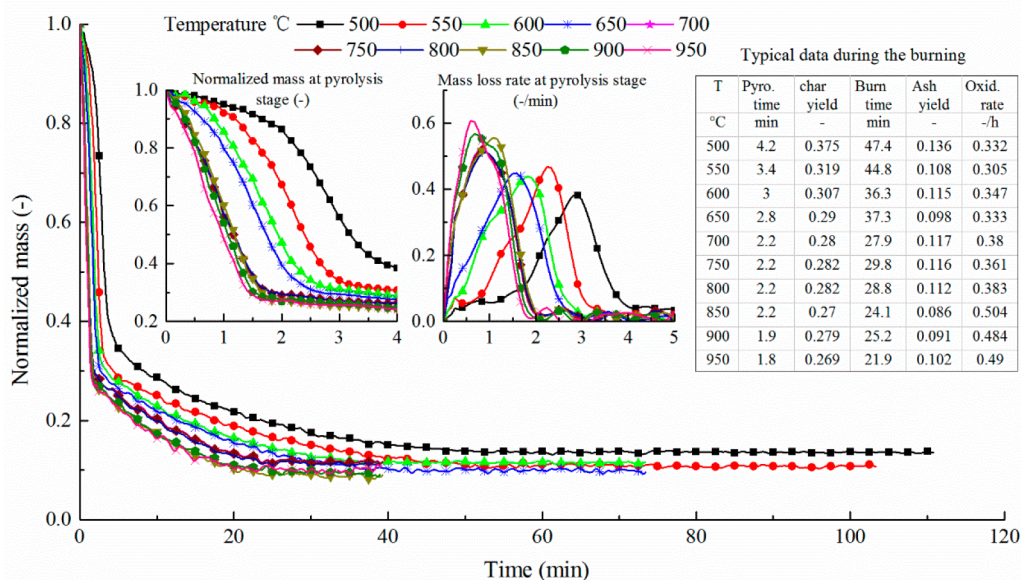
T	Pyro. time	char yield	Burn time	Ash yield	Oxid. rate
°C	min	-	min	-	-/h
500	4.2	0.375	47.4	0.136	0.332
550	3.4	0.319	44.8	0.108	0.305
600	3	0.307	36.3	0.115	0.347
650	2.8	0.29	37.3	0.098	0.333
700	2.2	0.28	27.9	0.117	0.38
750	2.2	0.282	29.8	0.116	0.361
800	2.2	0.282	28.8	0.112	0.383
850	2.2	0.27	24.1	0.086	0.504
900	1.9	0.279	25.2	0.091	0.484
950	1.8	0.269	21.9	0.102	0.49

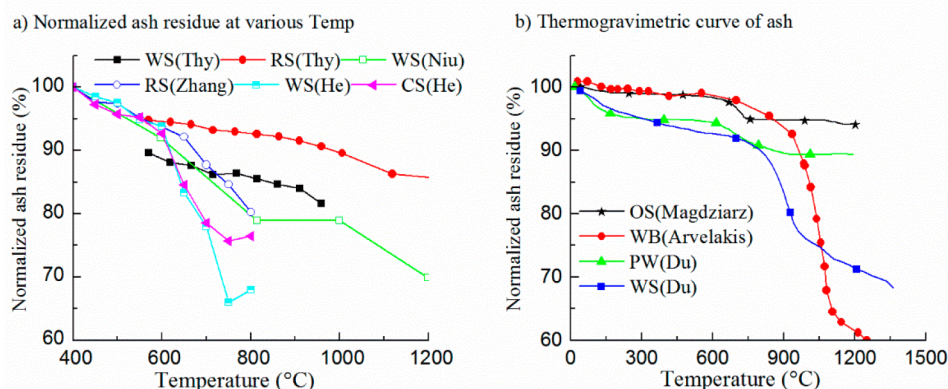**Figure 3.** Drying and pyrolysis stages of corn-stover pellets.

Figure 4. Normalized ash residues at different temperatures and thermogravimetric curves of biomass ashes (WS, wheat straw; RS, rice straw; CS, corn stover; OS, oat straw; WB, winter barley; PW, polar wood). Adapted from ref 56. Copyright 2015. Adapted from ref 57. Copyright 2015 Elsevier.

2.2. Scientific Basis of Low-Temperature Solid Combustion Technology.

Although there was no clear concept of low-temperature-solid combustion in the literature, some engineering attempts and scientific research provide the scientific basis of this idea. For example, a firebed cooling device was applied in a 12 kW underfeed pellet boiler, and it was found that 17 wt % dust decreased without impacting combustion quality.[27] A BB-100 technology recorded optimal combustion temperatures for wood and agricultural biomass of 760 and 675 °C, respectively.[38]

Our previous study on thermogravimetric of wood char[39] showed that char oxidation can be accomplished in a reasonable time (up to several minutes) at temperatures <500 °C. Smoldering combustion can survive with poor oxygen[40] and is a slow, low-temperature, and flameless form of combustion.[41,42] Yerman et al. reported that smoldering was achieved with 70% moisture contents of fuels.[43,44] Rahwan et al. showed that smoldering of sludge could be sustained with heating value of 1.6 MJ/kg.[45] Smoldering of biomass[46,47] showed that the ash was white and soft,[48] as shown in Figure 2, without any slags in the ash or solid deposition around the

reactor. The recorded temperatures inside the fuel bed are normally around 600 °C for agrostalks and 700 °C for wood char.

All of the above indicate that objectives of pollution reduction and ash recycling of biomass can be achieved using low-temperature-solid combustion technology. In fact, small-scale equipment has been set up, and primary experiments have been successfully performed in our group.

2.3. Resident Time of Biomass in Flame Chamber.

The residence time of biomass in the flame chamber is a key operation parameter, and it depends on the pyrolysis time. It can be measured using a Muffel furnace with a mass trace system. Our experiments on a single pellet of corn stover ($\Phi =$ 10 mm × 40 mm) in a horizontal tube furnace showed that the pyrolysis time at the temperature range of 500−900 °C is less than 4 min, as shown in Figure 3.

In our bench-scale combustor, the residence time of the corn-stover pellets in the flame chamber can be adjusted. Experiments showed that when this residence time is longer than 6 min, the pellets stick to the grate and slags appear. The indicates that the residence time should be well controlled.
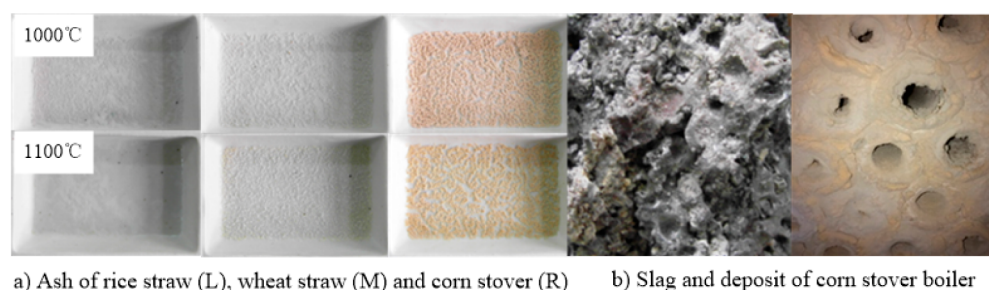
a) Ash of rice straw (L), wheat straw (M) and corn stover (R)   b) Slag and deposit of corn stover boiler

Figure 5. Photos of sintering ash and fouling waste in our experiments.

3. POTENTIAL IN POLLUTION REDUCTION

3.1. Reduction of Deposition/Fouling and Particle Emission.
One of the biggest problems in boilers of biomass, especially grass or agroresidues (high content of K, Na, N, and ash), is the deposition/fouling/sintering.[49,50] It causes a dramatic reduction of boiler efficiency and serious operational problems (frequent maintenance work and sometimes collapse of the equipment). The source of deposition/fouling/sintering and particle emission is the release of ash-forming elements from solid to gas. The reduction of this pollution can be estimated from the ash yield data at different temperatures.

It has been recorded that ash residue of biomass decreases significantly with increasing temperature.[37,51] Results on the measurement of ash residues at different temperatures[52,53] and thermogravimetric analysis of biomass ash demonstrate this decrease clearly.[54,55] Some examples[56,57] are shown in Figure 4. In Figure 4a, normalization of data is performed, taking the ash amount at 400 °C as the basis.

It can be seen that the reduction amount in the temperature range of 400−1200 °C varies considerably, from several percent to about 40%. For example, our experiments[56,57] showed that the mass decreases of ash for rice straw, corn stover, and wheat straw are about 20, 22, and 35 wt %, respectively, when the temperature increases from 400 to 800 °C. This is similar to those recorded in papers of Niu[51] and Du[53] but differs significantly from that of Thy.[32] The deviation might be due to the ash treatment method. In our experiments, ash yields of about 4 g were measured directly from the burning of raw material. In Thy's experiment, about 20 g of ash produced at 525 °C was pressed into pellets and heated at different temperatures in a furnace. During the release of inorganics from the ash pellets at a high temperature, there was great resistance, especially when sintering occurred.

For the pollution reduction estimation, data of the ash yield from direct combustion are chosen for calculation. It can be seen from Figure 4 that most of the decrease of ash yield occurs in the temperature range of 600−1000 °C. Decreases are more than 20% for most straws, accounting for more than 2/3 of the total decrease. This indicates that a relative reduction of deposit/fouling and particle emission of at least 60% can be achieved for those straws if the temperature of solid can be controlled to <600 °C.

It should be noted that the real decrease in the amount of fouling/deposit is affected by both the reduction ratio of ash and the content of ash. Here a boiler (350 kW, corn stover as fuel, provides residential heating for 4000 m^2) is taken as an example for a brief calculation. The fuel consumption of the boiler is about 100 kg/h, and the ash production rate is 100 kg/h × 0.05 kg ash/kg biomass = 5 kg ash/h. For a whole day, the total (deposit/fouling and particle emission) decrease

amounts to 5 kg/h × 24 h × 20% = 24 kg. Normally the surface of the heat exchange for this small boiler is about 25 m^2. This means that about 1 kg/m^2 deposit/particle emission can be reduced. This will improve the performance of the boiler dramatically.

3.2. Reduction of SO$_x$ and NO$_x$ Release.
SOx and NOx lead to acid rain, accelerate fouling and corrosion, and participate in the generation of photochemical smog. Thus, their concentrations in the flue gas of combustion systems are strictly controlled nowadays.[26]

Fuel-S is the only source of SOx, and the conversion rate varies with the type of biomass. Experiments[50] showed that 73, 44, 52, 51, 35, 70, and 32% of fuel-S from wheat bran, hay, sorghum, maize, straw, miscanthus, and vineyard pruning are converted into SOx, respectively. As to the effect of temperature, it has been recorded that the release of S from corn stover increases linearly with temperature (S% = 0.10 × T − 22) from 70% at 906 °C to complete release at 1234 °C.[33] This indicates low-temperature combustion has the potential for >30% SOx reduction.

There are three mechanisms responsible for NOx formation: the thermal mechanism (>1300 °C), the prompt mechanism (occurs at very low air/fuel ratios), and fuel-N conversion; of these mechanisms, fuel-N conversion plays the greatest role[47] in biomass combustion. It is recorded that the release of N of sewage sludge increases from about 50% at 350 °C to about 93% at 1000 °C during pyrolysis.[58] X-ray photoelectron spectroscopy (XPS) analysis showed that the main components of volatile nitrogen from coal are HCN, NH$_3$, and N$_2$ at temperatures of 853−1488 K. Higher temperature leads to significantly higher total emission of the three.[59] Release of HCN and NH$_3$ from soybeans in microwave pyrolysis[60] is similar to the above coal. All these show that there is about a 40% NOx reduction of low-temperature-solid combustion.

3.3. Reduction of Solid Waste.
Solid waste here refers to useless, unwanted combustion products in the solid state. High-temperature combustion of biomass produces a lot of slags.[51] Our experiments showed that ash of rice straw, wheat straw, and corn stover almost completely melt or stick to the crucible at temperatures >1000 °C, as seen in Figure 5a).

The hard, big slags, as shown in Figure 5b, are not allowed to return to the farm. They affect the field management, and their nutrients are often solidified via sintering. We think that water solubility of ash can represent to some extent the degree of sintering. It was found that water solubility of rice straw,[57] wheat straw, and corn stover[56] decrease from 37.5%, 50.1%, and 33.2% at 400 °C to 20.5%, 38.5%, and 26.4% at 600 °C and to 6.3%, 11.5%, and 7.2% at 800 °C, respectively. It can also be seen that a significant decrease of water solubility occurs at temperatures >600 °C.
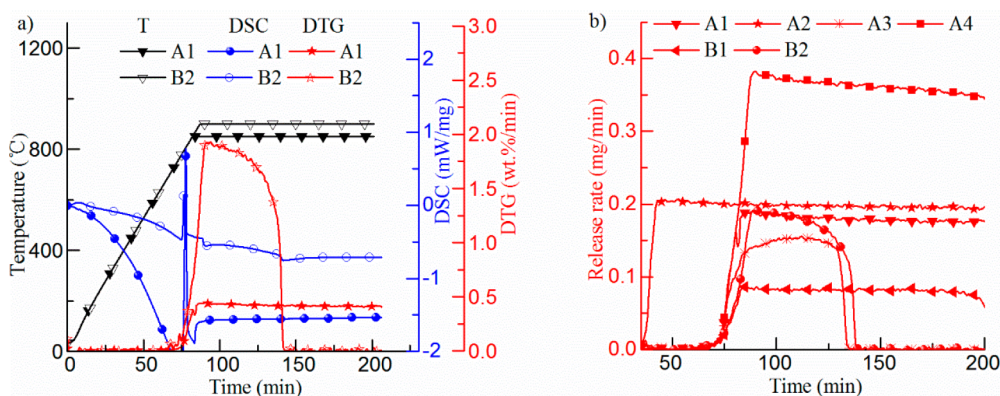
Figure 6. Results of thermogravimetric experiments. (a) DSC, DTG, and temperature history curves of KCl (A1) and a mixture (B2) of KCl and SiO_2. (b) Mass loss rates of all experiments. Adapted from ref 74. Copyright 2019 Elsevier.

Table 1. Correlations of Char Oxidation Rate and Ratio of CO/CO_2

reactions	rates	kinetics	ref	CO/CO$_2$ expression	ref
$\eta C + O_2 \rightarrow 2(\eta-1)CO + (2-\eta)CO_2$	$\omega = -k_d\rho_G Y_{O_2}\dfrac{M_C}{M_{O_2}}S$	$k_c = 10.3Te^{-74900/RT}$, $S = 6.3\ m^2/g$	76	$2512e^{-6240/T}$	78
		$k_c = 301e^{-149380/RT}$, $S = 6.3\delta_G^2/\delta^3$	77	$4.3e^{-3390/T}$	79
$C + CO_2 \xrightarrow{k_1} 2CO$ $C + H_2O \xrightarrow{k_2} CO + H_2$ $C + 0.5O_2 \xrightarrow{k_3} CO$	$\omega_c = -(k_1 + k_2 + k_3)\rho_C$	$k_1 = 1.5 \times 10^4 e^{-30000/RT}$ $k_2 = 7.5 \times 10^6 e^{-30000/RT}$ $k_3 = 3.01 \times 10^5 e^{-14900/RT}$	80	$1.0e^{-100.6/T}$	82
	$\omega_{O_2} = -(k_1 + k_2 + k_3)\rho_{O_2}$	$k_1 = 0.658e^{-74800/RT}$ $k_2 = 3.42e^{-130000/RT}$ $k_3 = 3.42e^{-130000/RT}$	81	$750e^{-7200/T}$	83
$\eta C + O_2 \xrightarrow{k_1}$ $2(\eta-1)CO + (2-\eta)CO_2$ $C + CO_2 \xrightarrow{k_2} 2CO$ $C + H_2O \xrightarrow{k_3} CO + H_2$ $C + 2H_2 \xrightarrow{k_4} CH_4$		$k_1 = 1.715Te^{-9000/T}$ $k_2 = k_3 = 3.42Te^{-15600/T}$ $k_4 = (3.42T \times 10^{-4})e^{-15600/T}$	84	$1.0/(0.02p_{O_2}^{0.21})e^{-3070/T}$	31

Deposition/fouling in high-temperature combustion, as shown in Figure 5b, is normally caused by reactions with irons in the surface of the heat exchanger, as a sequence, and this ash is not suitable to return to the farm either. The high content of K and other elements limit its utilization as cement.[61] The most popular disposal method is in landfilling. However, no country can afford enough land filling sites for the accumulation of ash every year.

In low-temperature combustion technology, there are no big slags in ash. After some simple treatments, all of the ash can be returned to the farm as fertilizer. This recirculation was a traditional method and is beneficial for the health of the ecosystem[49,57] and zero-cost waste disposal.

The ash content of agroresidues is normally high (2−15%), and it is estimated that approximately 480 million tons of biomass ash could be generated worldwide annually.[50] Taking China as an example, the amount of agroresidue is about 1900 million ton/year. If 1% of this residue is combusted at low temperature and the ash content is 5%, 0.95 million tons of solid waste would be reduced annually. At same time, 47500 tons of potassium would be returned to the ecosystem as fertilizer given 5% of accessible K[57] is there in the ash.

4. NECESSARY FUNDAMENTALS

The most important things for low-temperature-solid technology development are accurate prediction and control of the process, especially the change of the solid. Smoldering depends on heat exchange, the ambient oxygen concentration, and the content of moisture and inorganic material in solid fuel.[62] Boigné[63] developed kinetic models of biomass smoldering, in which reaction mechanisms of exothermic smoldering are described as endothermic pyrolysis and heterogeneous and exothermic char oxidation. Scott[64] studied multidimensional heat exchange and mass and momentum transfers by simulating smoldering. Fernandez-Anez[65] reported the characteristics of smoldering processes and developed the functional relationship between the refiled amount of fuel and the change of the combustion rate. Erland[66] reported that the

smoldering fronts propagates with a velocity of 0.4 mm/s in their experiment of smoldering. Chen[67] showed that the smoldering front propagates from the top to the bottom, where stable flame could be sustained to purify smoldering emissions. Combustion science offers knowledge to understand, model, handle, design, and optimize systems. Although there is some information in the literature that can be used as a reference for the design/operation of a low-temperature solid combustor, further investigations in some areas are still necessary, as stated in the following sections.

4.1. Release Rates of Inorganics. Release characteristics of inorganics during the combustion of biomass are often explained using thermodynamic equilibrium theory.[57,68] However, an equilibrium state is seldom reached in the process because of the relatively short burn-out time and the open reaction system. In recent years, the time-resolved release of potassium (K) was broadly investigated. Some researchers[69,70] developed kinetic models to calculate the release rate of K, and most of these kinetic models are based on the Arrhenius expression,[71,72] which states that the release rate is related to the mass of potassium. Even in some evaporation models,[71,73] the concentration of gaseous potassium inside biomass particles is assumed to be linearly proportional to the mass of potassium.

However, our experiments[74] showed that release rate has little relationship with the mass of potassium. In our work, the chemical form of potassium in corn stover was detected, and it was found that most K exists as potassium chloride (KCl). Based on this, the release of K from pure KCl and a mixture of KCl and SiO_2 at normal combustion temperatures was measured using simultaneous thermal analysis (STA). The differential thermogravimetric (DTG) analysis, differential scanning calorimetry (DSC) analysis, and evaporation history are shown in Figure 6. The quite flat DTG curves and release rate curves show that evaporation dominates potassium release at normal combustion temperature. A model to calculate the evaporation rate of KCl was developed and validated using data from our experiments and literature.

Theoretically, the method might be generalized to predict the release of other inorganics in biomass combustion. However, more experiments and theoretical analysis are necessary in a general sense, and the following problems must be clarified: (1) the original type of inorganics in biomass, (2) release rates of these inorganics, (3) the interaction of the inorganics during evaporation, and (4) the prediction of the global release of the inorganics.

4.2. Rate and Products of Char Oxidation. There are many correlations for calculating the rate and product of char oxidation, as shown in Table 1. Calculation results using these correlations differ significantly from one other. It is normally stated that more CO_2 than CO is produced at low temperatures (below 1562, 5078, ∞, 2231, and 1394 °C according to expressions in Table 1 from top to below) in the oxidation of coal char. However, Li's recent experiments[75] showed that more CO is generated at temperatures <650 °C. This is preferred in low-temperature-solid combustion because less air is necessary and less heat is generated in the char oxidation stage. Thus, it is easier to arrange air supply holes and the heat exchange surface.

The char oxidation rate and products are the keys to design the char oxidation chamber and to control the process. Because there are wide deviations in the literature on these properties, further investigation is necessary, especially for

biomass waste. To be more specific, these include the following: (1) the CO/CO_2 ratio of agroresidue char, (2) the kinetics of agroresidue char, (3) the effect of specific area and oxygen concentration, and (4) a practical calculation model or method for equipment design.

4.3. Fertilizer Property Change of Ash. Literature on the application of biomass ash as fertilizer[85,86] includes two groups: the possible amount of nutrients from ash and the impact of ash on the growth of the plant. It is concluded that considerable amount of nutrients can be returned to the ecosystem by recirculating ash,[87] and these nutrients do help the growth of plants.[88,89]

Quantitatively assessing the fertilizer property of biomass ash is difficult[85] because biomass ash contains almost all plant nutrients in tremendous types of phases.[90] The authors of this work developed a method including sequential extraction and matrix expression.[91] Based on this, the effect of the burning temperature on the fertilizer property of the ash from cornstover was analyzed. It was found that the fertilizer property is significantly affected by the burning temperature and changes dramatically in the temperature range of 600−700 °C, as shown in Figure 7. Many of our attempts to describe those
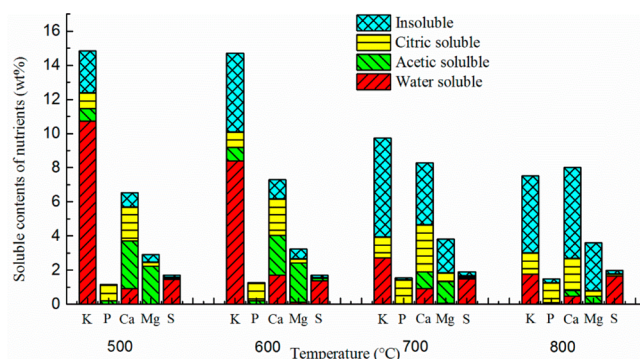

Figure 7. Solubility of nutrients in ash at different temperatures. Adapted from ref 91. Copyright 2018 Elsevier.

using existing kinetic forms have failed. Since solid/liquid reactions are involved in the process, the physical mechanism (melting, evaporation, flow, and transportation) might dominate the process rather than reactions. More experiments, observation, and analysis are necessary in this field.

Mechanism and calculation methods on the change of the fertilizer property of ash should be further investigated. To be more specific, these include the following: (1) the mechanism of the phase changes of ash and their kinetics, (2) interactions of components in ash at combustion temperature, and (3) practical calculation models or correlations to calculate the change of the fertilizer property in combustion.

4.4. Control of NOx and SOx. NOx species (normally 90% NO + 10% NO_2) are emitted in all combustion processes.[26] The formation of NOx from fuel-N dominates in combustion of biomass and is is very complex, being sensitive to fuel composition and combustion conditions. Some data on combustion of wood char and coal show that the release of N increases with the increasing temperature, as mentioned in section 3.2. It was also found[25,92] that oxygen availability affects the oxidation selectivity of fuel-N toward NO or N_2, and char/soot has the ability to reduce NO.

Release of SOx is normally not serious for biomass because S is not a macronutrient for plants and its content in most

biomass is low. In the two types of S, organic and inorganic forms, organic S makes up about 50 wt % of the total S in biomass. There are two steps in release S during combustion. The organic S is released at low temperatures, normally in a reduced form such as H_2S, while inorganic S is retained in the ash until the combustion temperatures exceed approximately 900 °C. Ren et al.[93] found that emission of S has a negative relation with Ca/S (x) and K/S (z), as $y_{SO_2} = 0.1022x^{-0.439}$ and $y_{SO_2} = 0.1207z^{-0.423}$, respectively, for biomass. Since there is large amount of K in the ash of agroresidues,[33,94] the release of SOx might be significantly reduced at optimal combustion conditions.

The ideal method is to convert all fuel-N to N_2 and all fuel-S to sulfate. The possible technology solution approaching this ideal method is based on further investigation/summary of the following: (1) the effect of temperature and reducing atmosphere on the reduction of NOx and its mechanisms, (2) the effect of temperature and alkali inorganics on the reduction of SOx and its mechanisms, and (3) a practical prediction model for combustor design.

5. CONCLUSION

Low-temperature-solid combustion technology applies a low temperature for the solid phase and a normal temperature for the gaseous phase. It has great potential in the economical reduction of deposition/fouling, emission, and solid waste in the combustion of biomass and solid waste. For better application, release rates of inorganics during combustion, rate and products of char oxidation, mechanisms on change of fertilizer property of ash, and the transformation of fuel S/N to NOx/SOx should be further investigated.

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Notes

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■ REFERENCES

(1) Williams, A.; Pourkashanian, M.; Jones, J. M. Combustion of pulverised coal and biomass. *Prog. Energy Combust. Sci.* **2001**, *27* (6), 587−610.

(2) Yin, C.; Rosendahl, L. A.; Kær, S. K. Grate-firing of biomass for heat and power production. *Prog. Energy Combust. Sci.* **2008**, *34* (6), 725−54.

(3) Míguez, J. L.; Morán, J. C.; Granada, E.; Porteiro, J. Review of technology in small-scale biomass combustion systems in the European market. *Renewable and Sustainable Energy Reviews* **2012**, *16* (6), 3867−75.

(4) Nunes, L. J. R.; Matias, J. C. O.; Catalão, J. P. S. Biomass combustion systems: A review on the physical and chemical properties of the ashes. *Renewable and Sustainable Energy Reviews* **2016**, *53*, 235−42.

(5) Saidur, R.; Abdelaziz, E. A.; Demirbas, A.; Hossain, M. S.; Mekhilef, S. A review on biomass as a fuel for boilers. *Renewable and Sustainable Energy Reviews* **2011**, *15* (5), 2262−89.

(6) Lu, J. W.; Zhang, S.; Hai, J.; Lei, M. Status and perspectives of municipal solid waste incineration in China: A comparison with developed regions. *Waste management* **2017**, *69*, 170−86.

(7) Makarichi, L.; Jutidamrongphan, W.; Techato, K-a The evolution of waste-to-energy incineration: A review. *Renewable and Sustainable Energy Reviews* **2018**, *91*, 812−21.

(8) Obernberger, I.; Brunner, T.; Barnthaler, G. Chemical properties of solid biofuels—significance and impact. *Biomass and Bioenergy* **2006**, *30* (11), 973−82.

(9) Wendt, J. Fundamental coal combustion mechanisms and pollutant formation in furnaces. *Prog. Energy Combust. Sci.* **1980**, *6* (2), 201−22.

(10) Vejahati, F.; Xu, Z.; Gupta, R. Trace elements in coal: Associations with coal and minerals and their behavior during coal utilization − A review. *Fuel* **2010**, *89* (4), 904−11.

(11) Williams, A.; Jones, J. M.; Ma, L.; Pourkashanian, M. Pollutants from the combustion of solid biomass fuels. *Prog. Energy Combust. Sci.* **2012**, *38* (2), 113−37.

(12) Stam, A. F.; Haasnoot, K.; Brem, G. Superheater fouling in a BFB boiler firing wood-based fuel blends. *Fuel* **2014**, *135*, 322−31.

(13) Carlson, C. L.; Adriano, D. C. Environmental impacts of coal combustion residues. *Journal of Environmental quality* **1993**, *22* (2), 227−47.

(14) Vehlow, J. Air pollution control systems in WtE units: an overview. *Waste management* **2015**, *37*, 58−74.

(15) Romeo, L. M.; Gareta, R. Fouling control in biomass boilers. *Biomass and Bioenergy* **2009**, *33* (5), 854−61.

(16) Nakanishi, E. Y.; Frías, M.; Santos, S. F.; Rodrigues, M. S.; Vigil de la Villa, R.; Rodriguez, O.; et al. Investigating the possible usage of elephant grass ash to manufacture the eco-friendly binary cements. *Journal of Cleaner Production* **2016**, *116*, 236−43.

(17) Carrillo, M. A.; Staggenborg, S. A.; Pineda, J. A. Washing sorghum biomass with water to improve its quality for combustion. *Fuel* **2014**, *116*, 427−31.

(18) Deng, L.; Zhang, T.; Che, D. Effect of water washing on fuel properties, pyrolysis and combustion characteristics, and ash fusibility of biomass. *Fuel Process. Technol.* **2013**, *106*, 712−20.

(19) Said, N.; Bishara, T.; Garcia-Maraver, A.; Zamorano, M. Effect of water washing on the thermal behavior of rice straw. *Waste Manag* **2013**, *33* (11), 2250−6.

(20) Batidzirai, B.; Mignot, A. P. R.; Schakel, W. B.; Junginger, H. M.; Faaij, A. P. C. Biomass torrefaction technology: Techno-economic status and future prospects. *Energy* **2013**, *62*, 196−214.

(21) Carroll, J. P.; Finnan, J. M. The use of additives and fuel blending to reduce emissions from the combustion of agricultural fuels in small scale boilers. *Biosystems Engineering* **2015**, *129*, 127−33.

(22) Niu, Y.; Wang, Z.; Zhu, Y.; Zhang, X.; Tan, H.; Hui, Se. Experimental evaluation of additives and K 2 O−SiO 2 − Al 2 O 3 diagrams on high-temperature silicate melt-induced slagging during biomass combustion. *Fuel* **2016**, *179*, 52−9.

(23) Wang, L.; Skreiberg, Ø; Becidan, M. Investigation of additives for preventing ash fouling and sintering during barley straw combustion. *Applied Thermal Engineering* **2014**, *70* (2), 1262−9.

(24) Becidan, M.; Todorovic, D.; Skreiberg, Ø; Khalil, R. A.; Backman, R.; Goile, F.; et al. Ash related behaviour in staged and non-

staged combustion of biomass fuels and fuel mixtures. *Biomass and Bioenergy* **2012**, *41* (0), 86−93.

(25) Bugge, M.; Skreiberg, Ø; Haugen, N. E. L.; Carlsson, P.; Houshfar, E.; Løvås, T. Numerical Simulations of Staged Biomass Grate Fired Combustion with an Emphasis on NOx Emissions. *Energy Procedia* **2015**, *75*, 156−61.

(26) Mladenović, M.; Paprika, M.; Marinković, A. Denitrification techniques for biomass combustion. *Renewable and Sustainable Energy Reviews* **2018**, *82*, 3350−64.

(27) Gehrig, M.; Pelz, S.; Jaeger, D.; Hofmeister, G.; Groll, A.; Thorwarth, H.; et al. Implementation of a firebed cooling device and its influence on emissions and combustion parameters at a residential wood pellet boiler. *Applied Energy* **2015**, *159*, 310−6.

(28) Villeneuve, J.; Palacios, J. H.; Savoie, P.; Godbout, S. A critical review of emission standards and regulations regarding biomass combustion in small scale units (<3MW). *Bioresource technology* **2012**, *111*, 1−11.

(29) Hurt, R.; Sun, J.-K.; Lunden, M. A kinetic model of carbon burnout in pulverized coal combustion. *Combustion and flame* **1998**, *113* (1−2), 181−97.

(30) Porteiro, J.; Patiño, D.; Collazo, J.; Granada, E.; Moran, J.; Miguez, J. Experimental analysis of the ignition front propagation of several biomass fuels in a fixed-bed combustor. *Fuel* **2010**, *89* (1), 26−35.

(31) Zhou, H.; Flamant, G.; Gauthier, D. DEM-LES simulation of coal combustion in a bubbling fluidized bed Part II: coal combustion at the particle level. *Chem. Eng. Sci.* **2004**, *59* (20), 4205−15.

(32) 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), 783−95.

(33) Johansen, J. M.; Aho, M.; Paakkinen, K.; Taipale, R.; Egsgaard, H.; Jakobsen, J. G.; et al. Release of K, Cl, and S during combustion and co-combustion with wood of high-chlorine biomass in bench and pilot scale fuel beds. *Proceedings of the Combustion Institute* **2013**, *34* (2), 2363−72.

(34) Li, X.; He, F.; Behrendt, F.; Gao, Z.; Shi, J.; Li, C. Inhibition of K_2SO_4 on evaporation of KCl in combustion of herbaceous biomass. *Fuel* **2021**, *289*, No. 119754.

(35) Zhou, J.; Masutani, S. M.; Ishimura, D. M.; Turn, S. Q.; Kinoshita, C. M. Release of Fuel-Bound Nitrogen during Biomass Gasification. *Ind. Eng. Chem. Res.* **2000**, *39*, 626−34.

(36) Li, X.; He, F.; Behrendt, F.; Dieguez-Alonso, A.; Sun, H.; Wang, H. Experiments on vapor pressure of KCl at different molar fractions in mixtures of KCl + K_2SO_4. *Acs Omega* **2022**, *7*, 36300−36306.

(37) Vassilev, S. V.; Baxter, D.; Andersen, L. K.; Vassileva, C. G. An overview of the composition and application of biomass ash. *Fuel* **2013**, *105*, 19−39.

(38) Fournel, S.; Palacios, J. H.; Morissette, R.; Villeneuve, J.; Godbout, S.; Heitz, M.; et al. Influence of biomass properties on technical and environmental performance of a multi-fuel boiler during on-farm combustion of energy crops. *Applied Energy* **2015**, *141*, 247−59.

(39) Anca-Couce, A.; Dieguez-Alonso, A.; Zobel, N.; Berger, A.; Kienzl, N.; Behrendt, F. Influence of Heterogeneous Secondary Reactions during Slow Pyrolysis on Char Oxidation Reactivity of Woody Biomass. *Energy Fuels* **2017**, *31* (3), 2335−44.

(40) Wang, S.; Ding, P.; Lin, S.; et al. Deformation of Wood Slice in Fire: Interactions between Heterogeneous Chemistry and Thermo-mechanical Stress. *Proceedings of the Combustion Institute* **2021**, *38*, 5081−5090.

(41) Wyn, H. K.; Konarova, M.; Beltramini, J.; et al. Self-sustaining smoldering combustion of waste: A review on applications, key parameters and potential resource recovery. *Fuel Process. Technol.* **2020**, *205*, No. 106425.

(42) Torero, J. L.; Gerhard, J. I.; Martins, M. F.; et al. Processes defining smoldering combustion: Integrated review and synthesis. *Prog. Energy Combust. Sci.* **2020**, *81*, No. 100869.

(43) Yerman, L.; Wall, H.; Torero, J.; et al. Smoldering Combustion as a Treatment Technology for Feces: Sensitivity to Key Parameters. *Combustion Science & Technology* **2016**, *188*, 968−981.

(44) Yerman, L.; Wall, H.; Torero, J. L. Experimental investigation on the destruction rates of organic waste with high moisture content by means of self-sustained smoldering combustion. *Proc. Combust. Inst.* **2017**, *36*, 4419−4426.

(45) Rashwan, T. L.; Fournie, T.; Torero, J. L.; Grant, G. P.; Gerhard, J. I.; et al. Scaling up self-sustained smouldering of sewage sludge for waste-to-energy. *Waste Management* **2021**, *135*, 298−308.

(46) He, F.; Behrendt, F. Experimental investigation of natural smoldering of char granules in a packed bed. *Fire Safety Journal* **2011**, *46* (7), 406−13.

(47) He, F.; Yi, W.; Li, Y.; Zha, J.; Luo, B. Effects of fuel properties on the natural downward smoldering of piled biomass powder: Experimental investigation. *Biomass and Bioenergy* **2014**, *67*, 288−96.

(48) He, F.; Yi, W.; Zha, J.; Li, Y. Experiments on smoldering of compressed agro-stalks in natural convection fixed bed stove. In *Proceedings of the 15th European Biomass Conference*, Berlin, Germany, May 8−11, 2007; ETA Florence Renewable Energies: Florence, Italy, 2007: pp 1646−1652.

(49) Fernández Llorente, M. J.; Carrasco García, J. E. Comparing methods for predicting the sintering of biomass ash in combustion. *Fuel* **2005**, *84* (14−15), 1893−900.

(50) Carvalho, L.; Wopienka, E.; Pointner, C.; Lundgren, J.; Verma, V. K.; Haslinger, W.; et al. Performance of a pellet boiler fired with agricultural fuels. *Applied Energy* **2013**, *104*, 286−96.

(51) Niu, Y.; Tan, H.; Hui, Se. Ash-related issues during biomass combustion: Alkali-induced slagging, silicate melt-induced slagging (ash fusion), agglomeration, corrosion, ash utilization, and related countermeasures. *Prog. Energy Combust. Sci.* **2016**, *52*, 1−61.

(52) Arvelakis, S.; Jensen, P. A.; Dam-Johansen, K. Simultaneous thermal analysis (STA) on ash from high-alkali biomass. *Energy Fuels* **2004**, *18* (4), 1066−76.

(53) Du, S.; Yang, H.; Qian, K.; Wang, X.; Chen, H. Fusion and transformation properties of the inorganic components in biomass ash. *Fuel* **2014**, *117*, 1281−7.

(54) Magdziarz, A.; Gajek, M.; Nowak-Woźny, D.; Wilk, M. Mineral phase transformation of biomass ashes − Experimental and thermochemical calculations. *Renewable Energy* **2018**, *128*, 446−459.

(55) Nurmesniemi, H.; Mäkelä, M.; Pöykiö, R.; Manskinen, K.; Dahl, O. Comparison of the forest fertilizer properties of ash fractions from two power plants of pulp and paper mills incinerating biomass-based fuels. *Fuel Process. Technol.* **2012**, *104* (0), 1−6.

(56) He, F.; Yu, R.; Zhang, Yi; Zhu, J.; Gao, Z.; Sun, P. Effects of ash forming temperature on water-soluble fraction of biomass ash and its elements. *Trans. Chin. Soc. Agric. Eng.* **2015**, No. 08, 227−232.

(57) Zhang, Y.; He, F.; Gao, Z.; You, Y.; Sun, P. Effects of ash-forming temperature on recycling property of bottom ashes from rice residues. *Fuel* **2015**, *162*, 251−7.

(58) Liu, T.; Guo, Y.; Peng, N.; Lang, Q.; Xia, Y.; Gai, C.; et al. Nitrogen transformation among char, tar and gas during pyrolysis of sewage sludge and corresponding hydrochar. *Journal of Analytical and Applied Pyrolysis* **2017**, *126*, 298−306.

(59) Kambara, S.; Takarada, T.; Yamamoto, Y.; Kato, K. Relation between functional forms of coal nitrogen and formation of nitrogen oxide (NOx) precursors during rapid pyrolysis. *Energy Fuels* **1993**, *7*, 1013−20.

(60) Zhang, J.; Tian, Y.; Cui, Y.; Zuo, W.; Tan, T. Key intermediates in nitrogen transformation during microwave pyrolysis of sewage sludge: a protein model compound study. *Bioresource technology* **2013**, *132*, 57−63.

(61) Rosales, J.; Cabrera, M.; Beltrán, M. G.; López, M.; Agrela, F. Effects of treatments on biomass bottom ash applied to the manufacture of cement mortars. *Journal of Cleaner Production* **2017**, *154*, 424−35.

(62) *SFPE Handbook of Fire Protection Engineering*, 5th ed.; Hurley, M. J.; Gottuk, D.; Hall, J. R., Jr.; Haarada, K.; Kuligowski, E.;

Puchovsky, M.; Torero, J.; Watts, J. M., Jr.; Wieczorek, C., Eds.; Springer. 2016.

(63) Boigné, E.; Bennett, N.; Wang, A.; Mohri, K.; Ihme, M.; et al. Simultaneous in-situ measurements of gas temperature and pyrolysis of biomass smoldering via X-ray computed tomography. *Proc. Comb. Inst.* **2021**, *38*, 3899–3907.

(64) Scott, S. N.; Keedy, R. M.; Brunini, V. E.; Kury, M. W.; Dodd, A. B.; Urban, J. L.; Fernandez-Pello, A. C.; et al. Validation of PMDI-based polyurethane foam model for fire safety applications. *Proc. Combust. Inst.* **2019**, *37*, 4009–4016.

(65) Fernandez-Anez, N.; Meyer, A. K.; Elio, J.; Kleppe, G.; Hagen, B. C.; Frette, V.; et al. Behaviour of smoldering fires during periodic refilling of wood pellets into silos. *J. Loss. Prev. Process. Ind.* **2021**, *72*, No. 104565.

(66) Erland, S.; Meyer, R.; Hagen, B. C. Fast moving smoldering fronts in thin liquid fuel films dispersed on inert porous media. *Fire Safety Journal* **2022**, *133*, No. 103645.

(67) Chen, Y.; Lin, S.; Liang, Z.; Surawski, N. C.; Huang, X. Smouldering organic waste removal technology with smoke emissions cleaned by self-sustained flame. *J. Clean. Prod.* **2022**, *362*, No. 132363.

(68) Jöller, M.; Brunner, T.; Obernberger, I. Modeling of Aerosol Formation during Biomass Combustion in Grate Furnaces and Comparison with Measurements. *Energy Fuels* **2005**, *19* (1), 311–23.

(69) Zhang, Z-h; Song, Q.; Alwahabi, Z. T.; Yao, Q.; Nathan, G. J. Temporal release of potassium from pinewood particles during combustion. *Combust. Flame* **2015**, *162* (2), 496–505.

(70) Fatehi, H.; He, Y.; Wang, Z.; Li, Z. S.; Bai, X. S.; Aldén, M.; et al. LIBS measurements and numerical studies of potassium release during biomass gasification. *Proceedings of the Combustion Institute* **2015**, *35* (2), 2389–96.

(71) Mason, P. E.; Jones, J. M.; Darvell, L. I.; Williams, A. Gas phase potassium release from a single particle of biomass during high temperature combustion. *Proceedings of the Combustion Institute* **2017**, *36* (2), 2207–15.

(72) Deng, S.; Wang, X.; Zhang, J.; Liu, Z.; Mikulcic, H.; Vujanovic, M.; et al. A kinetic study on the catalysis of KCl, K2SO4, and K2CO3 during oxy-biomass combustion. *J. Environ. Manage* **2018**, *218*, 50–8.

(73) Jones, J. M.; Darvell, L. I.; Bridgeman, T. G.; Pourkashanian, M.; Williams, A. An investigation of the thermal and catalytic behaviour of potassium in biomass combustion. *Proceedings of the Combustion Institute* **2007**, *31* (2), 1955–63.

(74) Li, X.; He, F.; Su, X.; Behrendt, F.; Gao, Z.; Wang, H. Evaporation rate of potassium in combustion of herbaceous biomass and its calculation. *Fuel* **2019**, *257*, No. 116021.

(75) Li, C.; Brown, T. C. Carbon oxidation kinetics from evolved carbon oxide analysis during temperature-programmed oxidation. *Carbon* **2001**, *39*, 725–32.

(76) Yang, Y. B.; Sharifi, V. N.; Swithenbank, J.; Ma, L.; Darvell, L. I.; Jones, J. M.; et al. Combustion of a Single Particle of Biomass. *Energy Fuels* **2008**, *22* (1), 306–16.

(77) Porteiro, J.; Granada, E.; Collazo, J.; Patiño, D.; Morán, J. C. A Model for the Combustion of Large Particles of Densified Wood. *Energy Fuels* **2007**, *21* (6), 3151–9.

(78) Gupta, P.; Sadhukhan, A. K.; Saha, R. K. Analysis of the combustion reaction of carbon and lignite char with ignition and extinction phenomena: Shrinking sphere model. *International Journal of Chemical Kinetics* **2007**, *39* (6), 307–19.

(79) Arthur, J. R. Reactions between carbon and oxygen. *Trans. Faraday Soc.* **1951**, *47*, 164–78.

(80) Peters, B.; Bruch, C. Drying and pyrolysis of wood particles: experiments and simulation. *Journal of Analytical and Applied Pyrolysis* **2003**, *70* (2), 233–50.

(81) Lu, H.; Robert, W.; Peirce, G.; Ripa, B.; Baxter, L. L. Comprehensive Study of Biomass Particle Combustion. *Energy Fuels* **2008**, *22* (4), 2826–39.

(82) Evans, D. D.; Emmons, H. Combustion of wood charcoal. *Fire Safety Journal* **1977**, *1* (1), 57–66.

(83) Saidi, M. S.; Hajaligol, M. R.; Mhaisekar, A.; Subbiah, M. A 3D modeling of static and forward smoldering combustion in a packed bed of materials. *Applied Mathematical Modelling* **2007**, *31* (9), 1970–96.

(84) Thunman, H.; Leckner, B.; Niklasson, F.; Johnsson, F. Combustion of wood particles–a particle model for eulerian calculations. *Combust. Flame* **2002**, *129* (1–2), 30–46.

(85) Vassilev, S. V.; Baxter, D.; Andersen, L. K.; Vassileva, C. G. An overview of the composition and application of biomass ash.: Part 2. Potential utilisation, technological and ecological advantages and challenges. *Fuel* **2013**, *105* (0), 19–39.

(86) Ingerslev, M.; Skov, S.; Sevel, L.; Pedersen, L. B. Element budgets of forest biomass combustion and ash fertilisation − A Danish case-study. *Biomass and Bioenergy* **2011**, *35* (7), 2697–704.

(87) Park, N. D.; Michael Rutherford, P.; Thring, R. W.; Helle, S. S. Wood pellet fly ash and bottom ash as an effective liming agent and nutrient source for rye grass (Lolium perenne L.) and oats (Avena sativa). *Chemosphere* **2012**, *86* (4), 427–32.

(88) Väätäinen, K.; Sirparanta, E.; Räisänen, M.; Tahvanainen, T. The costs and profitability of using granulated wood ash as a forest fertilizer in drained peatland forests. *Biomass and Bioenergy* **2011**, *35* (8), 3335–41.

(89) Freire, M.; Lopes, H.; Tarelho, L. A. Critical aspects of biomass ashes utilization in soils: Composition, leachability, PAH and PCDD/F. *Waste management* **2015**, *46*, 304–15.

(90) Vassilev, S. V.; Baxter, D.; Andersen, L. K.; Vassileva, C. G. An overview of the composition and application of biomass ash. Part 1. Phase−mineral and chemical composition and classification. *Fuel* **2013**, *105*, 40–76.

(91) Zhang, Y.; He, F.; Li, X.; Behrendt, F.; Gao, Z.; Yu, R. Fertilizer properties of ash from corn-stover pellets using the sequential extraction and matrix expression. *Waste management* **2018**, *82*, 111–7.

(92) Houshfar, E.; Skreiberg, Ø; Todorović, D.; Skreiberg, A.; Løvås, T.; Jovović, A.; et al. NOx emission reduction by staged combustion in grate combustion of biomass fuels and fuel mixtures. *Fuel* **2012**, *98*, 29–40.

(93) Ren, X.; Sun, R.; Meng, X.; Vorobiev, N.; Schiemann, M.; Levendis, Y. A. Carbon, sulfur and nitrogen oxide emissions from combustion of pulverized raw and torrefied biomass. *Fuel* **2017**, *188*, 310–23.

(94) Johansen, J. M.; Jakobsen, J. G.; Frandsen, F. J.; Glarborg, P. Release of K, Cl, and S during Pyrolysis and Combustion of High-Chlorine Biomass. *Energy Fuels* **2011**, *25* (11), 4961–71.