CHAPTER 2 BED AGGLOMERATION

2.1 Introduction

Particle agglomeration was early recognized as critical factor for the operation of fluidized bed in fuel conversion, iron ore reduction and cement processes [14-16]. However, it became useful and common for food and pharmaceutical industries, the agglomerates of material grains are intentionally produced in order to improve the powder properties [17]. Bed particle agglomeration latterly was found to occur in likelihood by a mechanism of sintering in the presence of a liquid phase [18]. As the sintering process progressed, the coalescence and densification were evident.

The bed particle agglomeration was experienced during various fuel conversion processes such as fluidized bed combustion (FBC) and gasification (FBG) of coal, biomass and refuse derived fuels (RDF) [12,19-23]. It was mainly attributed to the chemistry of ash and bed material [24-28]. The interactions between the released ash species and bed particles under high temperature during the normal bed operating conditions resulted in the presence of the compounds with low melting temperatures on the surface of bed particle. At certain critical conditions, these compounds presenting as liquid phase induced the permanent bonds between bed particles to form agglomerates, and defluidization then began.

There are a large number of previously intensive studies toward the bed agglomeration, many investigations focused on the plausible and governing mechanisms, prediction or prevention. The following information on bed agglomeration is the comprehensive compilation and review of the research literatures.

2.2 Ash chemistry of biomass

A wide variety of solid and liquid biomass materials, and biomass materials as the components of mixed fuels, are combusted in a wide range of combustion devices, for heating and power generation purposes. The general types of installations [29] can be classified under the following broad categories, depending on the scale of operation:

- The very small stoves, fires and boilers employed for domestic cooking and heating.
- The small and medium scale boilers employed for commercial, process and district heat supply.
- The medium and large scale boilers employed for combined heat and power, or power-only applications.
- The co-firing of biomass materials with coal in large industrial and utility boilers.

For the case of solid fuel, biomass materials contain noncombustible constituents, and the nature and behavior of these constituents have a significant bearing on the design, operation and performance of the combustor and boiler.

2.2.1 Chemical compositions of biomass ash

Composition and other relevant data for a wide range of biomass, biomass ash and other relevant materials are available in a number of databases of biomass properties on the internet [30-33] and of previous literatures in the biomass related field study, including from presently reviewed literatures [8,12,29]. All of the biomass and biomass-based waste materials are distinguished to other industrial solid fuels by having relatively low calorific values, high volatile matter contents and low bulk densities. They are the oxygen rich and carbon based fuel. Most of the biomass materials, in raw harvested form, also have very variable moisture contents, and it can be disadvantageous to dry and/or densify the biomass, prior to transportation, handling and storage as a fuel.

The reported ash data show fairly clear in some general trends of inorganic species, described below for woody fuels and agricultural residues. The wood materials, generally having very low ash contents (1-4 %), are particularly rich in calcium and very low in chlorine and sulfur. Some extraneous clay and quartz may be present from contamination with soil. The ash melting temperatures are generally very high. Agricultural residues have relatively higher ash content, ranging at a large variance from 2% to more than 20%. Their ash chemistry vary significantly but all are dominated by potassium, silicon and phosphorus compounds. Silicon is the abundant element. Their ash melting temperatures are therefore lower than those of wood, usually between 800-1000 °C. Some residues such as straws and grasses may also contain relatively high concentration of chlorine and sulfur.

Three different biomass ash systems have been generally described in terms of their ash chemical composition and their fusion behavior [34], viz:

- high silicon / high potassium / low calcium ashes with low fusion temperatures, in the agricultural residues.
- low silicon / low potassium / high calcium ashes with high fusion temperatures, found in woody materials.
- high calcium / high phosphorus ashes with low fusion temperatures, including manures, poultry litters and animal wastes.

The important inorganic elements in biomass from a view point of the bed agglomeration problems are the refractory silicon, the alkali potassium, the alkali earth calcium and the non-metallic chlorine, sulfur and phosphorus [12,24]. Potassium is well accepted by far as the most important element responsible for bed agglomeration and other ash-related problems in thermal treatments of biomass (given technical terms as combustion, pyrolysis and gasification).

2.2.2 Forms of inorganic in biomass

The form in which an inorganic element occurs in a solid fuel has a decisive influence on its reactivity and volatility in combustion and gasification. Inorganic material in low-rank solid fuels, including lignites and biomass, can be roughly divided into two broad fractions [35], viz:

1. Atomically dispersed inherent inorganic material

Inherent inorganic material exists as part of the organic structure of the biomass. It is most commonly and largely associated with the oxygen, sulfur and nitrogen-containing functional groups (carboxyl, hydroxyl, ketone or ether groups). The inorganic elements are associated chemically, in the form of cations or chelates (chelate; *a heterocyclic compound having a metal ion attached by coordinate bonds to at least two nonmetal ions*), with these organic functional groups in the suitable sites or are in the solution in inherent moisture as a soluble salt or are precipitated as a crystalline salt. It is also possible for some inorganic species to be present in a very fine particulate form within the organic structure.

2. Extraneous discrete mineral

This inorganic material is added to the fuel through geological processes, or during harvesting, handling and processing of the fuel. Biomass fuels are commonly contaminated with soil, sand, pebble, pieces of iron or tramp materials, which have become mixed with the fuel during collection, handling and storage.

The modes of occurrence and origins of the main inorganic elements in biomass based on the plant physiology [34] are summarized in Table 2.1, including the elements of interest, principal form of uptake, structural forms in plant, brief function description and main source of each element, and explain below viz;

- Silicon is taken up to plant by absorption of silicic acid from the soil and deposited as hydrated oxide ($SiO_2{\cdot}nH_2O$) in plant structure usually in an amorphous form, but occasionally in a crystalline form [36].
- Aluminum is toxic occurring in small quantities and its presence is usually a marker of contamination via dust, dirt or other soil constituents.
- Calcium is essential for cell wall stiffening and forms exchangeable bonds with cell walls. Major sources of calcium are lime, dolomite or gypsum in the soil amendment.
- Magnesium is exclusively part of chlorophyll essential for photosynthesis [37]. Soil minerals, organic material, fertilizers, and dolomitic limestone are sources of magnesium for plants.
- Sodium is not an essential element to plant, but it is toxic at higher than 2 wt% in soil.
- Potassium occurs as the univalent ion with high mobility and has an important function in osmotic process and metabolism [38]. It is supplied to plants by soil minerals, organic materials and fertilizers.
- Phosphorus, noted especially for its role in converting the sun energy to useful compounds for plant, is a vital component of DNA *(*Deoxyribonucleic acid; *the genetic memory unit*), RNA (Ribonucleic acid; *the DNA decoder*) and ATP (Adenosine-5'-triphosphate; *the chemical energy unit*) of plants [39]. Its uptake is mostly as the primary orthophosphate ion ($H_2PO_4^-$) from mainly fertilizer, but some also absorbed as secondary orthophosphate (HPO_4^{2-}) as increasing soil pH [36,39].
- Iron has two principal forms; chelates and cations. It is involved in nitrogen fixation and photosynthesis. Soil mineral is its main source.
- Sulfur in plants is in the form of sulfates and organic sulfur. It can be incorporated into plants both by absorption and assimilation of the atmospheric SO_2 and by absorption of the sulfur dissolving water.
- Chlorine in biomass occurs as a chloride iron. Its concentration is closely related to the nutrient composition of the soils.

Table 2.1 Element structures in biomass

Element	Uptake form	Structural examples in plant	Function	Source
Silicon (Si)	H_2SiO_3, $Si(OH)_4$	$SiO_2 \cdot nH_2O$, usually in amorphous form and occasionally in crystalline form	- A structural component of some plant species - Play a role in disease resistance in crop plants	Soil
Aluminum (Al)	Al^{3+}	Al^{3+}	- Toxicity of Al decreases the uptake and distribution of other elements	Soil, Dirt
Calcium (Ca)	Ca^{2+}	Ca^{2+}, CaC_2O_4	- Essential for cell wall structure - Form exchangeable bonds with cell walls for osmotic and signaling purposes	Lime, Gypsum, Dolomite
Magnesium (Mg)	Mg^{2+}	Mg^{2+}	- Exclusive component of chlorophyll [37] - A cofactor for many enzymatic reactions	Soil, Fertilizer, Dolomite
Sodium (Na)	Na^+, NaCl	NaCl	- It is not an essential element for plant - Its high concentrations in soil are toxic	Intrusion of salt water or a process additive
Potassium (K)	KCl	K^+(univalent ion) or in the organic matrix [38]	- High mobility with little structural function in every living plant and animal cell - Aid in osmotic and ionic regulation - Function as a cofactor or activator of many enzymes of carbohydrate and protein metabolism	Fertilizer, Organic materials
Phosphorus (P)	$H_2PO_4^-$, HPO_4^{2-}	$R\text{-}(PO_4)_2$, a vital component of DNA, RNA, and ATP [39]	- Play central role in plants in energy transfer and protein metabolism - Energy used by an organism in its daily operations is released when ATP reduces to ADP (Adenosine diphosphate) - Essential for all plant growth	Fertilizer

Table 2.1 Element structures in biomass (Continue)

Element	**Uptake form**	**Structural examples in plant**	**Function**	**Source**
Iron (Fe)	Fe^{2+}, Fe^{3+}	Fe^{2+} in the form of chelates and ion	- Involved in N-fixation and photosynthesis - To be active a transport[1] - Essential for reversible oxidation/reduction reaction	Soil
Manganese (Mn)	Mn^{2+}	Mn^{2+}	- Involved in photosynthesis - A constituent of enzymes arginase[2] [40] and phosphotransferase[3] [41]	Soil, Fertilizer
Copper (Cu)	Cu^{2+}, $Cu(OH)_2$, $Cu(H_2O)_6^{2+}$	Cu^{2+}, $Cu(OH)_2$, $Cu(H_2O)_6^{2+}$	- Constituent of several enzymes - Relatively immobile element, associated in plant structure - Important trace in plants reproductive growth stage	Soil, Additive
Sulfur (S)	SO_4^{2-}, SO_2	SO_4^{2-}, organic-S	- Involved in plant cell energetics	Atmospheric SO_2, Sulfur dissolved in water
Chlorine (Cl)	KCl, Cl^-	Cl^-	- Essential for photosynthesis - Function in osmoregulation[4] [42] of plants growing on saline soils	Soil, Salt water

Remark

[1] an exchange of molecules (and their kinetic energy and momentum) across the boundary between adjacent layers of a fluid or across cell membranes

[2] a manganese-containing enzyme It is the final enzyme of the urea cycle.

[3] a category of enzymes that catalyze phosphorylation reactions (addition of a phosphate (PO_4^{3-}) group to a protein or other organic molecule)

[4] the active regulation of the osmotic pressure of an organism's fluids to maintain the homeostasis of the organism's water content; it keeps the organism's fluids from becoming too diluted or too concentrated.

The further investigations [36,43] of the major inherent inorganic species of biomass provide a roughly qualitative and quantitative data of the major inorganic element speciation in three categories, viz:

- Water soluble, i.e. in free ionic form
- Organically associated
- Precipitated as relatively pure compounds, in crystalline or amorphous forms

A listing of these major inorganic species is presented in Table 2.2.

Table 2.2 Speciation of inorganic materials [36,43]

Element	**Class 1 – water soluble (free ionic form)**		
	Compound	**Formula**	**Share of total element (%)**
Si	Silicon hydroxide	$Si(OH)_4$	<5
Ca	Calcium nitrate, chloride, phosphate	$Ca(NO_3)_2$, $CaCl_2$, $Ca_3(PO_4)_2$	20-60
Mg	Magnesium nitrate, chloride, phosphate	$Mg(NO_3)_2$, $MgCl_2$, $Mg_3(PO_4)_2$	60-90
Na	Sodium nitrate, chloride	$NaNO_3$, $NaCl$	>90
K	Potassium nitrate, chloride	KNO_3, KCl	>90
P	Phosphate ion	PO_4^{3-}	>80*
S	Sulfate ion	SO_4^{2-}	>90*
Cl	Chloride ion	Cl^-	>90*
	Class 2 – organically associated (covalent or ionic bonding with tissue)		
Ca	Calcium pectate	macromolecule	0.8-2.6
Mg	Chlorophyll, magnesium pectate	$C_{55}H_{72}MgN_4O_5$, macromolecule-	8-35
P	Nucleic acid	PO_4^{3-}	Not reported
Fe	Organic complex, organic sulfates	Fe^{3+}, Fe^{2+}	>80*
Mn	Various organic structures	Mn^{2+}, Mn^{3+}, Mn^{4+}	>90*
S	Sulfolipid, poteins, amino acids	SO_4^{2-}, S	Not reported
	Class 3 – precipitated (pure compound, amorphous, crystalline)		
Si	Phytolite	$SiO_2{\cdot}nH_2O$	>90*
Ca	Calcium oxalate	$CaC_2O_4{\cdot}nH_2O$	30-85
P	Phytates	Ca-Mg(-K)-salt of $C_6H_6[OPO(OH)_2]_6$	Up to 50-86% in seeds
Fe	Phytoferritin	$(FeO.OH)_8.(FeO.OPO_3H_2)$	Up to 50% in leaf tissue

* No exact quantities have been reported. The quoted value indicates that the speciation is the dominant one for that element.

The data in this table indicate clearly that the alkali, phosphorus, sulfur and chlorine in the inherent inorganic material tend to be present largely in the soluble form, as simple inorganic salts. Silicon is present predominantly as silica in the precipitated form. The alkaline earth metals are more complex and can occur in a number of forms. The extraneous inorganic material can also be present in many forms. It takes the form of contamination with sand, soil or other mineral materials, tramp metal components, etc.

The modes of occurrence of inorganic species are further discriminated according to their solubility in a sequence of increasingly aggressive chemical solvents, namely "the chemical fractionation" [44-45]. It is developed originally for the characterization of coals and later adapted to characterize a number of biofuels [24,46-47]. The leaching solvents employed for this purpose are commonly: Water ⇒ Ammonium acetate solution ⇒ Hydrochloric acid solution. The following four modes of occurrence distinguished by this analysis are listed in Table 2.3.

Table 2.3 Modes of chemical fractionation results

Solubility	Likely form in the fuel
soluble in water	principally the water soluble salts, sulfur and chlorine
soluble in ammonium acetate (ion-exchangeable)	organically bound as cations and chelates
soluble in hydrochloric acid	generally acid soluble salts as carbonates and sulfates
insoluble	principally mineral formed as oxides, silicates or sulfides

It is generally considered that the water and acetate-leachable elements are relatively reactive and are more readily released into the vapor phase and the submicron sized aerosol fraction of the ash generated from the biomass during elevated temperature processes. The elements in the acid soluble and residue fractions are more immobile and tend to release into the coarser ash fraction.

As result, the biomass materials, in general, have significantly and relatively higher levels of water and acetate soluble species, with the majority of the potassium and chloride, and some of the calcium and magnesium, compared with coals. The fractionation results in details of each element are provided in Table 2.4 and discuss, viz

Table 2.4 Fraction and form of elements in chemical fractionation of biomass

Element	Fraction	Likely form	Description
Refractory Si, Al, Ti	Insoluble mainly	Oxide, Silicate	- Al and Ti in trace concentration - Much less reactive in volatilization and chemical reaction
Alkali K, Na	>90% in water soluble or ion exchangeable	Chloride, Sulfate, Other salts, Cations, Chelates	- Na in trace concentration - Easily volatilized or easily available for chemical reaction
Alkali earth Ca, Mg	Largely in an ion exchangeable or acid soluble	Cations, Chelates, Carbonate, Sulfate	- Lesser volatile than alkali
Cl	Water soluble mainly	Salt, Anions	- Present in an easily vaporizable form
S	Variable	Variable	- Variable forms, ranging from completely water soluble to completely insoluble
P	Variable	Variable	-
Noble metals (Fe, Mn, etc)	Acid soluble or insoluble	Variable	- Trace elements in biomass

- All refractory elements (Si, Al and Ti) are insoluble and likely in the oxide and silicate as the major form. Al and Ti are present in trace concentrations. These refractory components are thus assumed to be much less reactive in volatilization and chemical reaction in a high temperature process.

- The alkali and alkali earth elements (K, Na, Ca and Mg), which mainly occur in plant organic structures or reactive mobile inorganic components, are predominantly in the soluble fractions.
- Over 90% of potassium in non-contaminated biomass (no soil) is in the water soluble and ion exchangeable form, hence it is believed to be easily volatilized or easily available for chemical reaction, probably leading to the ash-related problems. Sodium presents only in a trace element.
- Calcium is largely in an ion exchangeable or acid soluble form, thus it is lesser volatile than potassium. Magnesium also shows the same.
- Chlorine is supposed to be present in an easily vaporizable form, since almost all of it in biomass is in a water soluble form.
- Noticeably, sulfur occurs in variable forms, ranging from completely water soluble in wheat straw to completely insoluble in switchgrass. However, the volatility of sulfur is insubstantially depended on its form in fuel, as it is oxidized to SO_2 in combustion and released as H_2S in gasification and pyrolysis [48].
- Phosphorus and the noble metals also occur in variable forms.

It further seems that the chemical fractionation results are fairly consistent with the biological functions of inorganic elements. Clay contamination can give increasingly a fraction of insoluble.

The chemistry of biomass ash differs considerably with the biomass type, cultivated soil, fertilizers, climate, maturity, harvesting, handling, etc., and also with employed analytical techniques and ashing temperature [49-53]. The inorganic classes in biomass are early discriminated by the aforementioned analyses based on either the plant physiology or chemistry. They provide useful information to assist in the advance prediction about the potential behaviors of ashes in the thermal treatments of specified biomass fuels. However, the careful interpretation from these results is needed.

2.3 Inorganic behaviors and bed agglomeration process

Despite the result of the complex interactions in both physically and chemically, the bed agglomeration is likely treated as basically three sequential steps [24];

- Firstly, the ash forming elements in fuel are released during thermal treatments, as the inorganic transformation,
- Secondly, they are transported to the surface of bed particles forming the coating, namely the inorganic migration, and
- Thirdly, the coated bed particles stick their neighbors and then form the agglomerates, this is the sintering.

A review in this section is performed to identify the behaviors of inorganic elements during elevated temperature processes. Their interactions with the bed particle relevant to bed agglomeration and the sintering processes are focused and then summarized to the mechanistic information.

2.3.1 Inorganic transformations

The physical and chemical transformations of inorganic matter in biomass combustion are typically illustrated in Figure 2.1. The mechanisms for transformations in biomass-fired boilers are mainly based on analysis of deposits from different locations in large scale or commercial scale boilers, including travelling grates and fluidized beds.

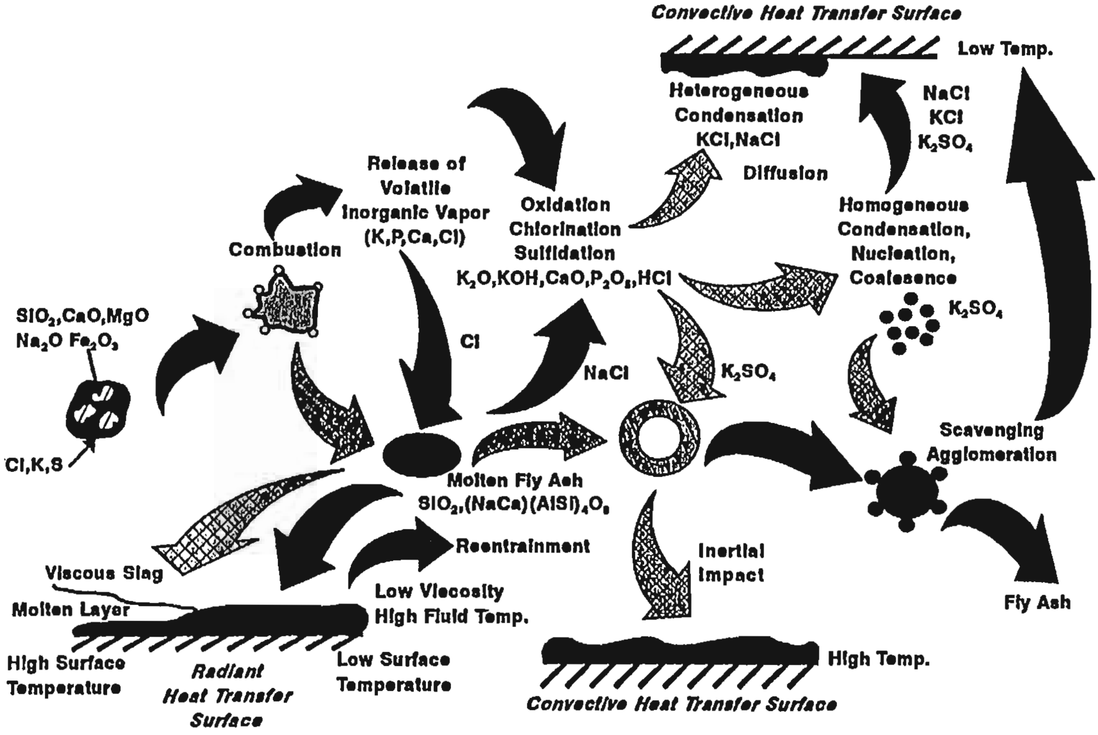

Figure 2.1 Transformation of mineral matters in biomass [54].

A certain part of the inorganic matters, derived supposedly from ionically or organically-bound inorganic, is released as a vapor phase. This volatilization of inorganic is a key role in fouling of biomass-fired boilers, (*fouling is defined as deposition in the heat-recovery section of the steam generator subjected to convective heat exchange by fly ash quenched to a temperature below its predicted melting point, condensation by volatiles, or sulfidation by* SO_3) [34]. The released ash constituents have else present in the fine liquid/solid of particulate matters (aerosols), coarse fly ash particles and sintered ash as bottom ash, which they can contribute to slagging and further to intensified fouling (*slagging is deposition of sintered ash on heat transfer surface and refractory in the furnace volume primarily subjected to radiant heat transfer*). However, there are some general agreements on the ash release behaviors and no exact ranges and temperature on the release quantities and the start of volatilization, respectively. These are obviously due to many factors affecting the release: the form of inorganic elements in biomass, heating rate and final temperature of fuel particle, presence of chlorine, sulfur and silica, ambient conditions (oxidizing: *combustion* or reducing: *pyrolysis, gasification*), etc [51].

Basically, most solid fuels exposed to a hot gas stream during combustion experience in three sequentially distinct stages of mass loss; (i) drying, (ii) devolatilization and volatile combustion, and (iii) char combustion. No release of inorganic species as well as chlorine and sulfur occurs in the drying step [55-68], indicating that they may not be associated with water in the fuel. Generally, a minor extent of inorganic elements starts to be released during devolatilization while the major releases part is in the char combustion phase. The transformation mechanisms of elements of interest, particularly of potassium that had been proposed specifically [69] as illustrated in Figure 2.2, can be summarized in Table 2.5 and explained; viz.

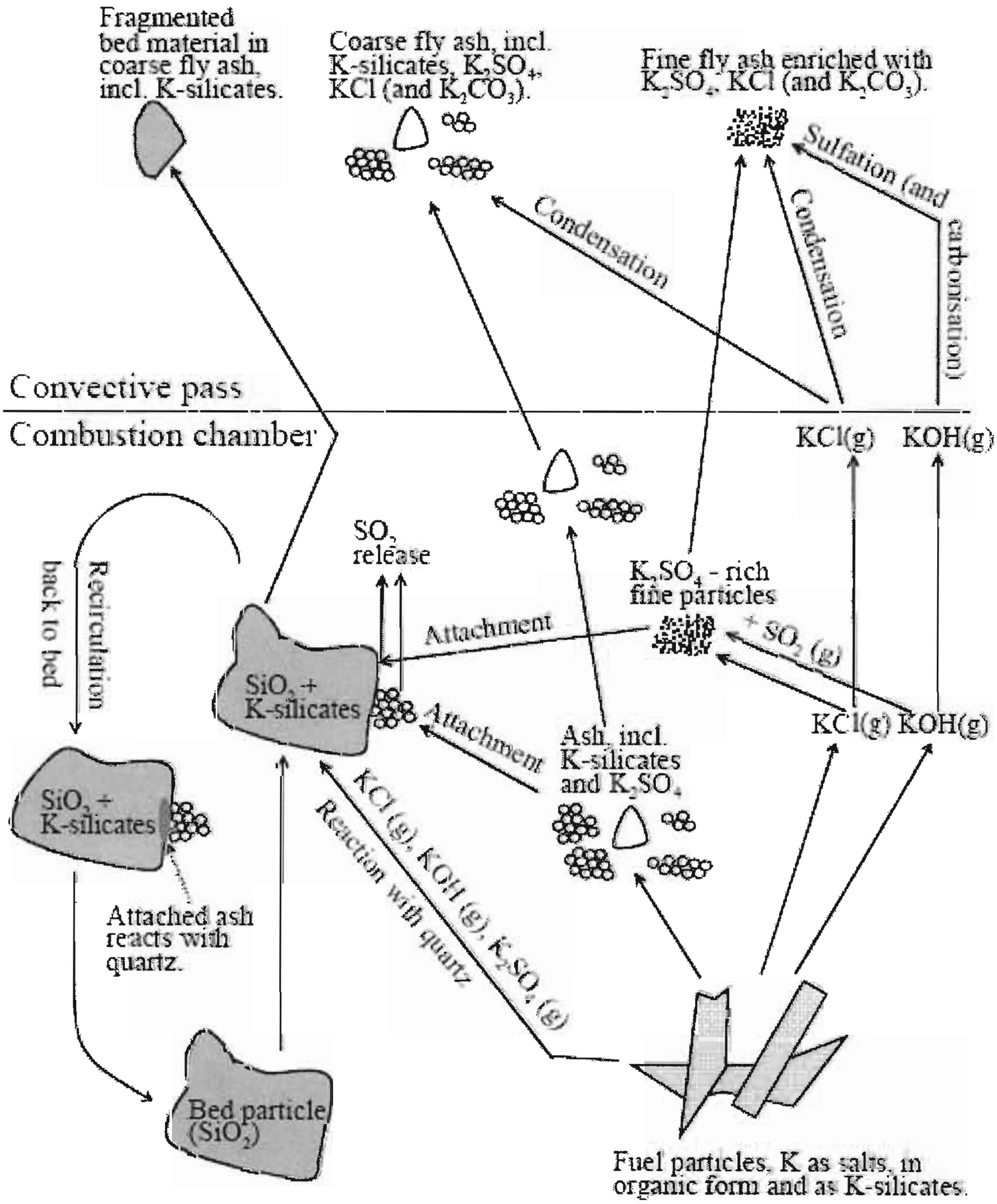

Figure 2.2 Behavior of potassium during biomass combustion [69].

Table 2.5 Fates of elements during heat treatment processes

Element	Transformation		Note
	Phase	Species	
Si	Molten	Silicates	-
	Solid	SiO_2 (Silica)	
Al	Solid	Al_2O_3, Silicates	-
Ca, Mg	Molten	Silicates	-
	Solid	Sulfate, Oxide and Chloride	
Na	-	-	Neglected in the account
K	Vapor	KCl, KOH, K_2SO_4	-
	Aerosol	K_2SO_4, K_2O, K_2CO_3	
	Molten	Silicates	
P	Solid	K_3PO_4, $K_4P_2O_7$, Silicates	-
Fe	Solid	Oxide form	-
S	Gas	SO_2, H_2S	-
	Aerosol	K_2SO_4	
	Solid	$CaSO_4$, $MgSO_4$	
Cl	Vapor	HCl, KCl	-
Trace	Variable	Variable	-

Potassium released from fuel particle includes (i) gaseous KCl, KOH and K_2SO_4, (ii) aerosol K_2SO_4, K_2CO_3 and K_2O, and (iii) K in the coarse particle mainly as silicates. If chlorine presents in biomass, especially the annual crop that has relatively large amount of potassium and chlorine, potassium will be released to the gas phase as KCl. This KCl is proved to be the major volatile K species and major volatile constituent [57,63]. The KCl release is initially in the devolatilization state and substantially on char combustion. The subsequent sulfation of KCl in both gas phase and condensed phase to form K_2SO_4 will be occurred, if SO_2 exists in the system [66]. The sulfation rate in the gas phase is significantly faster with occasionally up to complete conversion while that of the condensed phase is considerably slower with about 0.5-2% conversion. However, both rates are controlled by the availability of intermediate SO_3, depending on SO_2 and O_2 but not on H_2O concentration. A vapory K_2SO_4 is also directly released. As further suggested [66], the most in-flight KCl sulfation takes place in the gas phase while any sulfation of deposits likely occurs in the molten deposits. In the case of high water vapor concentration in the gas phase, KOH is formed and it is relatively stable [63]. KOH is yet still very reactive until it reacts to form the even more stable compounds by the reaction with vapor HCl to form gaseous KCl, the sulfation and carbonization to form aerosol K_2SO_4 and K_2CO_3 respectively or otherwise the absorption-reaction by some inorganic matters (chemisorption). The release of volatile alkali species out of fuel is however inhibited in consequence of the absorption onto the reactive char surface [60,61]. Solid K_2O is also an intermediate one among the released K species and it is unstable by thermal decomposition at temperature above 350 °C [70]. Since sodium is generally assumed to behave similarly with potassium and is further an insignificant content in biomass, the specific presence of sodium is always neglected in the account.

Chlorine is well already recognized as the facilitator of alkali volatilization, which can stabilize high temperature gaseous alkali species [59-62]. Its major amount in biomass is released to gas phase as HCl during devolatilization, this HCl is an important contributor to the high temperature corrosion in boiler [34]. Chlorine is hardly found in the non-volatile ash [24]. The KCl release to gas phase in char combustion is therefore determined by the existing chlorine in biomass char.

The main sulfur release in combustion is SO_2 [64]. In the devolatilization step, sulfur is released to gas phase from its primary binding sites in organic molecules, such as proteins or sulfolipids (a class of lipids which possess a sulfur-containing functional group), while sulfur in the form of inorganic sulfates may be partially reacted with char, and become attached to the char matrix or transformed to CaS/K_2S [61]. During char combustion phase, the inorganic sulfur bound to the char matrix is oxidized and released to gas phase as SO_2. However, the released gaseous sulfur species can be subsequently captured by reactive sites in the char, and become bound to the char. To the contrary in the reducing conditions, sulfur is largely converted to H_2S and the sulfation does not occur [51,64]. It was further suggested that the maximum achievable sulfur retention in fuel during heat treatments is largely determined by the content of silicate relative to calcium and potassium in biomass [64]. The interaction of gaseous sulfur species, as well as volatile alkali species, with char even inhibits their releases to gas phase.

The adsorption, mentioned above, and repeated desorption on the char surface allow resultantly the released alkali species to transform into thermally stable char-boned one and/or non-volatiles such as K-silicates, that is an important eutectics responsible for the bed agglomeration of biomass (Eutectics; *a mixture of substances having a minimum melting point*). Part of formed silicate fragments may partially or entirely be solidified in the deposition on convective surface as coarse fly ash from the entrainment of flue gas. In addition silica/silicate particles both from fuel as fly ash [34] and from silica sand (quartz sand); commonly used as the bed material, can absorb alkali hence creating the eutectics on their surfaces by the fluxing reaction [51].

Alkali earth elements, Ca and Mg, are hardly volatilized over the conventional temperature ranges of thermal treatments [51,61]. Therefore they are released mainly in char combustion and in association with the oxide and sulfate (by sulfation) groups, as the fine solid particle [46,53,69]. In some combustion cases of biomass rich in organically bound calcium [22,71-73] or co-combustion [74,75], calcium can cause problems by that it is involved to form the eutectics, while magnesium seems to be relatively more inert in eutectic formation. Calcium is an important bulk component in ash deposits of fouling but it is mostly not responsible for the initiation of deposits.

Phosphorus [76], aluminum [27], iron [12] and silicon [34,69] are mainly associated in oxide, silicate or potassium associated compounds as the fine solid particle with relatively high melting point, over than bed operating temperatures. The noble metals as the trace element in biomass have insignificant influences on the bed agglomeration [24,51], and there are a number of intensive studies on their behaviors and environmental impacts during combustion with a number of biomass [77-81].

The release behaviors of biomass ash forming elements during thermal conversions are influenced significantly by the chemical properties of biomass and operating temperature. The physical state (vapor, gas, molten or solid) and species of released ash have a remarkable effect on the form of ash deposition and on the physical and chemical interactions between the ash constituents and specific surface, for example the convective tube bank in fouling, the furnace wall for slagging and the surface of bed particle in bed agglomeration. Only extensive interactions between the ash forming constituents and bed particle are emphasized.

2.3.2 Inorganic migrations

The deposition mechanism of the ash forming elements from the burning fuel particle to the surface of bed particle to form the deposits as coating can be typically illustrated in Figure 2.3, including partly in Figure 2.1 and 2.2, and summarized: viz,

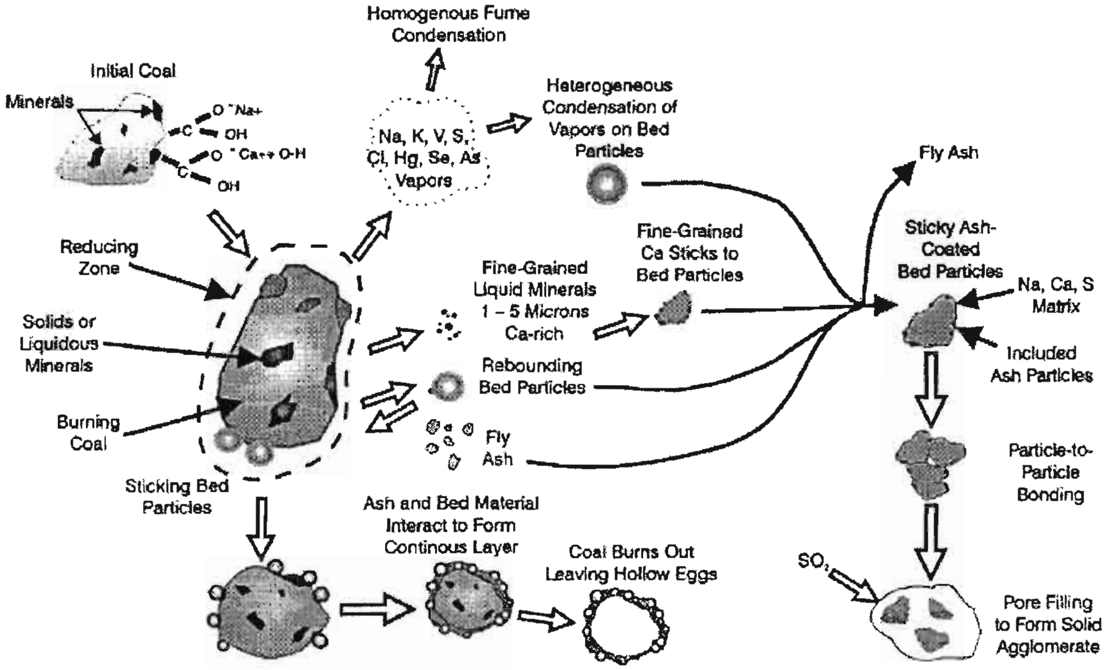

Figure 2.3 Mechanisms of ash-bed interaction [82].

1. Condensation

The submicron fly ash particles in size approximately between 0.02-0.8 μm had been identified in the elemental mass size distribution of K, S and Cl, of the ash matrix elements (Si, Ca, K, P, S and Cl), at downstream of cyclone during fluidized bed combustion of high alkali wood residues [69], and waste sludge mixtures [81]. This indicates that a certain part of the ash species is volatilized and these volatiles prefer nuclei condensation into submicron size as the homogeneous condensation, while the non volatile species remain mostly in the coarser particles (approximately 1-100 μm) [83]. Approximately half of gaseous KCl condenses into the aerosol particles, whereas the other half is found to condense on the coarser particle, or contact surface, as the heterogeneous condensation [69].

2. Adhesion

Aerosols that are originated from both non-volatile ash compounds (below 5 μm) and sublimed inorganic volatile compounds as freely fine particulate matter can be attached to bed particle surface, or relevant surface of constructions, via surface forces (the force that acts across an internal or external surface element in a material body) [84]. This attachment includes adhesion of the molten or solid ash on the surface of burning char particles with bed particle by the random collision, and the coagulation/fusion of coarse ash particles by sintering process.

Some certain compounds firstly formed or located in the proximity of the bed particle surface by above mechanisms can extend their transformation into the core of bed particle [28]. For instance [24,84], the possible decomposition of alkali sulfate in the formed coating layer or diffusion of alkali compounds can be the source of free alkali metals that subsequently form the silicates extending inward the sand grain by the reaction with silicon of quart sand, as the sand particle residence time increases.

3. Chemical reaction

In some case, the gaseous inorganic species are absorbed on the surface of bed particle, or relevant silica/silicate particles of ash, by chemical reaction (chemisorption). The evidences of gas phase alkali reaction with silica sand have been revealed in a literature [85]. The chemical reactions of alkali with silica sand also include the decomposition of alkali sulfates, carbonates and chlorides by reaction with silicon of sand, forming K-silicates.

Building up the coating layer on bed particle, the ash forming elements released from the burning fuels migrates by the processes such as the condensation of volatile inorganic species, the adhesion by random collision of particulates either as freely or on the burning fuel surface, and chemical attack of gaseous ash species. The ash deposition on the bed particle is probably dominated by the combination of them. Subsequent chemical reactions within the coating layer or inward the bed particle may occur. As the continuous deposition on the bed particles proceeds under prolonged operation, the coating thickened up to certain critical conditions (e.g. viscosity or thickness) leads to the formation of permanent bonds between the bed grains, and then agglomerates are formed. The extensive particle bonding mechanisms are therefore mentioned as following, and the relevant sintering mechanisms to the bed agglomeration are focused.

2.3.3 Particle interactions

Interparticle forces (or intergranular force), well defined same as intermolecular forces [86], are the forces of attractions that exist between individual particles in a material. These cause the material to exist in a certain state of matter. Interparticle forces between particles can occur due to a variety of causes. In fluidized bed [87], they are mainly associated to van der Waals interaction, liquid bridge and sintering.

1. van der Waals forces

"van der Waals forces" is a collective term taken to include the dipole/dipole, dipole/non-polar and non-polar/non-polar (dispersion) bonding forces arising between atoms, ions or molecules [88]. As illustrated in Figure 2.4, they are defined for two spherical particles as;

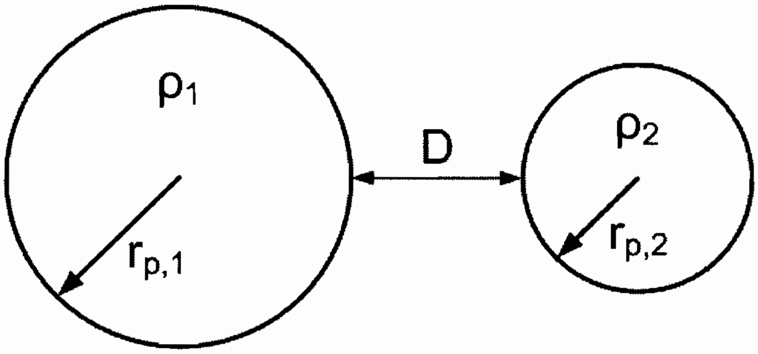

Figure 2.4 van der Waals interaction between two spheres [88].

$$F_{VW} = \frac{A}{6D}\frac{r_{p,1}.r_{p,2}}{(r_{p,1}+r_{p,2})} \qquad (2.1)$$

where A is the Hamaker constant (materials-dependent), r_p is particle radius and D is the surface separation between two particles, which takes a minimum value of the order of the intermolecular spacing. However, some confusion has risen between the expressions for intermolecular and interparticle van der Waals forces. To clarify, a previous study [88] showed the results that van der Waals forces increase in proportion to particle size, and are independent of it if asperity contact is assumed. They further revealed that the spherical particles with asperity contact in diameter of order 100 µm exhibit interparticle van der Waals forces to equal their single particle weight, while to much lesser for particles in diameter of order 1 mm. This is in accordance with common experience; dust particles of about 100 µm or below are commonly found adhering to all kinds of surface and resisting the gravity force, whereas particles of 1 mm or larger will only adhere to surface in the presence of some additional adhesives from the chemical reaction or sintering, for example.

2. Liquid bridges

If the surface of a particle has a film of mobile liquid at point of contact with other particles, or surfaces, liquid bridge will be formed, as shown in Figure 2.5. They are of practical importance in agglomeration processes, driers and in some types of reactors.

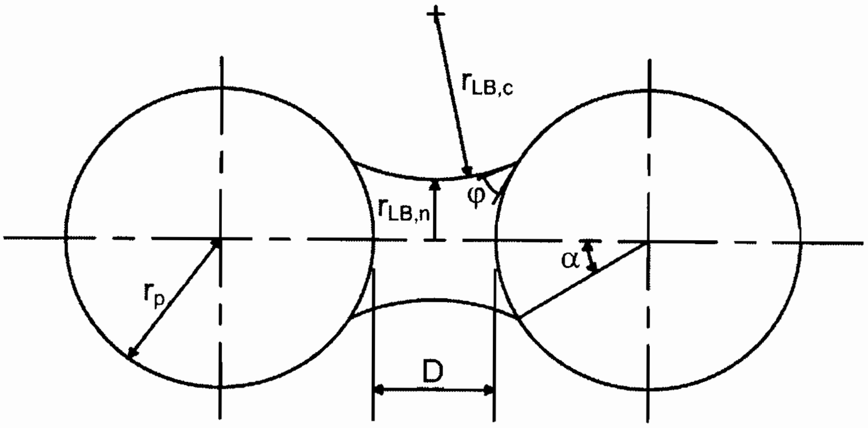

Figure 2.5 Liquid bridge between two equal spheres [88].

Liquid bridges are more complex than van der Waals forces in that they exhibit both static and dynamic forces, i.e. capillary and viscous forces, respectively, and are dissipative of energy [87]. Their magnitudes and forces can be varied by altering the amount of free liquid and its properties, particularly surface tension and viscosity. The static liquid bridge force (capillary force) arises from the sum of the surface tension force and the force arising from the pressure deficit in the liquid bridge.

$$F_{LB,S} = 2\pi r_{LB,n}\gamma + \pi r_{LB,n}^{2}\Delta P \qquad (2.2)$$

where ΔP is the reduction of pressure within the bridge with respect to the surrounding pressure; γ is the surface tension. This reduced pressure is given by according to Laplace equation [89];

$$\Delta P = \gamma\left[\frac{1}{r_{LB,c}} - \frac{1}{r_{LB,n}}\right] \qquad (2.3)$$

The liquid bridges also dissipate energy by viscous force (dynamic liquid bridge force). This force always opposes to the relative movement, unlike the surface tension force, and it becomes appreciable if separation rates are high. The viscous force between two spheres being separated at a rate equal to the relative particle velocity can be determined, to a first approximation, by Reynolds' lubrication equation [90].

$$F_{LB,V} = 12\pi\mu_f r_p^2 V / D \qquad (2.4)$$

where μ is fluid dynamic viscosity, and V is particle-particle relative velocity. The comparison between capillary force and viscous force [88] indicated that viscous force can become significantly for separation rates (V) above approximately 1 cm s^{-1}, if particle separation (D) is small (around 2 μm). However, viscous force becomes comparable with capillary force for separation rates above 1 m s^{-1} at larger separation (above 10 μm) and increasing bridge angle (α).

3. Sintering

The forces arising from sintering are quite different in kind from two above mentioned mechanisms. Sintering is a time-dependent process in which material migrates, due to diffusion, viscous flow or combination of mechanism, to the region of contact to form a neck. That the bed particles are adhered to a sticky ash melt or bonded together by a molten ash layer, as a neck, on their surfaces is characteristic for the silicate and salt systems is described by this sintering mechanism.

In fluidized bed, sintering starts when a neck is formed between bed particles, resulting in the initially porous network in agglomerates. A sinter neck of sufficient size becomes permanent, resisting the breaking due to the movement of solids and gas, and eventually leads to defluidization. In general, the rate of adhesive material migration is a sensitive function of temperature [87]. In viscous sintering, the migration is driven by surface energy minimization (which is relatively independent of temperature) and opposed by viscosity (which is strong function to temperature) [87,91]. This indicates that sintering occurs much faster at higher temperature for high temperature sintering of ash in combustion and gasification. It may be noted that the effect of temperature on sintering is quite different from its effect on dynamic liquid bridge forces (viscous forces), where reduced viscosity by increasing temperature lead to decreasing forces (Eq. 2.4), decreasing energy disruption in collision and decreasing probabilities of agglomeration and growth (at which the fractional liquid loading remains constant).

In the previous studies on the sintering behaviors of ashes from coal, peat and biomass under FBC conditions [92-97], three mechanisms are considered to be significant viz;

- Partial melting
- Viscous flow
- Chemical reaction

They depend significantly on the ash chemical and mineralogical composition, the temperature history of the ash particles and gas components.

Partial melting sintering (Reactive liquid sintering or diffusion sintering)

It is a sintering in the presence of a reactive non-viscous liquid consisting of molten alkali salts, or other crystalline materials, where the solid phase is partly soluble in the liquid at the sintering temperature. The amount of liquid determines the neck formation. Decreasing temperature below their solidus temperatures (the temperature at which melting of a substance begins) gives crystallization of bonding agent and densification of agglomerates. It was suggested that this mechanism is likely predominant for fuels with high alkali, sulfur and chlorine ashes [51].

Viscous flow sintering (Viscous sintering or Vitrification)

It is sintering due to viscous flow of a vitreous silicate phase. When a silicate ash is heated above its solidus temperature, it becomes highly viscous liquid. Due to its high viscosity, the liquid remains viscous on rapid cooling below the solidus temperature [51]. The presence of silicate compounds in ash deposits on either bed particle or silicate/silica fly ash particle gives rise to the formation of the liquid layer of silicate eutectics on the surface of the particles under sintering temperature. Flowing of this viscous molten layer forms a neck between adjacent particles. Upon cooling, this neck is solidified to a glassy phase.

The dependence of this mechanism on properties of fly ash particle for typical fly ash agglomeration is given by Frenkel equation [98];

$$X^2 = \frac{3 \cdot r_p \cdot \gamma \cdot t}{2 \cdot \mu} \qquad (2.5)$$

where X^2 is equivalent neck contact area; γ is surface tension of the vitreous phase and t is time. Neck growth (X(t)) is controlled by time and viscosity, which is varied significantly with temperature and chemical composition of material. Sintering is inhibited by the crystallization on the surface [51].

Chemical reaction sintering

This is a sintering due to reaction between the particles or the particles and the gas, to form a third compound binding the particles together. This mechanism was found to be responsible for the sintering of coal and biomass ashes rich in calcium [23,50]. It is caused by the carbonation and sulfation of CaO with CO_2 and SO_2, respectively, resulting in the particle to particle bonding via thermodynamically stable $CaCO_3$ and $CaSO_4$ crystals, respectively. These mechanisms can be relevant to the deposit hardening and bond strengthening, where ash is firstly formed on/between particles and then reacts in the post combustion zone in CO_2/SO_2 rich environment. Sulfation of CaO is stable over a wider temperature range (carbonation: 600-800 °C, sulfation: above 500 °C). Calcium sulfate bonding was mentioned to be important in a deposit hardening mechanism when firing coals rich in organically bound calcium and sulfur or when adding finely ground limestone for sulfur capture [23,34]. Submicron CaO particles deposit on the surface via thermophoresis (the migration of a particle in response to a macroscopic temperature gradient) and then become sulfate by the reaction with SO_2 or SO_3. Locally low oxygen partial pressure can additionally give rise to the formation of $CaSO_4/CaS$ eutectic (eutectic point 830 °C) [34].

2.3.4 Summary of mechanistic bed agglomeration

A summary of the mechanistic bed agglomeration processes including sub processes has been provided in the state-of-art [99] and pictorially illustrated only for the bed particle agglomeration in Figure 2.6.

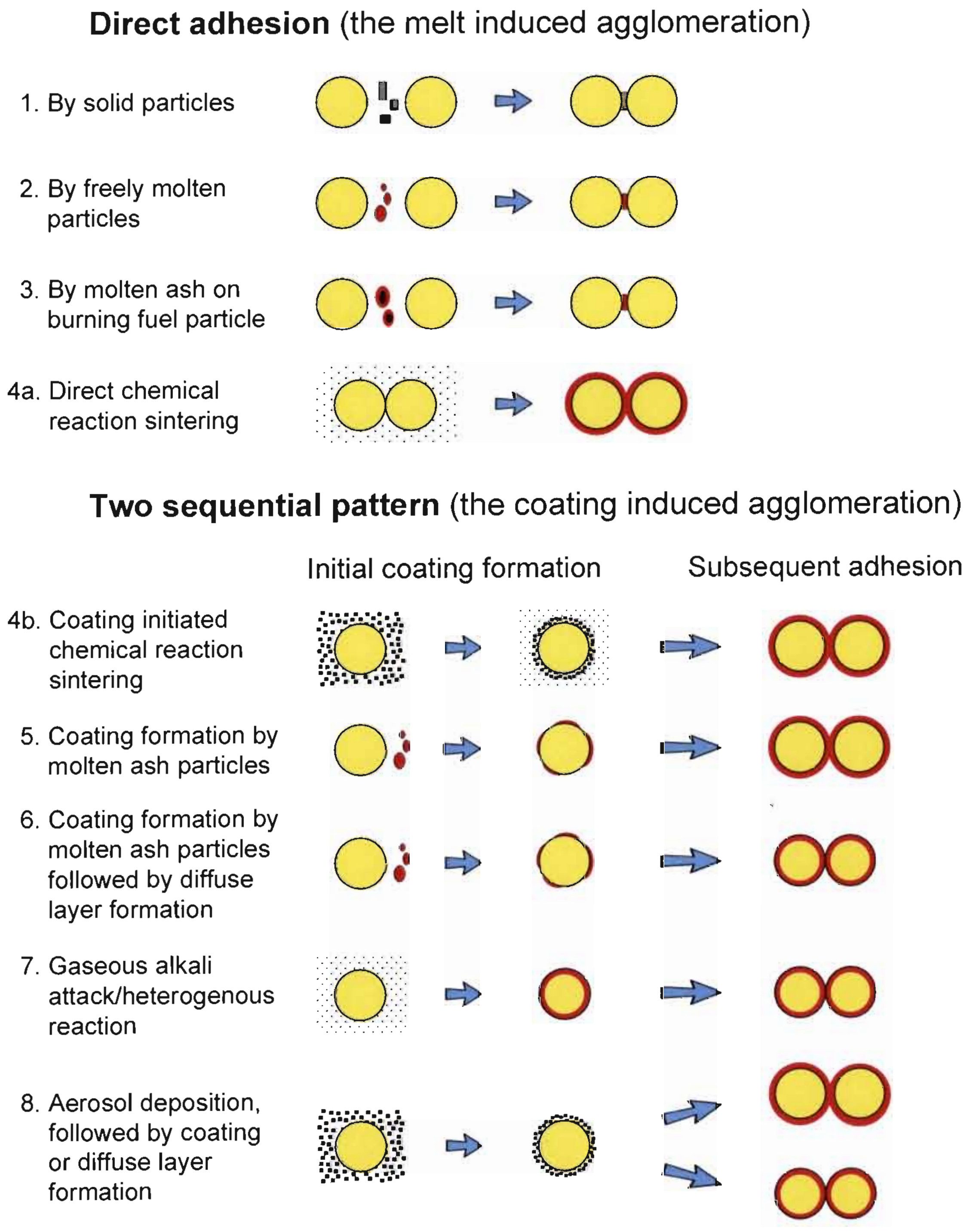

Figure 2.6 A summary of the different proposed bed agglomeration mechanisms [99].

The mechanisms can be divided into two main categories;

- Direct adhesion, as described in 1-4a
- Two sequential pattern initiated by the coating formation, as described in 4b-8.

The formation of coating layer can be initiated by: chemical reaction sintering; molten ash particle; chemical reaction with gas phase alkali species; and deposition of particulate matter followed by either coating formation or chemical reaction with bed particle. The molten ash fraction can be released in the form of the freely molten particle and the molten layer on fuel particle.

The two sequential processes, specifically named the coating induced agglomeration [72], including the direct chemical reaction sintering (4a) have been suggested to be dominating in the presently mechanistic bed agglomeration. Direct adhesion by the molten ash as freely and on burning fuel particle, dubbed as the melt induced agglomeration, have also been suggested and seem less likely, while the direct adhesion by solid ash particle is seemed unlikely.

Although the differently suggested mechanisms and sub processes (Fig. 2.6) may be dominating to bed agglomeration for different fuels and operating conditions, the molten phase formation seems to initiate the bed agglomeration and the coating induced agglomeration is likely dominating mechanism, particularly for biomass fuels. The formation of low melting point ash consisting mainly of alkali salts or alkali silicates is significantly dependent upon the ash chemistry and temperature. The gas phase reaction and/or aerosol deposition seem to be further important in some biomass for enhancing the melt formation and accelerating the defluidization [51,85].

2.4 Influence factors on bed agglomeration

2.4.1 Ash chemistry

It shows clearly that the ash chemistry plays an important role, as largely described in section 2.2. The most undesirable inorganic elements in biomass are alkalis in combination with sulfur, chlorine, phosphorus and silicon. Calcium causes problem in some cases of combustion of a fuel with a rich in organically bound calcium, or co-combustion of these fuels with a high sulfur fuel. The bed agglomeration is found to be a strong function of the level of these elements in fuel [19,69,82,100]. The large amount of these elements by either inherence in fuel, impregnation by additive impletion or fuel treatments can facilitate the bed agglomeration [20,24,101-102]. A high amount of volatile potassium in biomass also enhances the formation of melts due to the chemical reaction. Chlorine facilitates bed agglomeration due to the low melting point of chlorides and further provides the chemical reaction to form the eutectics. The same tread goes for sulfur. Sulfates originated from the reaction of alkali with SO_2 have very low vapor pressure and easily condense on surface, such as bed particles, to form the liquid layer. Both silica/silicate particles which absorb alkalis forming the low melting point compounds as coating layer and even originally released silicate particles are capable to sintering.

2.4.2 Bed material

The chemical reactions between bed material and ash are also an effect. It becomes clear from presently reviewed literatures that silica sand, commonly used, is not a suitable bed material in FBC and FBG of high alkali fuels, due to further formation of eutectics on its surface by the chemical reaction of silica with alkali. Alumina sand does not react with the ash and make possible higher bed operating temperatures [27,103]. Pure hematite is reported as the most suitable bed material in combustion of high alkali biomass [104]. Dolomite and limestone seem to be also unsuitable [105] and limestone as bed materials shows a high tendency to bed agglomeration [19]. The extensive reviews of different bed material as a practical prevention option of bed agglomeration will be mentioned later.

2.4.3 Fluidization condition

Defluidization by bed agglomeration is widely accepted as a result of competition between the strengthening adhesion of bed particles by the molten ash formation and sintering process, and the breaking of agglomerates due to mechanical forces of collision induced by the fluidization [82]. The movement of bed particles is also important because of the corresponding transfer of heat, and it is significantly dependent upon the bed operating condition. An ineffective/obstructed bed particle movement can easily lead to local bed temperature derivations, resulting in a further and potentially self-enforcing obstruction of particle movement and subsequent hot spots in bed, that promote the local bed sintering. This is a good reason why the bed operating variables have an important role in the bed agglomeration process.

The contributions of the bed operating variables on the tendency of bed agglomeration have been studied in the controlled fluidized bed reactors and described in term of the agglomeration temperature (T_{ag}) [106-108] and the defluidization time (t_{def}) [108-111]. The temperature at the start of defluidization during an increase or step up of fluidized bed temperature by either external heat sources or conditions, in which a certain amount of ash is early contained in bed by combustion or gasification at a given ashing temperature, is termed the agglomeration temperature. The definitions of the defluidization time are variable. The time between the commencement of segregation-defluidization and agglomeration can be termed, and is normally represent the time available to restore the operating conditions, such that agglomeration is prevented [108]. The time interval between the start of fuel conversion processes and the complete defluidization is also termed. The contributions of operating variables can be summarized in Table 2.6.

Table 2.6 Contribution of operating variables to bed agglomeration tendency

Contribution	**Tendency; represented by**	
	T_{ag} (or T_S)	**t_{def}**
Temperature	- (Ashing)	+ (Combustion)
Heating rate	0	N.T.
Fluidizing air velocity	-	-
Bed particle size	+	+ and -
Fuel particle size	-	0
Static bed	+	N.T.
Ambient condition (Air to fuel ratio)	0	0

where the defludization by bed agglomeration is accelerated by an increased magnitude of a variable is described by the plus (+), the opposite trend is referred to the minus (-), 0 is a sign of unobtrusively effect and N.T. is no experimental investigation. The higher tendency implied by lower bed agglomeration temperature and shorter defluidization time can be caused by lower ashing temperature, higher combustion temperature and lower fluidizing air velocity, for example. The major differences between combustion and gasification of fuel with high sulfur are that sulfates do not form in gasification and the much higher fuel particle temperature is in combustion. Sulfation, as well as carbonation, can facilitate the bed agglomeration. The air to fuel ratio which represents the effect of these ambient atmospheres, however, does not show clearly an influence.

The tendency for the colliding particles to stick together or the agglomerates to break apart is directly proportional to the particle adhesive properties and to the area of contact, and inversely proportional to particle momentum [15]. The formers are affected substantially by the chemistry and physic of particle, while the later is reflected to the bed hydrodynamics of fluidization.

2.5 Laboratory prediction

A number of laboratory methods are performed in order to assess the slagging, fouling and agglomeration propensity of a fuel. Some methods show low accuracy in their predictability and some give unclear support in the prediction, while some are not ever used to predict the bed agglomeration. They suffer from the fact that ash produced in laboratory is different substantially from actual ash generated in FBC and FBG. It is due to many influence factors in ash formation that can not be adequately simulated in the laboratory. These respect importantly to the ash partitioning, gas-solid reaction, and absorption and condensation of vapor alkalis. The predictive value of below mentioned laboratory methods is therefore hard to access.

2.5.1 Fuel analyses

Indices derived from the ash chemical composition

Several defined empirical indices are used commonly to assess the propensity of fireside ash-related problems during combustion of coal and biomass. They are formulated by only using the basic ash chemical composition derived from the standard methods of ash analyses. They include, for instance, Alkali index (AI) [112], Base-to-Acid ratio ($R_{b/a}$) [113] and Bed agglomeration index (BAI) [105]. These indices have correlated the ash composition to predict the standard deformation and fusion temperatures of coal ashes [114].

$$AI = \frac{kg(K_2O + Na_2O)}{GJ} \tag{2.6}$$

$$R_{b/a} = \frac{\%(Fe_2O_3 + CaO + MgO + K_2O + Na_2O)}{\%(SiO_2 + TiO_2 + Al_2O_3)} \tag{2.7}$$

$$BAI = \frac{\%Fe_2O_3}{\%(K_2O + Na_2O)} \tag{2.8}$$

Alkali index expresses the quantity of alkali oxides in the fuel per unit of fuel energy. The maximum alkali input, in kg/GJ, into the boiler is divided into: 0-0.17 does not give problems, 0.17-0.34 become problematic and need to frequent outages and lower furnace exit temperature, while >0.34 give certain to unmanageable problems. The label for each compound in Base-to-acid ratio and Bed agglomeration index makes reference to its weight concentration in the ash. Of the fuel ash, the increasing $R_{b/a}$ values indicates the increasing fouling tendency while the decreasing BAI represents the increasing bed agglomeration problem. These indices are fuel specific and can not definitely take the effects of the boiler operating parameters and the complex behaviors of inorganic elements during conversion into consideration. Nevertheless, they can be the approximately secure basis for decision making.

Ash thermal behaviors based on chemical fractionation with TPEC

Based on the chemical fractionation analysis in section 2.2.2, the ash forming elements are divided into two parts, "a mobile part" and "an immobile part" [24]. The mobile part consisting of water and ammonium acetate leachable elements are supposedly in the form of volatile and submicron aerosol during heat treatments, while the immobile part comprising of acid leachable and residue elements are present as the coarse ash found in bed. Their individual contents of mobile and immobile parts give more information about the propensity of fouling and bed agglomeration, respectively, than total content. These chemical fractionation data are then used to establish the ash melting behaviors, as a function of temperature, based on the thermodynamic multi-component, multi-phase equilibrium calculations (TPEC) [24]. This procedure is based on Gibbs' free energy minimization on the database of elements and chemical reactions. The estimated initial melting temperatures of these melt profiles are marked and then verified with the agglomeration temperatures from actual fluidized bed experiments [115,116] and the evaluated melting temperatures based on SEM-EDS + phase diagram analyses of coating/neck materials in agglomerates [24]. Their predictability shows fairly in accuracy. It was further revealed that the chemical fractionation analysis can yield 5-15% higher total alkali concentrations than the analysis of ash prepared at 600 °C [51].

TPEC method is useful to enhance understanding of the complex ash behaviors. However, TPEC's small imperfection is thermodynamically based calculation procedure that assumes the system to be in equilibriums, while the real process may not reach [51] and, importantly, the better quality of database in chemistry and thermodynamics is required for the higher accuracy of prediction.

Agglomeration and deposition problems are sometimes reported even though the fuel analyses indicate an unproblematic fuel [51]. It may be that the fuel quality varies beyond what is indicated by even frequent fuel analyses. Therefore, the homogenization of the feedstock is needed and may be worthwhile in order to limit the risk of frequent agglomeration and deposition problems due to such fluctuation in fuel quality.

2.5.2 Static methods

The methods below are the conventional and developed laboratory procedures based on analyzing the laboratory ash in order to characterize the ash thermal behaviors.

ASTM standard ash fusion test

Standard ash fusion temperatures are determined according to ASTM-D1857. This well-known method is developed to access the slagging propensity of coal and coke in stoker type boilers. It is based on visual observation on the deformation of an ash cone during heat treatment. The characteristic temperatures include Initial deformation temperature (IDT), Softening temperature (ST), Hemispherical temperature (HT) and Fluid temperature (FT). However, bed agglomeration problems sill occur despite the relatively low temperature in fluidized bed during conversion below the ASTM initial ash deformation temperature. The ashes substantially melt at 200-400 °C below the visually determined initial deformation temperature [117]. The melting process is not the shape phenomena, but the gradual process [114]. The characteristic temperatures of this method are affected by the size and geometry of ash cone, fineness of ash, heating rate and atmosphere.

Simultaneous thermal analysis (STA; TGA-DTA and TGA-DSC)

TGA, DTA and DSC are termed as Thermo gravimetric analysis, Differential thermal analysis and Differential scanning calorimetry, respectively. These methods are conventional analyses to study the ash thermal behaviors, such as the melting and volatilization behaviors of ashes, or to study in advanced applications such as characterizing the sorbents for alkali capture and the reactions between bed materials and alkali salts [118]. They are based on the simultaneous measurement of heat effects in ash samples (endothermic or exothermic processes) and weight loss. These methods can be useful to determine the initial melting temperature and to estimate the volatilization of elements. However, interpretation of the results without the knowledge of mineralogical composition of ash is a very difficult task due to many processes that can occur simultaneously in ash (decomposition, volatilization, evaporation, melting, and reaction with gas) and many disturbing effects (the combustion of residual carbon, absorption of gases and reaction of artefacts from low temperature ashing) [51]. Therefore, these methods do not clearly support the bed agglomeration.

Thermo-mechanical analysis (TMA, or shrinkage method)

This method is based on the measurement of volume changes and softening of ash samples during heat treatments to determine the sintering tendency, initial melting temperature and initial sintering temperature. It has been used to identify the initial sintering temperature of spent bed material and found well correlation between this temperature and temperature where agglomeration started in circulating fluidized bed (CFB) combustion of high sodium low rank coals [119]. The initial sintering temperature from TMA is the same as temperature where melting started in TGA-DTA, so that partial melting is probably the sintering mechanism, however it is substantially less than the ASTM initial deformation temperature. Additionally, the sintering rate of ash has been correlated to the decreasing rate of pressure drop across an ash pellet sample in a tube like holder for some certain time during heat treatments. The sintering changes the porosity of ash pellet by shrinkage [120-121]. This method has been applied for coal ashes only. The dilatometer is a scientific instrument that also employs this method.

Compressive strength measurement

This laboratory method is applied for determining the sintering tendency of ashes based on the compressive strength test on heat-treated ash pellets. The pellets of laboratory ash samples including the mix of ash with bed materials or additives [34,93-94,122] are heat treated at given temperatures and conditions. After cooling the crushing strength of pellets is measured. The temperature of treatments which the corresponding crushing strength deviates from the base line strength is then referred to the initial sintering temperature. This method is very useful for revealing the mechanism behind agglomeration and comparing different fuels for their sintering and agglomeration propensity, but it does not give absolute initial agglomeration temperature due to many other important factors beside ash chemistry.

High temperature light microscope (HTLM)

This advanced practical method is used to evaluate the melting quantification of biomass ash on the basic of the change in light transparency during melting [123]. As a part of the ash is molten, it becomes transparent. The transparency change on the plate area of spread ash is detected by the advanced image analyses and then converted to the melt fraction, relative to the area fraction. This method detects the onset of melting of ash samples significantly lower than STA and fusion test [124]. HTLM method is used to study the characteristics of ash fusion and deposit formation, but it is not ever applied to predict the bed agglomeration.

Heat treatment and subsequent SEM analysis

The common heat treatment of mixtures of ashes and bed materials is used to study their agglomeration characteristics in associate with Scanning electron microscope (SEM) [21,27,125-126]. The agglomeration temperatures determined correspond very well with experience in lab scale FBG [21,27]. This test can be used to obtain a first indication and comparison of the agglomeration propensities of the mixture of bed material and ash, but it does not give the absolute results of initial agglomeration temperature, again due to many other important factors beside ash chemistry.

Flow properties heat treated ash

A method is developed to evaluate the agglomeration propensity of ash from petroleum coke, based on the hot angels of repose and internal friction [127]. When desired temperature in a vertical stainless steel cylindrical heater is reached, the ash is allowed to flow from the cylinder through a small hole in the bottom. The repose and internal friction angel are then taken as an indication of the flow ease of ash at a given temperature. These results have been compared to the results from compressive strength method and SEM analysis of deposit from full-scale FBC to determine the sintering mechanisms. This allows determination of the ash agglomeration mechanism.

As mentioned, the ash prepared in laboratory by standard methods can not be representative in the attributes of actual ash formed in fluidized bed. Ashing temperature above 600 °C generally specified in the standard methods gives significant loss of alkali, artificially increasing the fusion temperature [51,53]. Although a study on ash behaviors has used ashing procedure at 350 °C [53], the low temperature ashing with long oxidation times gives rise to the formation of artifacts from organically bound inorganic elements which are not normally found in conventional biomass ash; e.g. potassium nitrate and perchlorates [34].

2.5.3 Dynamic methods

By the above reasons, the test in the controlled laboratory scale fluidized bed facilities seems to be the best laboratory method for the characterization and prediction of the bed agglomeration. From literatures, there are four methodologies to determine the tendency of bed agglomeration during FBC and FBG, which is reported in Table 2.6. The onset of defluidization and bed agglomeration is mainly detected by bed pressure monitoring.

- A certain amount of biomass is combusted at a fixed temperature (ashing), subsequently the biomass feeding is stopped and the bed temperature is increases by the external heat sources until the agglomeration occurs (sudden drop in pressure and sudden change in temperature) [22,106-107,128]. Bed agglomeration temperature, T_{ag}, is then recorded.

- Biomass is gasified in the bed at a fixed temperature for a certain time while the fuel feed rate and airflow are kept constantly. Subsequently the bed temperature is raised stepwise at certain temperature interval and time by the external heat sources until agglomeration occurs [51], and T_{ag}, is then recorded.
- A fixed amount of biomass is combusted batchwise at a constant temperature with the bed containing a fixed weight of bed material. After the fuel batch is depleted eventually, the test ends, the spent bed is then discharged and the reactor is emptied. A new experiment is then carried with the fresh bed material at a stepwise higher temperature. These procedures are repeated until the sign of defluidization is observed [51], and T_{ag}, is then recorded.
- At fixed operating conditions (temperature, airflow, bed particles size, mass of bed material, air to fuel ratio, etc), the steady state combustion of biomass is carried out until the signs of beginning defluidization are observed or complete defluidization is reached [109-111]. Defluidization time, t_{def}, is then recorded.

All above laboratory methods, mentioned in this section, for the prediction of bed agglomeration and their predictabilities are then summarized in Table 2.7.

Table 2.7 Summary of the laboratory prediction methods

Method	Method description	Predictability	Reference
Fuel analysis			
Indices	Chemical compositions of biomass ashes are determined by standard methods and then are correlated into the empirical indices.	- It is used mainly as the criteria for decision making	[34,72,112-113]
Chemical fractionation with TPEC	Increasingly aggressive solvents leach the same sample in a series of three sequential leaching, producing four samples for characterization. TPEC is used to estimate the ash behavior by which the leached compositions are the input data.	- Predictability is moderate.	[24,47,115-116]
Static methods			
ASTM standard ash fusion test	Four characteristic temperatures are identified according to standardized description (Visual observation of ash cone during heat treatment in electrical furnace).	- It predicts too high agglomeration temperature and the predicted trends are false as well.	[34,46,50,114]
STA	The heat effects and the weight loss of the ash samples are measured simultaneously. Detectable processes are melting, decomposition and chemical reactions.	- The STA measurements do not clearly support the melt formation and the bed agglomeration.	[50-51,118,124]
TMA	The change in volume or length of a pulverized ash sample pellet is measured during heating. Shrinkage indicates sintering or melting.	- This method is superior to the ash fusion test and shows fairly well agreements in the prediction for coal ashes.	[102,119-121]
Compressive strength	The ash sample is pulverized and palletized to the cylindrical pellet and then heated in a control condition. After cooling, the ash pellets are crushed in standard compression-testing equipment and the compressive strength is taken as a measure of the degree of sintering.	- This test is good for predicting the agglomeration trends except for the case at which interaction between ash and bed material takes place. - It is very useful to reveal the mechanism behind agglomeration.	[34,92-93,122]
HTLM	The ash sample spread over the flat plate is heated at a specific condition. The melted fraction is relative to the area fraction that becomes transparent.	- To ever compare the onset of melting temperature with STA and standard fusion test, but not used to predict the bed agglomeration temperature.	[123-124]

Table 2.7 Summary of the laboratory prediction methods (Continue)

Method	**Model description**	**Predictability**	**References**
Heat treatment and subsequent SEM analysis	Mixtures of ashes and bed materials are heated in an oven for a certain condition and period. The heat treated ash samples are then analyzed chemically and morphologically by SEM.	- Not used to predict bed agglomeration temperature. - Good to reveal the mechanisms behind agglomeration/sintering.	[21,27,125-126]
Flow properties heat treated ash	Ash is heat treated in vertical cylinder. When desired temperature is reached, the ash is flowed to the small hole at bottom. The repose and internal friction angels are measured as an indication of the flow ease of ash.	- No temperature is predicted and the predictability of this method is not very promising.	[127]
Dynamic methods			
Bubbling Fluidized bed combustion facilities	Combust a certain amount of fuel at a fixed temperature (ashing) and subsequently stop fuel feeding and rise the bed temperature externally until bed defluidization occurs, referring to the bed agglomeration temperature.	- This method includes interactions between ash and bed materials. - Bed agglomeration temperature is determined.	[22,106-107,128]
Bubbling Fluidized bed gasification facilities	Biomass is converted to ash at low bed temperature in gasification. Subsequently bed temperature is raised stepwise by external heater until bed defluidization occurs. The fuel feed rate and air flow rate are kept constantly.	- This method includes interactions between ash and bed materials. - Bed agglomeration temperature is determined.	[51]
Bubbling Fluidized bed combustion facilities	A fixed amount of fuel is combusted in a fixed mass of bed material at a constant temperature. After fuel batch is depleted, the bed is discharged and the reactor is emptied. A new experiment is then carried with the fresh bed material at a stepwise higher temperature. The procedures are repeated until sign of bed agglomeration is observed.	- Bed agglomeration temperature is determined.	[51]
Bubbling Fluidized bed combustion facilities	Steady state combustion at constant bed condition (air velocity and bed temperature) is proceeded until eventually bed is defluidized.	- Defluidization time and fuel consumption are determined.	[109-111]

2.6 Bed diagnostic tool

The conventional monitoring in thermal based fluidized bed applications or otherwise is principally based on the bed pressure, either local or different, and temperature measurements. In normal operation, bed pressure drop which directly related to the mass of bed can be described by the balance between the net gravitational force and the friction force exerted by fluid, as mentioned in Chapter 1, while in abnormal condition of bed during agglomeration, the adhesive force between bed particles is taken into consideration in the above force balance [18]. The isothermal condition inside fluidized bed is due to the intense in-bed heat transfer as a consequence of turbulent bed mixing. It seems clearly that the bed pressure indicates the better perception to any abnormal bed conditions [82,129]. An analysis method developed uses the short term predictability of time series of local bed pressure fluctuations to detect early changes in the hydrodynamic states of bed, named EARS (Early Agglomeration Recognition System) [130-131]. The incipient bed particle agglomeration causes changes in the hydrodynamics. This analysis gives the time period between the detection of a significant change in the hydrodynamics and the moment when the bed is defluidized, sufficiently large to take preventive measures, i.e. increasing gas velocity. This method has been further evaluated into the industrial scale fluidized bed boilers [132].

2.7 Measures for prevention

Some measures to prevent or delay bed agglomeration, and other ash-related problems, for an existing installation include viz:

- Alternative bed material,
- Chemical additive,
- Co-firing, with coal or forest wood residue,
- Fuel pre-treatment,
- Fluidized bed operation control,
- Bed management,
- Other measures

2.7.1 Alternative bed material

According to section 2.4.2, a number of alternative bed materials have been studied their bed agglomeration characteristics to serve as a practical option of the bed agglomeration prevention. Some less Si and Si free bed materials show inapplicable or the promotion on bed agglomeration, while many can reduce evidently the bed agglomeration problems. They include alumina, granite, gabbro, corundum, mullite, hematite ore, pure hematite, feldspar, magnesite, dolomite, limestone, bauxite, calcined sillimanite, calcite, ceramsite, GR GRANULE, lignite ash with high Al_2O_3 content, pure CaO, $CaSO_4$ and $CaCO_3$, blast-furnace slag and patented AGGLOSTOP^{TM} [19,25-28,51,73,100,103-105, 122,133-136].

The Al species bed materials for instance alumina, bauxite, corundum and ceramsite (a clay mineral rich in Al_2O_3) delay evidently the bed agglomeration since they do not interact chemically with biomass ash to further form the eutectic compounds. However, the coatings of silicate compounds on the surface of bed particles, as an evidence of the ash deposition, is still existed in the previous illustrative results [27,103], and possibly leads to defluidization. The lignite ash with high Al_2O_3 content is also inert to bed agglomeration. The use of alumina and mullite (aluminosilicates clay) in stead of silica sand has once been found that it does not change the agglomeration temperature [51].

The Fe species bed materials as hematite ore, pure hematite and blast-furnace slag show the potential mechanism of prevention. If sufficient Fe_2O_3 is present in the bed material, or otherwise in the ash of residues burnt, the agglomeration rate may be reduced since Fe_2O_3 may react preferentially with the alkali and present in bed as the fine particle of the eutectic mixtures with relatively high melting temperatures, in occasionally excess of 1135 °C [104-105].

The different effects of alkali earth based bed materials, such as magnesite, dolomite and limestone, on bed agglomeration are reported, but they are all unsuitable to be the bed particle [105]. Their high attrition rates which are several times higher than that of silica sand do not make possible to maintain sufficient bed inventory. Limestone particle show a high tendency to agglomeration due to a decrease of ash deformation temperature [114], while dolomite can extends the operation by several hours, due to the formation of high melting point Mg rich mineral phase in ash.

As mentioned above, the bed agglomeration is determined by the two competitive processes i.e. physical and chemical. Although the uses of different bed materials in stead of silica sand can inhibit efficiently the chemical reaction of ash with bed material, the physical transformations of ash (condensation or melt adhesion) are an influence and become dominating the bed agglomeration process. FBC or FBG with some bed materials is still eventually ended at defludization, or even increase other ash related problems.

2.7.2 Chemical Additive

The identified mechanisms of additives to reduce or delay bed agglomeration in FBC and FBG are revealed viz [51];

- Physical absorption: the molten phases are absorbed within porosity of additive particles.
- Chemical absorption: the problematic elements are absorbed chemically into the stable compounds with high melting point. This effect includes the absorption of the molten phases, fixation of volatile alkali species and the removal of sulfur prior to reaction with ash to form the compounds with low melting points.
- Powdering: the additives generate the molten phases which act less sticky to surface of bed and ash particles in order to reduce the rate of bed agglomeration.

The additives that at least in some cases offer the above positive effects are listed in Table 2.8, including the principal components.

Table 2.8 List of additives preventing bed agglomeration

Effect	Additive	Principal component	Reference
Physical absorption	Gibbsite	$Al(OH)_3$	[51,137]
	Calcined dolomite	$CaO.MgO$	[138]
	Sintered magnesite and Periclase	MgO	[51]
	Calcined alumina	Al_2O_3	[139]
Chemical absorption	Coal ash	Fe, Ca rich	[51,134]
	Aluminosilicates (Clay minerals)	$Al_xSI_yO_z$ (Al_2SiO_5 for Sillimanite)	[51,119,137]
	Bauxite	Rich Al_2O_3 + less SiO_2	[25]
	Kaolinite,Kaolin	$Al_2O_3.(SiO_2)_2.(H_2O)_2$	[82,137-138,140]
	Dolomite	$CaMg(CO_3)_2$	[51,137-139]
	Emathlite		[141]
	Diatomaceous earth (Diatomite)	SiO_2	[142]
	Limestone, Calcite	$CaCO_3$	[25,138]
	Magnesite	$MgCO_3$	[25]
Powdering	Coal fly ash	Ca, Mg rich	[139]
	Dolomite	$CaMg(CO_3)_2$	[143]
	Aluminosilicates	$Al_xSI_yO_z$	[51,140]
	Pure magnesium oxide	MgO	[114]
	Pure calcium oxide and carbonate	CaO, $CaCO_3$	[114]
	Calcined dolomite	$CaO.MgO$	[51]

It has been suggested that bauxite, kaolinite, kaolin (the rock that is rich in kaolinite) and emathlite (a rich Al additive) are promising alkali vapor sorbents. Aluminosilicates as clay minerals including kaolin seem to be preferable for the reaction with the molten phases. Gibbsite and porous calcined alumina reduce the available melt by soaking the molten species. Limestone and dolomite are the common commercial sulfur capture additives. Noticeably, dolomite can further affect the combustion of some biomass to form Ca-Mg rich layers with high melting points and these layers protect the bed particles from agglomeration [143]. In contrary, limestone can have the adverse effects in that it facilitate the bed agglomeration and increase problems of fouling and erosion in biomass fired fluidized beds by decreasing the ash deformation temperature [114]. The use of additive to reduce the bed agglomeration problem is considered primarily a selective prevention method since it is a conventional chemical treatment for FBC and FBG of coal and biomass [11-12].

2.7.3 Co-firing

Co-firing to achieve a higher ash melting temperature or lower alkali input into the system is to blend a problematic biomass with coal, forest wood residue or waste sludge. It includes co-combustion and co-gasification. This prevention method is considered as a good alternative to using additives. The mechanism primarily considered to be responsible for the positive effect of co-firing is that a major part of alkali from biomass is bound chemically into the high melting compounds found in co-fuels, such as aluminum silicates, magnesium aluminum silicates or iron species of coal and wood [12,113,144]. In addition, the low content of alkali and chlorine in coal gives the dilution effect so that the volatile alkali and chloride species may not condense due to resultantly very low vapor pressure.

The general criteria for the pairing of biomass-biomass, biomass-coal or biomass-waste fuel (sludge) in co-firing are given below [51],

- Co-firing of fuels having alkali and high chlorine concentrations should be avoided. Chlorine causes the high mobility of alkali during fuel conversions.
- Co-firing of fuels rich in KCl and high sulfur (some coals) should be avoided. Sulfation of KCl in gas or molten phase is the main reason.
- Co-firing of high alkali and high silica fuels should be avoided. The alternative bed material (not silica) is preferred as an optional solution.
- Co-firing of high alkali fuels with high magnesium or iron fuels should be considered.

The examples of successful co-firing experiences include; (i) the combustion of lucerne-coal and olive flesh-coal provided the stable operation possible for entire duration of experiments (10 hrs), instead of less than 30 min for their own biomass combustion [144]. Blending these fuels with coal also increased significantly their initial bed agglomeration temperatures, and further obtained 80% of sulfur retention in the bottom ash; (ii) Wood and rice straw were blended during combustion and this mixed fuel could delay bed defluidization by at least 50% fraction of wood [113]; (iii) The bed agglomeration risk seemed low, indicated by the increase of bed agglomeration temperatures, when straw was co-combusted with sewage sludge [51].

The ash characteristics of biomass and co-fuels, as another biomass, wood, coal or waste sludge, indicate a first sign for co-firing that cause more or less trouble than either of biomass used separately. The thermal behaviors of mixed ash analyzed by laboratory methods may provide the further possibilities of co-firing. However, the possible and appropriate combination of biomass with co-fuels needs further intensive experimental investigations in fluidized bed furnaces.

2.7.4 Fuel pre-treatment

The removal of problematic inorganic materials described largely in section 2.2.2 is an effective option of prevention [51,58]. The different inorganic materials provide the different effects on fluidization. Too large fraction of coarse particle impacts negatively to the quality of fluidization. The inert extraneous discrete particles such as soil, sand, pebble, pieces of iron or tramp materials, including coarse char particles under slow reaction conditions, can accumulate in bed to a concentration that limits the local bed circulation and subsequent heat transport and eventually destabilize the fluidization properties. Such destabilization easily leads to hot spots in bed that promotes the local sintering due to the obstructed heat transport. The major part of the whole bed may be involved in this irreversible process within a short time. These extraneous particles can also have the participation in sintering [51]. Mechanical breaking, crushing, washing, sieving, magnetic separation or fluid dynamic separation may be the solutions of separating out of fuel and bed material. The attached sand and soil can be removed more easily by sieving, if fuel is dry.

The inherent inorganic material being the main cause of bed agglomeration can be extracted out of biomass by leaching [24,45,58]. The biomass fuels leached by hot water show clearly the less problem of bed agglomeration, while the extensive bed agglomeration is observed for the untreated biomass [71,145-146]. The loss of alkali and other problematic elements, particularly chlorine and sulfur, in biomass by leaching is the main reason for this treatment.

Fuel pre-treatments particularly the leaching can reduce efficiently the risk of bed agglomeration because it eliminates the large fraction of alkali and chlorine elements as well as sulfur of inherent inorganic material before they are transformed to the problematic compounds during FBC/FBG. However, the excessive water content more hinders the combustion process and limits the availability of the fuel fired FBC/FBG. Otherwise, the removal of sand, soil and other inert contaminate materials can prevent the deterioration of fluidization quality only in a minor extent.

2.7.5 Fluidized bed operation control

As mentioned in section 2.4.3., defluidization is described as a part of the formation of stable bond between bed particles and the breaking of agglomerates. The breaking is significantly dependent upon the bed operations, particularly fluidizing air/gas velocity and operating temperature.

Velocity control

High fluidization velocities lower the tendency for bed agglomeration and deposition problems due to an increasing breaking force, and enhancing ash entrainment [147-148]. In some occasions, agglomerates already formed are disintegrated by temporarily increasing the gas velocity, which may mainly work on weakly bonded agglomerates that typically formed rather fast at relatively high temperatures [149]. However, increasing the gas velocity may also show a negative result when the agglomerates are bound with the stronger bond and settled on the base of bed. These agglomerates with slowly settling are more typically formed in the lower bed temperature ranges. Increasing the gas velocity in the primary zone (bed zone that is closely above the air/gas distributor) may even provide a worse situation by reducing the bulk density in the still fluidized areas adjacent to the agglomerates and thereby reducing the buoyancy forces acting on the agglomerates [51,149]. A suitable way in this case is to frequently or occasionally drain the bed, even if the boiler has to be shutdown. A sudden increase of air flow during combustion at an inappropriate stoichiometric ratio may also result in an overshoot of temperature, which is the worsen situation. However, simply increasing the fluidizing gas velocity does also result in the increasing loss of heat by flue gas and entrained unburned carbon.

Temperature control

Agglomeration is in most case caused by the melt formation of ash forming constituents at particle surface, which then glue particles together. It is therefore a straightforwardly logical measure to avoid agglomeration by combustion/gasification at a sufficiently low temperature below the initial agglomeration (sintering) temperature, or initial melting temperature [150]. However, there are several temperature related effects to be concerned.

Lowering bed temperature of FBG by decreasing air-fuel ratio is undesirable, as this generally gives a lower carbon conversion and higher tar concentration in the gas [51]. Increasing the excess air ratio in FBC is also difficult, as it can cause extinction of the flame at the bottom of the bed. Furthermore, a low bed temperature may cause a high CO emission [104]. Increasing air flow to lowering the bed temperature can result in the unacceptable carbon losses due to a high elutriation. A better way to achieve a lower bed temperature for a given air-fuel ratio is therefore the addition of steam, flue gas or nitrogen to the fluidizing gas [114], or otherwise additional heat transfer area in bed or freeboard. Freeboard temperatures in biomass combustion are generally 100-200 °C higher than bed temperatures due to the volatile combustion [34].

Temperature overshooting during start up in combustion and gasification (start up and shut down usually in "combustion mode") is also a serious problem [51]. A delayed reaching the set point temperature often results in a major increase of a fuel feed rate, due to the natural impatience of operators. It results to an unrecognized excessive amount of fuel in bed. This fuel starts to react at a much faster rate shortly before reaching the set point of operation temperature, and thus gives overshoot bed temperature. A similar risk exists when changing to a less reactive fuel [11]. A good procedure during start up is to observe the temperature response on a short feeding stop, before an assigned operation temperature is reached. It is also a good start up not to exceed a previously experienced or calculated feed rate. To avoid temperature excursions during start up and shut down, it is simply patient and careful [51,82].

In addition, the local temperature peaks established by the locally poor bed circulation from the large bed area or inappropriate design of furnace chamber or fluidizing gas distributor should be avoided. Several measures are mentioned [51];

- improving the distribution of fuel and oxygen,
- better mixing by providing a more aggressive stage of fluidization in critical areas,
- moderating the temperature near gas nozzles e.g. adding steam in gasification or circulating flue gas in combustion,
- inducing further upwards streams through critical in-bed areas,
- allowing a higher particle flux, through critical part of a CFB reactor.

Fluidized bed reactors used for energy production are operated at specifically designed load conditions, e.g. steam or gas capacity. Increasing the fluidizing gas velocity by raising the gas flow merely delays the defludization state, due to the limited capacity of the designed air/gas flowing devices (blower or compressor). The temperature of burning char particle, especially in the high oxygen concentration zone inside the bed, is considerably higher than the mean temperature of the surrounding bed particles [51,96]. This high surface temperature of char particle can enhance the melt formation of eutectics on the char surface. Measures such as improved distribution of combustion or gasification agent (e.g. improved nozzle design) may be a solution, in order to avoid high concentration of oxygen in areas with high concentration of char. Oxidation or gasification at low (average) temperature also limit this problem due to the generally slowed reaction kinetics and higher margin from bed temperature to initial temperatures of melting and eutectic formation, resulting in a lesser formation of the melts [107,109].

Temperature control and velocity control are relevant operation. The operation controls as increasing gas velocity or decreasing bed operation temperature are an urgent prevention that delays the bed agglomeration. The furnace/nozzle designs and operations resulting to reduce effectively the poor bed circulation and poor fuel distribution is a solution to achieve this measure. However, the above operations out of the design conditions increase directly the losses of heat and carbon conversion of fuel, leading to the loss of boiler efficiency and the high emission. It is therefore seen to be a less extractive measure of bed agglomeration prevention.

2.7.6 Bed management

The bed properties on a continuous FBC/FBG after considerably long operating hours are largely different from the original properties of initially loaded bed particles. It includes a change in bed particle size, both larger and smaller than the initially loaded bed particle, as well as a change in chemical compositions of bed material. It is mainly due to the substantial contamination of the inorganic constituents from fuels and inherent fluidized bed behaviors [34,54]. The regular sampling and analysis of the bed material during operation and periodical refreshing the bed inventory, before a critical alkali concentration [104] or critical bed defluidization level is reached, is a necessary measure. The refreshment of bed inventory is a discharge of old bed material in the reactor and an addition of the new one.

In cases where some oversize particles are not possible to be removed by the fuel preparation, the fluidized bed chamber should be designed in such a way that the worst possible type of tramp material; passing through the preparation and feed system, and the agglomerates; formed in bed, can be efficiently drained out. The suggested design means for effective draining are mentioned viz; [51]

- designing for a light state of fluidization in the bed bottom (bed regime below the air/gas distributor), in order to loose the bed lock up,
- keeping the flow high enough to the vigorous and stable fluidization at the reactor bottom, at all times,
- inclining the bed bottom against draining opening/means,
- using directional air/gas distributor,
- using nozzle shaped in order not to hold up the irregular bed components,
- providing an open type of bed drain [151], instead of a base plate with nozzles.

A periodical addition of the fresh bed material keeps the bed sufficiently well sized and chemically corrected. The addition is considered in term of the mass ratio of batch fed fuel to bed particle. The potential needs for the bed refreshment is partly or fully covered by adding the chemically active particles to absorb sulfur, chlorine and alkali components.

2.7.7 Other measures

Carbonation and sulfation of CaO are a main agglomeration mechanisms based on chemical reaction (in section 2.3.3), according to below reactions.

Carbonation: $CaO + CO_2 \rightarrow CaCO_3$ (exothermic)
Sulfation: $CaO + SO_2 + \frac{1}{2}O_2 \rightarrow CaSO_4$ (exothermic)
$CaCO_3 + SO_3 \rightarrow CaSO_4 + CO_2$ (exothermic)

The potential of these reactions to be taken place is increased by [34,51,66] viz,

- the presence of a high CaO concentration,
- a high partial pressure of CO_2 and SO_2/SO_3,
- decreasing bed temperature

An extension of the agglomeration due to carbonation and sulfation is particularly presented, when the high Ca fuels, bed materials or additives are used and temperature of local bed is decreased to form the thermodynamically stable Ca compounds. The particle stagnation is also a further effect, as badly fluidized zone in bed [51]. The possible preventions are suggested as;

- avoid stagnant zones such as the area near gas distributor grids, in particle return duct and particle coolers.
- limit the CO_2 or SO_X concentration in critical areas, e.g. (i) limiting the char concentration; (ii) adding steam, circulated flue gas or nitrogen; (iii) designing the chamber in such a way that liberate of SO_X out of bed as well as its subsequent absorption are primarily taking place , e.g., in the vigorously fluidized main reactor chamber,
- choose proper bed materials/additives,
- provide sufficient clearance and cleaning in hear absorption surfaces
- precautions in design of the flue gas and product gas coolers against deposition,
- avoid the combination of pressure and temperature that enhance the tendency for Ca compounds to alternate between calcinating and re-carbonating/re-sulfating conditions.

The formation of agglomerates/deposits based on condensation of vapor KCl on the particle surface/heat absorption surface and the subsequent sulfation forming K_2SO_4 is a risk, according to reaction;

$$2KCl + SO_2 + 2H_2O \rightarrow K_2SO_4 + 2HCl$$

It is a severe problem when high alkali and chlorine fuel is co-combusted with a high sulfur coal, for example. Some possible solutions are viz;

- avoid the combination of inputs of K/Na, chlorine and sulfur (e.g. co-firing straws/grasses and a high sulfur coal),
- limit the release of alkali to gas phase and/or promote its rebinding into non-sticky solid phase (e.g. using additive or free Si bed materials),
- provide sufficient clearance and cleaning in hear absorption surfaces,
- provide some rows of so called screening tubes in front of superheater surfaces in the convective pass, deposits will form on the screening tubes but tend to peel off due to thermal stress induced by a relatively low surface temperature.

Depending on the application and choice of fuel, an option of prevention or the combination of these can be the effective measure to reduce the bed agglomeration problem. The prevention methods to be success need the intensive experimental and practical experiences.

In above reviews including the further reviews of mathematical prediction in Chapter 4, despite the substantial efforts toward the bed agglomeration, the intimate understanding in its phenomena is still far from being complete. The several significant inconsistencies and uncertainties are shown in the present literatures. It is due to the fact that the bed agglomeration is a consequence of physically and chemically complex interactions in micro level between many different compounds. The intensive chemistry of bed agglomeration is hence important and needs to be studied in greater detail, in order to obtain more effective prediction and tackling for the success of applying FBC to produce energy from the specific biomass.