Defluidization Investigation into Bubbling Fluidized Bed Particles with Alkaline Addition during Pyrolysis

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Abstract Some unwanted inorganic materials, such as alkaline compounds contained in biomass, have the potential to create slagging formations with oxide compounds from either inside or outside the bubbling fluidized bed (BFB). The process involved 88-125 μm silica sand and clay (bentonite) as bed particles during pyrolysis with KCl addition at 700°C to represent biomass under superficial- N_2 -velocity operation. Agglomeration formation was confirmed by the decrease in the average ΔP of the experiment, which theoretically should take place during the addition of KCl, while the defluidization condition was confirmed by a consistent average ΔP particle deviation, even after further KCl additions. Investigation of 0.005 and 1 g encapsulated KCl periodical addition showed that the silica sand has a tendency to form agglomeration faster than bentonite, specifically after 0.0211 g of KCl addition (0.0032% of total silica sand mass). Meanwhile, the bentonite has a tendency to achieve defluidization formation more easily than silica sand according to deviation analysis. The ability of silica sand to maintain fluidization longer than bentonite indicates that silica sand is the better particle for this process.

1 Introduction

Increasing the efficiency of biomass energy production by utilizing proper thermal conversion processes to achieve good product quality can save energy and increase the use of cleaner energy. The bubbling fluidized bed (BFB) pyrolysis process is a technique which involves the efficient combustion of raw materials at high temperatures via particle circulation supported by N_2 flow in the superficial velocity condition. Particle fluidization ensures that thermal conversion is run optimally during the process. Therefore, the size, type, and flowrate velocity of particles in circulation have a significant effect on the completion of the reaction.

Silica sand particles already have numerous applications in fluidization. This work will consider the competitiveness of another particle with similar properties. The use of clay with a high silica content should reduce the likeliness of particle degradation, even in high-temperature conditions. However, it is possible that defluidization phenomena will take place during the reaction, causing a decrease in the efficiency of the process. The increase in particle size likely occurs during thermal processing due to the agglomeration formation in the bed particles. It is affected by the presence of some alkaline compounds contained inside raw biomass, such as K, which easily associates with some oxide compounds to increase the particle size until the particle fluidization stops. Therefore, defluidization analysis becomes important when comparing silica sand and clay

(bentonite) during BFB pyrolysis and will be observed in detail in this work.

2 Method

2.1 Particle circulation preparation

Both silica sand and bentonite particle mixtures were dominated by oxide compounds, contained particles of heterogenous sizes, and were provided by Japanese companies. The densities of silica sand and thermal bentonite were estimated to be 2 and 2.9 g/cm^3 , respectively, which places them in Group A according to the Geldard Classification (Kunii and Levenspiel, 1991). Sieving and milling were carried out by a mechanical sieve and mortar to obtain homogenous particle sizes of 88–125 μm . Particles were placed into the BFB chamber, which has a vertical height of 500 mm and an inner diameter (ID) of 43 mm, before start-up. The total initial bed particle mass was around 65 g, and it was located 30 mm above the 50 μm porous distributor plate at the bottom of the chamber. The particle size was selected to prevent back pressure and ensure fluidization could take place after achieving the minimum fluidization velocity (U_{mf}) of N_2 . Therefore, the U_{mf} had to be determined both at room temperature (24°C for silica sand and 19°C for bentonite) and pyrolysis temperature (700°C). Figures 1 and 2 show the U_{mf} analysis for silica sand and bentonite.

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Figure 1. The U_{mf} analysis of silica sand at 24°C (room temperature) and 700°C (pyrolysis temperature)

Figure 2. U_{mf} analysis of bentonite at 19°C (room temperature) and 700°C (pyrolysis temperature)

The ratio between room and pyrolysis temperatures in Figure 2 indicates that the U_{mf} value is 3–4 times higher at the pyrolysis temperature for bentonite. The U_{mf} estimation was considered when setting the N_2 velocity to approximately 0.012 m/s, or 2 litres per minute (L/min), to create a superficial velocity condition at 700°C.

Bentonite has a high moisture content, which evaporates during heating and fluidization of the particles, thereby decreasing the particle mass. The presence of water implies that flocculation easily occurs and decreases the capability to form chemical bonds with other bed particles. This also relates to its capability to swell up to several times its initial size in atmospheric conditions (Basnayaka *et al.*, 2018). Therefore, thermal pre-treatment was needed to ensure its readiness for use in the pyrolysis process.

2.2 Raw material preparation

The raw material was biomass containing a rich supply of organic compounds, which are easily reacted and released from the chamber at 700°C. However, some biochar would remain inside the BFB chamber due to its inorganic components, which would mix with the fluidized particles. KCl is used to represent the inorganic compounds found in biomass. The 88–125 μ m KCl was obtained by grinding powder to obtain the same particle size as the bed particles. After that, it was placed into commercial capsules of various sizes so that 0.005 g and 1 g of KCl could be added at 15 min intervals. The use of an empty capsule made it easier to input KCl into the BFB chamber as shown in Figure 3. The empty capsule mass was approximately 0.1 g, and it was composed of 89.2% cellulose, 2% TiO_2 , 1.3% KCl and 1% other compounds;

therefore, it combusted almost perfectly during the process.

Figure 3. Preparation of encapsulated KCl

2.3 BFB pyrolysis operation

BFB pyrolysis was commenced by heating up BFB with an electrical microheater to achieve a temperature of 700°C. This took approximately 60 min supported by continuous N_2 supply from the distributor section. Three ball valves on the top of the bed acted as nozzles for inputting encapsulated KCl. KCl was added every 15 min, supported by N_2 from the top reactor to avoid backflow. Three pressure probes were introduced into the bottom of the reactor (P1), the filter pipeline (P2), and the exhaust line (P3) to record the pressure difference (ΔP). A thermocouple was set and placed into the BFB chamber to maintain temperature at 700°C. A packaged sintering filter was installed into the updraft BFB discharge line to catch fine particles before being emitted to the atmosphere.

Figure 4. Bubbling fluidized bed (BFB) pyrolysis system

The differences in mass inside the bed reactor and the sintering filter, before and after pyrolysis were calculated to determine the total remaining bed particle masses, amount of elutriation, and the loss mass. A detailed description of the BFB system is provided in Figure 4.

3 Results

3.1 Defluidization analysis of silica sand particles

Defluidization analysis was carried out based on the pressure drop (ΔP) during the experiment. To maintain the fluidization condition inside the bed, KCl was added in 15 min intervals to decrease continuously and getting loss capability. Thermal gravimetric analysis (TGA) of the endothermic reaction at 700°C under N_2 atmosphere, as shown in Figure 5, confirmed that the silica sand and KCl were more difficult to degrade than the cellulose capsule

during pyrolysis. The amount of mass loss was predicted to come from the cellulose capsule degradation, which almost completely volatilized during pyrolysis.

Figure 5. TGA on (a) KCl, (b) Empty capsule, and (c) Silica sand

The average ΔP was calculated experimentally to determine the agglomeration and defluidization conditions associated with the change in ΔP within an interval of 15 min. The ΔP values by theory and elutriation analysis were calculated using Pascal's law, as shown in equations 1 and 2, to confirm the ideal process in which all the particles do not degrade.

$$\Delta P \text{ by theory} = \frac{m_{\text{bed particle}} \times g}{A_{\text{BFB}}} \quad (1)$$

$$\Delta P \text{ by elutriation} = \frac{(m_{\text{bed particle}} - m_{\text{filter particle}}) \times g}{A_{\text{BFB}}} \quad (2)$$

Therefore, those ΔP values always should to be higher than ΔP by experiment.

3.1.1 Analysis of silica sand with 0.005 g KCl added/15 min

This was the lowest interval analysis to identify the initial agglomeration formation before reaching the defluidization condition. In this step, ΔP by experiment increased gradually after initializing the N_2 supply and adding several capsules. The particle fluidization slightly decreased ΔP although fluidization still occurred until the last KCl addition, when the total added KCl was 0.21 g, as seen in Table 1. The initial agglomeration is indicated

in Figure 6 by the decrease in particle fluctuation, where the standard deviation decreases from 0.00551 KPa at the initial fluidization to become 0.00349 KPa after several KCl additions. Analysis of average ΔP confirmed that the agglomeration was formed after 0.02 g of KCl was added or 0.032% of the initial bed particle mass. The increase in agglomeration was taking place continuously in accordance with the decrease in average ΔP by experiment of 0.497%.

Figure 6. Agglomeration of silica sand with 0.005 g KCl added/15 min against ΔP by theory and elutriation movement, based on (a) ΔP deviation, (b) Average ΔP by experiment, (c) ΔP by experiment (raw data)

The agglomeration formation was confirmed by sieving the bed particle after pyrolysis to obtain particles larger than 125 μm (+125 μm). After sieving, 0.82 g of agglomerated particles were obtained, as can be seen in Table 1 and Figure 7.

Figure 7. The mixed bed particle (silica sand) after pyrolysis within 0.005 gr/15 min interval KCl addition (a) Before separation, (b) After separation

The silica sand particles were almost stable. Table 1 shows that the total emitted bed particle mass was 4 g and the total accumulated filter particle mass was 0.2 g. This

stable performance resulted in a small mass loss of approximately 3.8 g.

Table 1. Mass loss calculation of silica sand BFB with 0.005 g KCl added/15 min (left) and 1 g KCl added/15 min (right)

Parameter	Value	Parameter	Value
Bed reactor		Bed reactor	
1. Silica sand input mass	65.24 g	1. Silica sand input mass	65.17 g
2. Total KCl addition mass	0.21 g	2. Total KCl addition mass	40.58 g
3. Total cellulose capsule mass	3.71 g	3. Total cellulose capsule mass	7.45 g
4. Total bed particle mass before pyrolysis (1.1 + 1.2 + 1.3)	69.16 g	4. Total bed particle mass before pyrolysis (1.1 + 1.2 + 1.3)	113.20 g
5. Total bed particle mass after pyrolysis	65.16 g	5. Total bed particle mass after pyrolysis	106.00 g
5.1. +125µm particle size	0.82 g	5.1. +125µm particle size	2.67 g
5.2. +88-125µm particle size	58.26 g	5.2. +88-125µm particle size	86.73 g
5.3. -88µm particle size	6.08 g	5.3. -88µm particle size	16.60 g
6. Total emitted bed particle mass (1.5 - 1.4)	4.00 g	6. Total emitted bed particle mass (1.5 - 1.4)	7.20 g
Sintering Filter		Sintering Filter	
1. The mass before pyrolysis	670.10 g	1. The mass before pyrolysis	670.20 g
2. The mass after pyrolysis	670.30 g	2. The mass after pyrolysis	670.70 g
3. Total accumulated filter particle mass (2.2 - 2.1)	0.20 g	3. Total accumulated filter particle mass (2.2 - 2.1)	0.50 g
Total mass loss		Total mass loss	
The difference of emitted bed particle and accumulated filter mass (1.6 - 2.3)	3.80 g	The difference of emitted bed particle and accumulated filter mass (1.6 - 2.3)	6.70 g

3.1.2 Analysis of silica sand with 1 g KCl added/15 min

More KCl was added in the experiment to determine the new defluidization condition, as agglomerations were completely formed with less KCl. It lasted 10 h, or 40 additions of KCl, reaching an added mass of 40.58 g. The defluidization condition was confirmed when the movement of ΔP stopped or, when particle movement was stable even with further KCl addition. The defluidization condition occurs when ΔP deviation is stable compared to ΔP deviation when the N_2 supply is stopped. Before achieving defluidization, ΔP changes as the bed particles find more stable formations. In this phase, fine and bed particles react, creating larger particles and incremental changes in ΔP . On complete defluidization, even KCl addition does not significantly change the ΔP value.

Figure 8. Defluidization investigation of silica sand with 1 g KCl added/15 min against ΔP by theory and elutriation movement, based on (a) ΔP deviation, (b) Average ΔP by experiment, and (c) ΔP by experiment (raw data)

Figure 9. Defluidization investigation of silica sand with 1 g KCl added/15 min based on % average ΔP by experiment rate

Figure 8(a), confirms agglomeration formation. Meanwhile, the defluidization condition was not yet achieved after comparing the ΔP deviations, which still fluctuated until the last addition of KCl, compared to the ΔP condition N_2 supply stopped, 0.00189 KPa and 0.00152 KPa respectively. There are five agglomeration areas depicted in Figure 9 according to the change of ΔP by experiment rate. The 1st and 2nd areas show the most significant change, where the bed particle vigorously reacts with KCl to make a large agglomeration. The decreased rate of the 1st and 2nd area was 0.1% and 0.84% respectively, with the total added mass of KCl at the end of the 2nd area being 10.18 g, or 15.613% of the initial bed particle mass, as shown in Figure 8(b). Meanwhile, the 3rd area shows the most stable condition with a slightly increased rate of 0.03%, and total added mass of KCl at 24.37 g or 37.395%. In this case, only a small amount of agglomeration was formed. The 4th and 5th area confirm a small increment of agglomeration formation with total added mass of KCl at 33.48 g or 51.378% and 39.56 g or 60.707%, respectively. The stability condition confirmed the rate of change amount at 0.109% and 0.040% respectively as well.

Figure 10. Mixed silica sand and KCl particles after pyrolysis within 1 g KCl added/15 min interval reaction (a) Before, and (b) After the sieving process

Agglomeration was proved by the presence of a higher bed particle size after pyrolysis, as can be seen in Figure 10. The mass balance in Table 1 confirmed that there was 2.67 g of agglomerated particles obtained from the sieving process. That agglomeration has a weak structure which was very easy to break down with vibration during sieving. Sintering of the agglomeration is relevant as higher

temperatures would increase agglomeration (Kunii and Levenspiel, 1991). The mass loss was confirmed to be 6.7 g.

3.2 Defluidization analysis of bentonite particles

Bentonite was selected to be used as another bed particle. It has the potential to be considered as a support catalyst to increase reaction efficiency. However, according to TGA, not only was the empty capsule but degrading, but also approximately 10.9% of the bentonite as shown in Figure 11. The high degradation rate increases the disparity between ΔP by experiment and ΔP by theory and elutriation.

Figure 11. TG analysis on clay (bentonite)

3.2.1 Analysis bentonite with 0.005 g KCl added/15 min

The identification of agglomeration in this case was carried out by adding a total of 0.3 g KCl. Using a similar method to the silica sand, agglomeration formation was shown with ΔP deviation 0.03461 KPa as shown in Figure 12(a). It was achieved after 0.09 g of KCl was added or 0.14% of the initial bed particle mass as shown in Figure 12(b).

Figure 12. ΔP by experiment values based on (a). Deviation data, (b). Average data and (c). Raw data against ΔP by theory and elutriation between bentonite and 0.005 g KCl added/15 min.

The analysis shows that the bentonite takes longer to form an agglomeration than silica sand. The degradation of bentonite changes its structure, meaning ions inside the compound will react with some ions supported with its high adsorption capability during the process (Petrovic *et al.*, 2014). The high degradation of bentonite was proved by the 11.81 g of accumulated fine particles inside the sintering filter, as shown in Table 2.

Table 2. The mass loss calculation of BFB analysis using bentonite with 0.005 g KCl added/15 min (left) and 1 g KCl added /15 min (right)

Parameter	Value	Parameter	Value
Bed reactor		Bed reactor	
1. Bentonite input mass	65.07 g	1. Bentonite input mass	65.19 g
2. Total KCl addition mass	0.31 g	2. Total KCl addition mass	40.65 g
3. Total cellulose capsule mass	5.56 g	3. Total cellulose capsule mass	7.61 g
4. Total bed particle mass before pyrolysis (1.1 + 1.2 + 1.3)	70.94 g	4. Total bed particle mass before pyrolysis (1.1 + 1.2 + 1.3)	113.45 g
5. Total bed particle mass after pyrolysis	47.57 g	5. Total bed particle mass after pyrolysis	91.29 g
5.1. +125μm particle size	0.42 g	5.1. +125μm particle size	4.66 g
5.2. +88-125μm particle size	20.66 g	5.2. +88-125μm particle size	69.89 g
5.3. -88μm particle size	26.49 g	5.3. -88μm particle size	16.75 g
6. Total emitted bed particle mass (1.5 - 1.4)	23.37 g	6. Total emitted bed particle mass (1.5 - 1.4)	22.15 g
Sintering Filter		Sintering Filter	
1. The mass before pyrolysis	698.70 g	1. The mass before pyrolysis	670.30 g
2. The mass after pyrolysis	710.51 g	2. The mass after pyrolysis	678.70 g
3. Total accumulated filter particle mass (2.2 - 2.1)	11.81 g	3. Total accumulated filter particle mass (2.2 - 2.1)	8.40 g
Total mass loss		Total mass loss	
The difference of emitted bed particle and accumulated filter mass (1.6 - 2.3)	11.56 g	The difference of emitted bed particle and accumulated filter mass (1.6 - 2.3)	13.75 g

Figure 13 shows some small agglomerations from both before and after the mechanical sieving process. Table 2 confirmed that the total agglomerated particle mass was 0.42 g.

Figure 13. Bentonite after pyrolysis with 0.005 g KCl added/15 min (a) Before separation, (b) After separation

3.2.2 Analysis clay (bentonite) against 1 gr/15 min interval KCl addition

The ΔP deviation for 10 h with a total of 40.65 g KCl added was compared to the ΔP deviation once the after N_2 supply stopped. This showed that the initial defluidization condition was achieved when the ΔP values were 0.00216 followed by slight change 0.00224 until the last addition compared to 0.00221 KPa respectively as shown in Figure 14(a). Figure 15 confirmed the agglomeration was formed in 4 phases, based on average ΔP by experiment rate. The 1st area was the most significant change in agglomeration with 3.05 g KCl added or 4.671% of the initial bed particle mass, the ΔP rate decreased by 0.549% as shown in Figure 14(b). A small agglomeration took place in the 2nd area with 5.08 g or 7.796% of initial bed particle mass. The 3rd

area shows the beginning of defluidization, involving continued agglomeration formation with added KCl of 32.5 g or 49.855% of the initial mass. In the 4th area, the defluidization formation continued to stabilization. The experiment was carried out until the last KCl addition, totalling 40.65 g or 62.355% of the initial bed particle mass.

Figure 14. (a). ΔP deviation, (b). Average ΔP and (c). ΔP by experiment (raw data) against ΔP by theory and elutriation of bentonite with 1 g KCl added/15 min

Figure 15. Defluidization investigation of bentonite with 1 g KCl added/15 min based on % average ΔP by experiment rate

The analysis in Table 2 shows that bentonite has a higher potential to emit a large amount of fine particles than silica sand, which will be remained inside the filter.

Figure 16. Bentonite and KCl particles after pyrolysis with 1 g KCl added/15 min interval reaction (a). Before, and (b). After the sieving process

The high volume of fine particles causes a lot of agglomeration, as the particles mix easier and have a higher surface area when smaller. After being sieved, the agglomeration size is larger than the initial particles (+125 μm) with a total mass of 4.66 g collected, as seen in Table 2 and Figure 16. This shows that the agglomeration was tightly bound with the KCl even after separation, unlike with the silica sand agglomeration in Figure 10 which broke up due to vibrations during the mechanical sieving process.

4 Conclusion

The defluidization condition was preceded by agglomeration formation. Silica sand tends to agglomerate faster than clay bentonite. However, bentonite tends to degrade and reach the defluidization phase first by forming larger, sintered agglomerated particles.

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