Particle settling in high viscous pyrolysis char suspensions

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Abstract

At Karlsruhe's bioliq® project, dry lignocellulosic biomass are converted through fast pyrolysis process into a high energy char powder and pyrolysis condensates (organic and aqueous). The char and aqueous condensate are mixed to a suspension known as bio slurry or bio syncrude that has suitable for long time storage and also lead to lower costs for long distance transport.

In the present work, suspensions of char in the aqueous phase obtained in the fast pyrolysis of straw were prepared with the aim of studying the influence of different variables like the char char concentration (23.4, 26 and 31.2%), the settling height (150, 84 and 20 cm) and the temperature (20, 35, and 45 ^{0}C) on the settling of the char particles. The result shows that, the settling velocity decreases with the increase of the char concentration in the suspension. However the settling height of the tower does not affect the settling trend of the particles, i.e. the hydrostatic pressure of the suspension does not influence the particle settling. On the other hand, the increase of the temperature from room temperature (20 ^{0}C) to 35 ^{0}C and 45 ^{0}C lead to an increase of the particles settling. Therefore, it is possible to conclude that the bioslurry should be stored at lower temperatures. Finally, bioslurry stability was determined using for coal water slurry and stability values of 80 and 79% after 7 days were found for 26 and 31.3% concentration slurries, respectively.

Key words: bio slurry, particles settling, concentration, stability

1. Introduction

Discovery and use of fossil fuels are unquestionable the fundamental role in building our modern civilizations. At present, more than 80 % of the world's energy consumption is based on fossil fuels [1]. However, this resource is depleted because of the limited reserves and the increasing consumption of energy. With the current consumption trends, world energy demand is estimated to increase by 50% between 2005 and 2030 [2]. By looking forward to these challenges, Karlsruhe Institute for Technology (KIT) is working on the so called bioliq process. The concept of bioliq which approaches two step process. First step, within a radius of approximately 25 km, the low energy local residual biomass, i.e. straw (2 - 2.5 GJ/m^3) are collected and processed in a decentralized plant by fast pyrolysis. The main objective of the fast pyrolysis is the production of adequate organic and aqueous liquid for complete char suspension [3]. The fast pyrolysis is carried out at 500^{0}C with residence time of 2-3 seconds. Regarding the operating parameters of the reactor and the used biomass, 50-70% of condensates and 15-30% pyrolysis char and about

15- 20% gas are obtained. The pyrolysis gases are condensed in two steps for obtaining organic condensate (pyrolysis tar) and aqueous condensate (pyrolysis water). These obtained products are mixed together to produce high energy bio slurry as an intermediate product. In the second step, this product can be transported efficiently and economically over long distances to centralized plants. In this central plant, all bio-slurries are collected from different decentralized plants and converted into synthesis gas and finally into high energy synthetic fuels. The concept of decentralized and centralized process plant for converting biomass to liquid is more efficient and economical [4].

For easy transport, loading and unloading, the biosyncrude should be particularly storage stable and pumpable, and therefore the settling of the char particles has to be avoided. But it is natural that the particle might settle in the suspension, due to their higher particle density, concentration present in the suspension or properties of the condensate. Bio slurry might be required to store for a period of time because it is not always possible to gasified immediately after the production. So for storing and transporting it is important, that the slurries remain uniform in solid concentration or the sediments formed in the storage tank be loosely packed so that it can be re-stirred and pumped.

The aim of this work was to characterize the particle settling varying the following variable:

- concentration of the char in the bio slurry.
- height of the settling tower.
- storage temperature.

Particle settling

For the low concentration slurry, settling takes place freely following the Stokes equation [5], as in equation 1. But for the concentrated slurry, the settling becomes a complex process. Also interactions between the particles form flocs or coagula. So, according to the particles present in the suspension, the settling can be defined as; discrete, flocculent, hindered settling, or compressive settling.

$$V_s = \frac{(\rho_p - \rho_f)\, g\, d^2}{18\, \mu} \qquad \text{Equation 1}$$

Batch sedimentation or zone settling

In batch processing, initially the sedimentation tower contains a homogenous mixture. Figure 1 represents a typical batch settling column test on a suspension showing zone settling characteristics. As the settling takes place, at the top of the tower a clear liquid interface is formed (A). As the particles settle down, a uniform concentration zone (B) and a non-uniform zone (C) is formed. At the bottom, solid particle compressed and formed stronger sediment (D) with the increasing storage time.

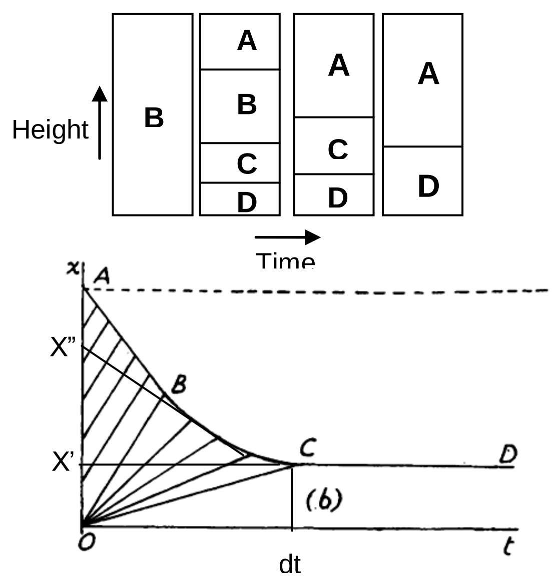


Figure 1: Zone settling behaviour in typical batch sedimentation [6]

A: clear liquid, B: uniform mixture, C: non uniform mixture, D: sediment

In Figure 1, initially, the suspension settles at a constant rate in the section A to B, and if the particles become of fairly uniform size, sharp discontinuities form between these layers. Between the regions B and C there may or may not be distinct continuity. As the time increases, the upper discontinuity meets the lower and the region B disappears. Then a gradual compression of the regions C and D occurs until finally the sediment formed. The slope of the settling curve at any point represents the settling velocity of the interface between the suspension and the clear liquid.

In batch settling test the settling velocity for any given concentration can be obtained and the concentration at the interface can be determined.

$$\mathrm{C}' = \mathrm{C}\,\frac{x}{\mathrm{x}'} \qquad \text{Equation 2}$$

2. Materials and Methods

Char

For the slurry preparation, the unmilled straw char from the fast pyrolysis step of the bioliq process was used. The straw char contains 54.3% carbon and has also a high ash content of 35.8%. The char has a calorific value 20.5 MJ/kg .The straw char has a low bulk density of 250 kg/m^3 due to the formation of agglomerates having interspaces between the individual particles, as well as intra-particle pores. The straw char contains a high porosity of 50-80%, which strongly influences the slurry preparation because initially the liquid is drawn by capillary forces in the pores or interspaces of agglomerates, and so a significant part of the liquid is immobilized.

Aqueous condensate

For the aqueous condensate, the heating value is too low for the direct gasification and so it necessary to increase this value by the mixture with char. The aqueous condensate consists of 84.4% water with having mass density of 1020 kg/m^3 and higher heating value of 7.13 MJ/kg.

Bio slurry

Bio slurry is a suspension of pyrolysis condensates and pyrolysis char. In this study, the bio slurry was prepared by mixing the aqueous condensate and the char in a colloidal mixer from MAT Company. In this mixer, the shear rate is high enough to completely destroy the solid char agglomerations.

For the present study, one ton of bio slurry mixture is prepared in the beginning and is stored in an IBC. Due to the particle settling the mixture becomes non-homogenous after an hour. So to maintain the mixture homogenous, a motor is used to stir the bio slurry continuously at around the speed of 800 to 1000 rpm. This first prepared bio slurry named as “alpha” with the lowest concentration of 23.4%. The second bio slurry with higher concentration was prepared by adding the slurry from alpha slurry experiments and the prepared slurry named as “beta” with the concentration of 26% and the third bio slurry with higher concentration of 31.3% was prepared by adding the higher concentrated slurry from beta slurry experiments.

Experimental strategy

For the study of the particle settling of the bio char particles in the bio slurry, the sedimentation method was used. In the sedimentation method, the bio slurry is allowed to settle in a sedimentation tower for a set period of time. The measurement of the char concentration at different levels of the tower was determined at different time intervals of 4 hours, 8 hours, 1 day, 3 days, 7 days and 14 days. To find out the influence of the char concentration in the slurry, experiments were carried out with three different concentrated slurries. With the beta slurry, experiments were done to find out the influence of the height for the particle settling in the slurry mixture. For this study, experiment was carried out with the beta slurry in big tower filled full level (150 cm) and around half level (84 cm) and also in the small scale cylinder with (20 cm).

To find out the influences of the temperature in the settling of the particles in the slurry mixture, the experiment was performed in different temperatures, i.e. room temperatures, i.e. 20±2^{0}C (TR), 35^{0}C (T35) and 45^{0}C (T45) in a small scale tower with the beta slurry. In the big scale tower, the experiment was done only at room temperature.

Experimental setup

For characterizing the particle settling of bio slurry the experiments were done in a two different scales.

Big scale tower

In a big scale experiment, a tower with 150 cm in height, 55 cm in breadth and 55 cm in width, which has a capacity of 450 L, was used. To sample the slurry, 25 outlets were fixed at the front side of the tower. The distances between two outlets were 6 cm.

Small scale cylinder

For the small scale experiment, cylinders with a vertical height of 20 cm were made out of 5 segments and the bottom side is closed with a cover. Each segment has a diameter of 5 cm and a height of 4 cm. At first, two segments are joined together with tape. To increase the height of the cylinder another segment is kept in top of the fixed segments and joined with the tape.

Experimental procedure for measuring the solid concentration distribution

For the measurements of the big scale tower sample, the slurries and allowed to settle for the defined sedimentation interval. The slurry was taken out from each outlet and measured the weight of the sample. As the char particle is porous, it soaked the condensate and formed solid or substances of very low volatility. Therefore the sample slurry is diluted with ethanol and stirred for around 20-30 seconds for proper mixing before filtration. Thus porous particles and the gaps between the particles are filled with ethanol and due to the low boiling temperature of ethanol it dried easily. After the filtration, the char is dried in the oven for minimum 6 hours at around 100^0 C to evaporate all the ethanol and condensate from the char particles. At last, the solid weight of char from each outlet was measured. By this method, we distinguished the phase separation zone and a solid concentration in different time intervals.

For the measurements of the small scale tower, the tape was cut stepwise from top of the column down, and the sample was kept in the beaker. At first, the sample tower was kept in the beaker and the tape between the first segment and second segment was cut with the knife. The first segment with sample was drawn out from the settling cylinder and kept in the beaker. Sequently the second, third, fourth and fifth segments were drawn out and kept in different beaker. The weights of the each beaker with the slurry sample and segment were measured. Then the similar procedure was followed as in a big scale tower for measuring the solid concentration at different segments.

Influence of temperature

To find out the influences of the temperature in the settling of the particles in the slurry mixture, the experiment was performed in different temperatures. The experiments at the 20^0C were carried out in the room temperature with $\pm$ 2^0C. While for the higher temperature at 35^0C and 45^0C, till the defined settling time of 4 hours, 8 hours, 1 day, 3 days, and 7 days at the constant temperature in the oven. After the defined time, the measurement of solid concentration on each segment was meaure.

Static stability test

The calculation of bio slurry stability was carried out with a equation used for the coal water slurry method [7]. A bio slurry sample was filled in a small scale tower (with 20 cm height) and measures the weight of slurry sample. Then the slurry was kept in a room temperature for 7 days. After 7 days, the slurry tower, then was turned upright for 4 minutes to let the slurry flow adequately from the tower. Afterwards, the mass of the non-flowing parts of the bio slurry was measured. The stability of bio slurry could then be calculated using the equation:

$$S_{sta} = (1 - \frac{M_N}{M_I}) \times 100 \qquad \text{Equation 3}$$

with S_{sta} as the static stability (%), M_I as the initial mass of the bio slurry sample (g) and M_N as the mass of the non-flowing bioslurry (g).

Settling test in graduate cylinder

A slurry was filled in a graduate cylinder at room temperature. The experiment was carried out with different initial settling height of 250 mm, 200 mm, and 150 mm. As the particle start to settle, the position of the interface between the settled particles and an almost particle free condensate was noted after a time interval of 30 min. The experiment was stopped when there was no change in the interface height. Then the height of the interface was plotted versus time. The settling velocity of the particles V_c in a suspension was determined by measuring the slope of the linear portion of the height against time.

Viscosity measurement

The viscosity was measured with the rotational rheometer. The viscosity was measured with the defined speed (shear rate) between 1 to 100. For all measurements, helical spindle was used, due to its high accuracy of viscosity values and to avoid turbulent rheological regime. Result

Analysis of slurry parameter

Particle analysis

The size and shape of particles regulate the flow and compression properties. From the Stoke's equation, it's seen the particle size is directly proportional to the settling velocity, thus the larger particles are expected to settle faster than the small particles, but in the experiments, no different particle size distribution could be found of the height, which is justified with the high solid concentration and the hindered settling. The particle size distribution X_{50} of all three slurries was below 30 μm. X_{95} for the alpha, beta and theta slurry is almost 84 μm, 80 μm, and 70 μm respectively. The mean sizes of the particles in the alpha, beta, and theta slurry were 40.7±0.6, 38.8±0.8, and 36.2±1.2 μm respectively. The decrease can be explained by the stirring treatment in the IBC.

Viscosity analysis

Figure 2 describes that the characteristics of the slurries at 20^0C generally present non-Newtonian behaviour. The viscosity of the slurry varied as the shear rate was changed. Pseudo-plastic or shear thinning behaviour is characterized by the decrease in viscosity as the shear rate increases. A similar trend was found at higher temperature (i.e. 35^0C and 50^0C). It should be mentioned that the viscosity strongly decreases with increasing shear speed.

As expected viscosity increases with the increase in particle concentration. Theta slurry with 31% concentration had a higher viscosity than the alpha and beta slurries with concentrations of 24.3% and 26% respectively. The viscosity increases because of the frictional forces between the particles become significant, and also the blockage of free condensate occur. Thus, the lubrication effect of free-flowing condensates are become ineffective [8].

Figure 3 shows the viscosity as a function of the temperature for different slurries at 50 rpm. As expected the viscosity of the slurry decreased as the temperature increased. This is because of cohesive forces between the particles decrease with the increasing temperature. Thus, the forces of attraction between particles decreases, which reduces the viscosity of the slurry.

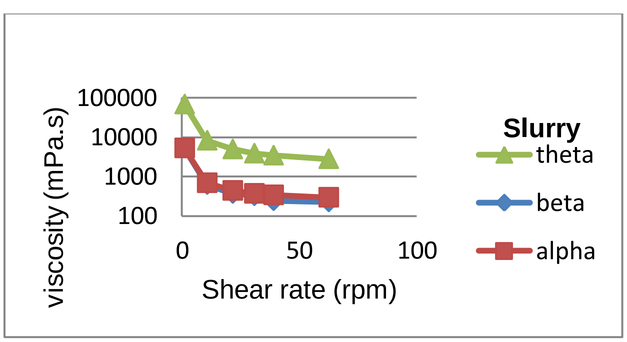


Figure 2: viscosity of slurry as a function of the shear rate at 20^0C

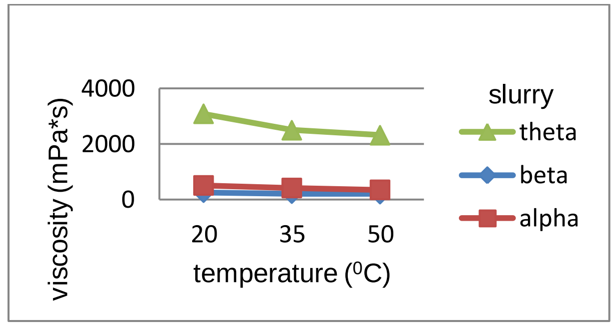


Figure 3: viscosity as the function of temperature

Characterization of sedimentation

Influence of concentration of char

Comparing the results obtained with slurry theta and beta it can be seen that with the higher concentration of the slurry the less the concentration change at the lower level corresponding to the outlet number 25. In fact, it seems likely that the initial concentration of around 31% is closer to the maximum packing density. Also, it can be seen that after 24 hours a relative sediment concentration has formed 17 for beta slurry and from outlet number 15 for the theta slurry. After this, the particle settling process becomes slower because the displaced liquid has to flow through the small spaces between the particles and the resistance to the flow of liquid progressively increases.

Comparing the results presented in Figure 4 and Figure 5, it is possible to conclude that the concentration changes after 24h were lower in the experiment with the theta slurry. In fact, for this slurry the larger variation obtained was off about 5% in the outlets 15, whereas for the beta slurry, the decrease of the concentration was off about 15% in the same outlets. At 336 hours, it was observed that, slurry with an initial concentration of 31.3% (theta slurry), the interface level between the particles and condensate is up to the height of 15 cm. Whereas, slurry with a lower concentration of about 26% (beta slurry), particles tend to settle down around the height of up to 21 cm.

The average concentration of the sediments may be calculated from the data in Table 1 obtained from the experiments. The average concentration was initial concentration times the initial height by sediment height. The result of average concentration of the sediment was calculated as in Table 1. This shows that the calculated average concentration is nearly the same concentration obtained from the experiment.

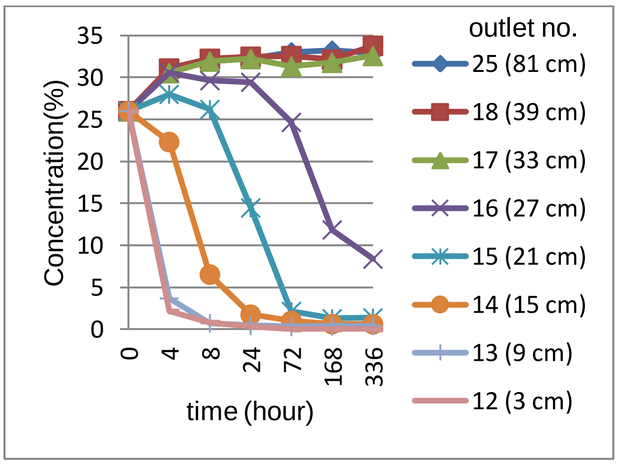


Figure 4: concentration measurement in different time intervals for beta slurry

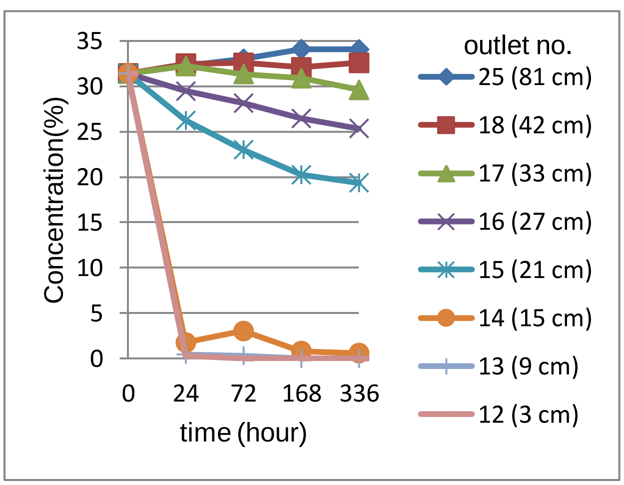


Figure 5: concentration measurement in different time interval for theta slurry

Influence of settling height

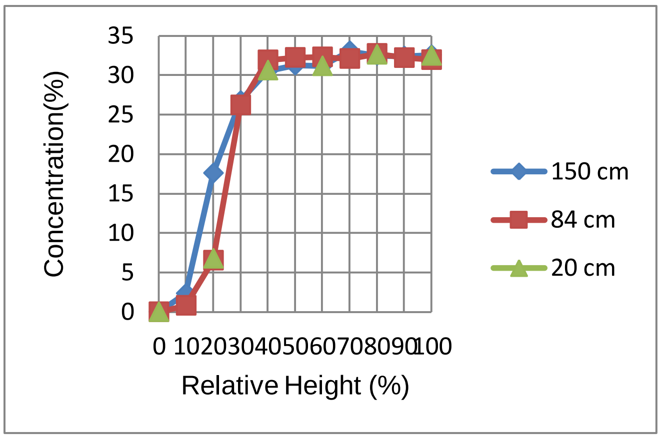
Figure 6 shows the settling of char particles as a function of the relative height at different time intervals at 8 hours and 168 hours. At 24 hours and 78 hours the graphs show the similar result. The result clearly shows that, the height of the settling tower did not affect either the settling trend or the consistence of the sedimentation. From all these figures at different interval of time, there the concentration of the char particles in different level or relative height is almost same and the solid concentration in the bottom region was also almost the same. This means that the hydrostatic pressure of the suspension did not influence the particle settling. Therefore, small scaled experiments can be scaled up.

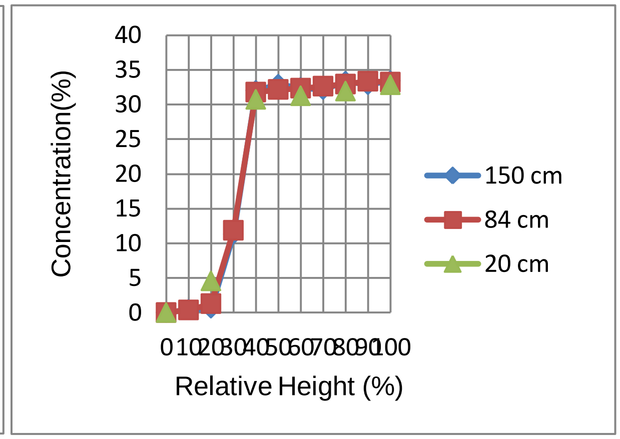
Influence of temperature

Figure 7 shows the previous results, but only for the first segment (height 4 cm) and the last segment (height 20 cm). Thus, it is clear that the increase of the temperature favours the sedimentation rate because after 4 hours, at room temperature the concentration of char at the top segments goes down to 14%, while at 35^{0}C and 45^{0}C this concentration is 5% and 4% respectively. In the bottom segments, the char concentration at room temperature and at a temperature 35^{0}C and 45^{0}C has a difference of around 3%. However, for the bottom segment the influence of the temperature is not important. These results indicate that, in order to avoid the sedimentation of the char particles, it is better to store the bioslurry at lower temperature.

Table 1: average concentration of sediment

Initial slurry concentration (%)	Initial height (cm)	Interface height (cm)	Relative interface level (%)	Sediment height (cm)	Average concentration of sediment (%)
26	84	21	25	63	34.7
31.3	84	15	17.9	69	38.01





(a) (b)

Figure 6: char concentration as a function of the column height (a) after 8 hours, (b) after 7 days

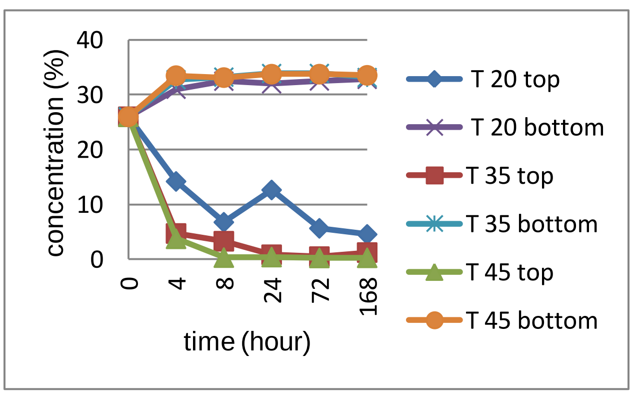


Figure 7: concentration as a function of temperature for first (top) segment and last (bottom) segment

Static stability

To estimate the bio slurry stability, the standard method for coal water slurry was adapted. For the coal water slurry (CWS), a stability of more than 70% was suggested [9]. As illustrated in Figure 8, using the same method, the static stability for the beta slurry and theta slurry was found at 80 % and 79% respectively. Liu et al.[7] refer a stability of 90% for a CWS with a concentration of 62.7 % and Abdulla [9] present a stability of 82% for 20% concentration of biochar in biooil of malle biomass.

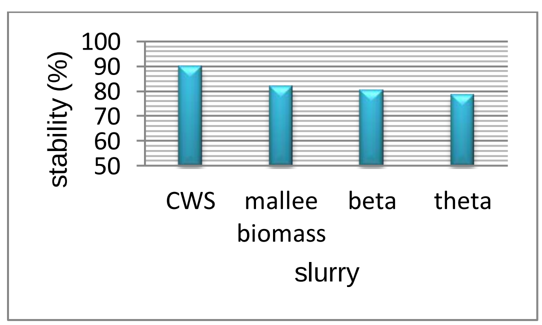


Figure 8: static stability of bioslurry

Settling test in a graduate cylinder

The settling behaviour of slurries in a batch settling test is illustrated in Figure 9, which shows the settling rate of alpha,beta and theta slurry samples in a sedimentation cylinder as a function of time for different initial settling heights of 250 mm. The figures for height of 200 mm, and 150 mm show the same trend. At the beginning of the experiment, the concentration is uniform throughout the cylinder. A short time after placing the slurry in the cylinder, a sharp interface is formed, separating the clear liquid in the upper part and settling particles in the lower part. In the area beneath the interface all particles go down at the same rate, so that the interface is also displaced at the same rate. By the time in the lower section of the cylinder, particles with a higher concentration amass. After a while, the particle-liquid interface approaches the region of concentrated particles and its rate of displacement starts to fall gradually because the resistance to the upwards flow of condensate through the particle increases. After some time, the settling rate becomes almost constant over the increasing time.

From the slope of the linear decreasing portion of the settling curve, zone settling velocity of the particles V_c in aqueous condensate suspension was determined and the results are presented in Table 2. The measured values show that, the settling velocity decrease with increasing concentration. A similar trend was found in the big scale experiment. Furthermore, it is possible to conclude that the height has no influence over the settling velocity.

Table 2: settling velocity of suspension for alpha slurry (23.4%), beta slurry (26%) and theta slurry (31.3%)

	settling velocity (mm/h) / *concentration (wt. %)*		
height (mm)	*23.4*	*26*	*31.3*
250	7.9±2.2	6.7±1.1	4±0.9
200	6.9±2.2	5.7±0.6	3.6±0.4
150	6.5±1.7	5±1.0	3±0.6

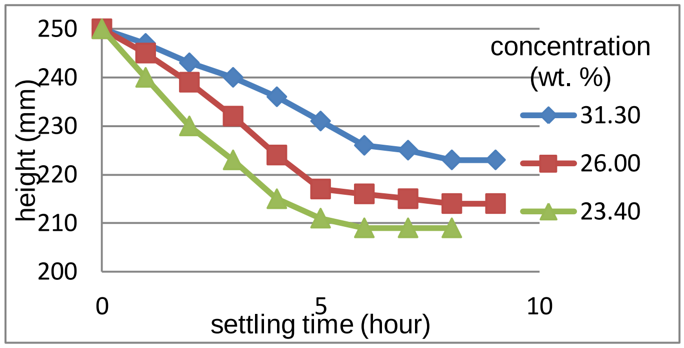


Figure 9: interface height against time plots for zone settling of different concentration slurries (a) at the initial settling height of 250 mm

3. Conclusion

Three bio slurries identified as “alpha”, “beta”, and “theta” with respectively, 23.4 wt. %, 26 wt. %, and 31.3 wt. % of char particles. The particle size distribution of all three of the slurries corresponds to an X_{50} was below 30 µm and X_{95} was below 85 µm. From the viscosity analysis, the bioslurries characteristic showed non-Newtonian behaviour and pseudo-plastic or shear thinning behaviour. Furthermore, the viscosity of the slurry increase with the increase of the particle concentration, but as expected decreases with increasing the temperature.

It seemed that with a higher initial concentration of 31.3% the particle moved closer to the maximum packing density, thus there were fewer changes in the concentration at the lower levels. The settling rate was lower for the most concentrated slurry because the resistance to the upward flow of the fluid increases.

The sedimentation rate of the char particles and the solid concentration in the bottom region are not affected by the change of initial settling height. Thus, it can be concluded that the hydrostatic pressure of the suspension has no impact on the particles settling. Therefore, small scaled experiments can be scaled up.

As an increasing the storage temperature from room temperature to a temperature of 35^0C and 45^0C, the increase the settling rate. Therefore, it is possible to conclude that for storing the bioslurry lower temperatures are better suited.

Finally, using the Kynch theory of sedimentation, the settling velocity of the particles in the suspension was calculated. The settling velocity of the particles decreased with the increased of the suspension concentration and with different settling height there is no influence.

The phase separation occurs within an hour, so it is recommended to keep the slurry stable and homogeneous by a continuous stirring process.

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