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Enzyme digestion of biofiber from mechanical heat treated municipal solid waste: accessing kinetic and rheological design data using a pilot-scale high-solids mixer

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Abstract

Mechanical heat treatment of municipal solid waste offers a route for the production and separation of a biofiber fraction with high organic content, which is a potential source of sugars for biochemical conversion to chemicals and fuels. This paper describes a study of the enzymatic digestion of this biofiber fraction using a 50L commercial vertical mixer, applying a commercial cellulase. Power measurements, with calibration of mixer constants using standard Newtonian and non-Newtonian fluids were used to determine apparent viscosity of biofiber mixtures, effective shear rate and Reynolds and Power Numbers. Measurements could be easily carried out at high solids contents, >25% dry weight, where initial biofiber mixtures had high viscosity, typically 100-150 Pa·s, with strong shear thinning behavior. Microscopy showed that the biofiber contained many individual wood and other plant fibers, which would entangle and so resist shear forces. Partial alignment of these fibers would be responsible for the shear-thinning effect. The fibers were repeatedly cut and reduced in length as a result of enzymatic hydrolysis, responsible for the large fall in viscosity during digestion. The viscosity of the biofiber slurries were monitored up to 48 hours digestion time, with analysis of samples to determine sugar monomer content. Digestion kinetics were analyzed using an exponential recovery model, where glucose yields of around 35% were found for digestion of a biofiber derived from standard and also high paper MSW mixtures. Further yield optimization would be required to achieve commercial viability.

Keywords: municipal solid waste; biomass; mixing; digestion; rheology; pilot-scale

Highlights

1. Real-time enzymatic digestion of MHT biofiber was followed using a commercial mixer

2. Apparent viscosity, shear-rate and rheological indices were calculated

3. Viscosity loss during digestion is due to cutting of fibers, which reduces tangling

4. Standard and high paper MHT biofiber fractions were prepared and digested in the mixer

5. Glucose yields of 35% require further optimization for commercial acceptance

1. Introduction

Municipal solid waste (MSW) is defined as a refuse stream collected by local authorities after preliminary sorting to remove recyclable components [1]. The residual MSW stream therefore contains a mixture of ill-defined, non-recyclable components, including some plastics, packaging, food, contaminated papers, wood products and other items. The stream is problematic in that the wide variety of constituents and their intimately mixed nature makes post-sorting and separation challenging using physical and mechanical means [2]. The stream accounts for around 40% of all household and business waste in the UK, depending on region and depending on efficiency of recyclables separation. Therefore, even in the best case a much greater effort is required in order to seek better recycling and/or recovery routes for these significant material volumes [3].

In recent years there has been interest in a variety of industrial refining techniques for better utilization of MSW [4]. Typically, refining concepts involve the separation of the incoming feedstock into different fractions, which are recovered and passed on for further processing as intermediates, either for materials, chemicals or energy generation [5]. Fractionation may be carried out by a variety of means including chemical or thermo-chemical [6], biochemical [7, 8], or by physico-chemical processing [9]. A variant of physico-chemical processing is described as Mechanical Heat Treatment (MHT), which may be particularly suited as the first fractionation step of an integrated route for refining MSW feedstocks at large scale. MHT requires the mixing and heating of batches of MSW feedstock in a rotating autoclave, with injection of steam at temperatures between 140-160°C [10]. The combination of mechanical tumbling and steam environment causes the organic derived paper, card, food and vegetable constituents to break down into a fine fibrous material, with millimeter dimensions or less, which can referred to as MHT-biofiber. In contrast, packaging, containers and other synthetic polymer items either remain unaltered in shape, or otherwise are softened and congealed into larger more compact pieces, typically of centimeter dimensions or more. After treatment the entire contents of the autoclave are ejected and passed through a mechanical sieve, to separate the coarse synthetic polymeric fraction from the fine organic fiber fraction. Both fractions can then be consolidated and removed for onward processing [11].

The MHT-biofiber fraction contains a higher proportion of plant cell-wall polysaccharides than the original MSW feedstock, which therefore makes it attractive as a source of sugars for fermentation. In particular, glucose and xylose, derived from cellulosic and lignocellulosic cell wall components, can be utilized as feedstocks for yeast or bacterial fermentation, for production of ethanol or butanol transport fuels or other platform chemicals [12]. The use of enzymatic digestion for generation of glucose and other sugars from agricultural and industrial biproducts has been well studied [13]. However, little work has been published on the application of analogous techniques for saccharification of MHT-biofiber, which may equally or more attractive from an environmental perspective. In addition, the initial MHT treatment may provide a degree of physico-chemical action, which may reduce the recalcitrance of lignocellulosic cell wall components towards enzyme digestion [14].

This study has therefore focused on an investigation of the enzymatic digestion of MHT-biofiber, to determine its potential as part of an integrated process for sugar production. A schematic overview of a possible process is shown in figure 1. Furthermore, since the production of MHT-biofiber requires efficient mechanical tumbling action, the process must be operated at pilot scale or greater. Therefore, it was appropriate in this study to carry out investigations also at pilot scale, in order to provide commercially representative data, suitable for engineering design and scale-up. Previous studies by the collaborating autoclave technology provider (Wilson Biochemical Ltd) had confirmed that MHT-biofiber generated using a 50 L vessel was representative of that from full commercial scale [15]. Therefore to integrate with this scale, the current study employed a 50 L capacity enzyme digester, which was adapted from a commercially available food cooker/mixer, retrofitted for measurement of mixer rotational power. The cooker/mixer rig could be operated with biofiber mixtures at high solids contents, at precisely controlled temperature and mixing speed. The arrangement allowed the generation of realistic kinetic and rheological process data, vital for design and optimization.

The properties and composition of representative batches of MHT-biofiber were examined using different physical, chemical and microscopic techniques, in order to better understand the effects of MHT treatment, and how this related to the action and efficiency of enzyme digestion of the resultant biofiber. Rheological analyses were performed using theoretical techniques developed for mixer technologies, which allowed the apparent viscosity and other rheological parameters to be determined under different mixing conditions and also in real time during digestion. The kinetics of enzymatic digestion were analyzed using sampling protocols, with trends superimposed against viscosity data for better understanding of process and mechanistic relationships. A commercial enzyme cocktail recommended for saccharification of lignocellulosic materials was chosen for the study, again to provide realistic data for scale-up. The experimental methodologies and rationale behind the study will be useful for developments in the wider biotechnology and waste processing industries.

2. Materials and Methods

2.1 Biofiber feedstocks.

The biofiber used in this study was produced using a pilot-scale rotating autoclave, designed for a typical batch size of MSW around 50 L (Wilson Biochemical, Chesterfield, UK). Each run led to the generation of around 20 L volume of wet MHT-biofiber product, which was appropriate for subsequent enzyme digestion trials. A batch of biofiber was prepared by MHT processing of a simulated standardized MSW feedstock, comprising of 45% paper and cardboard, 15% food waste, 10% wood, 22% plastic, 3% garden waste, 5% metals [16]. Also, a paper rich MSW feedstock was prepared, consisting of 80% paper and cardboard and 20% plastic, which generated an organic rich biofiber product, as might be the result of collection of office paper waste. Following earlier trials, a standardized temperature of 160°C was selected for production of the batches of biofiber, with a process time of 60 minutes [17]. On exiting the autoclave, the treated material was immediately passed manually through a 10 mm screen. The separated fine biofiber fraction was collected and frozen for storage, and rethawed for use as required. Typically, the moisture content of the as-made biofiber was around 70% on total wet weight. Previous analyses had shown that the biofiber from the standardized MSW comprised of approximately 58% w/w lignocellulose, of which 65.5% was cellulose (38% of total fibre), 27.6% was lignin (16% of total fibre) and 6.9% was hemicellulose (4% of total fibre) [18]. The high cellulose content suggested that the biofiber would be a practicable fermentation feedstock.

2.2 Enzyme for digestions

A commercial Cellic CTec-2 enzyme cocktail was used for all digestions, which consisted of an aggressive cellulase also with xylanse activity (Novozymes UK). The cellulase activity was determined as 203 FPU/g and β-glucosidase activity as 4900 CPU/g, according to standard methods [19].

2.3 Pilot-scale mixer for enzyme digestions

An adapted commercial cooker/mixer was employed for rheological studies of biofiber and for enzyme digestion experiments (model number CT50E, DeDanieli Snc, Italy). This was a single axis vertical design, with inner bowl height and diameter of 400 and 420 mm respectively, giving a 50L total capacity and ~35L maximum working capacity, with a close-fitting lid with silicone rubber seal around the stirrer shaft. A small port was cut in the lid of the bowl to allow for chemical and enzyme additions through a dispensing tube, with a slightly larger port cut to allow pH measurements and sampling. The bowl was heated via an electrically heated oil filled jacket, with temperature control of the bowl contents at better than +/- 1^{o}C. A modified gate stirrer was installed, with horizontal angled blades, with Teflon scraper bars at base and wall. This was mounted co-axially with a fixed set of horizontal baffles, as shown schematically in figure 2. The stirrer speed was continuously adjustable from 20 to 80 rpm. The total active input power to the drive at a given speed was measured in kilowatts using a retrofitted digital three phase power meter.

2.4 Measurement of rheology of biofiber and standard fluids

A single batch of golden syrup (GS) was obtained from a commercial supplier (HH Industries Ltd, UK), which was selected to act as a Newtonian rheological standard fluid. In addition, a batch of dry powdered carboxymethyl cellulose (CMC) was purchased from a local store (Solvite Ltd). This was made up in aqueous solution at 4.7 % (w/w) concentration, with mixing to avoid agglomeration of dry particles, then standing for 24 hours at ambient temperature before measurements. The equilibrated solution acted as a non-Newtonian fluid.

The standard fluids were first characterized using a laboratory rotational viscometer, with a concentric cylinder geometry, with a matt surfaced inner cylinder at a gap width of 1 mm (RheolabQC, Anton-Paar Gmbh). The viscosity behavior of the fluids was measured using an upward and downward shear-rate sweep, from 2 to 50 /sec, measured over 100 points in each direction at 0.5 sec/point, at 20°C. The thermally dependent viscosity behavior of the golden syrup was also determined using a stepwise temperature sweep from 15 to 45°C, at a shear rate of 10/sec.

The rheological characteristics of the commercial cooker/mixer rig were determined using the two rheological standard fluids, using methodologies described in the theory section below. Volumes of 18 L of CMC or GS fluid were transferred to the bowl, which were mixed at stepwise increasing speeds from 20 to 80 rpm, at a temperature of 20°C. Increments in speed were performed in the upward and then downward direction, with a 30 second stabilization period at each increment, then measurement of total active power averaged over the following 30 seconds. The active power required to rotate the stirrer in the empty vessel was also measured at the corresponding speed increments, which was subtracted to give the power required under mixing conditions, as required for calculations. In addition, the thermal behavior of the golden syrup was determined at stepwise increasing temperatures in the commercial cooker/mixer, from 17 to 40°C, at a rotational speed of 21 rpm, with stabilization for 3-5 minutes at each temperature, with measurement of average total active power at each increment.

A batch of 20 kg of biofiber made from standard MSW was made up at 25 % weight on solid, assuming an approximate density of 1.1 would give a volume of 18 L, equivalent to the volumes and nominal fill-factor of the rheological standards in the commercial mixer. This was mixed with stepwise upward and downward incrementation of rotational speed, as for the standard fluids, also at a temperature of 20°C.

2.5 Analysis of sugar yield

The total theoretical availability of sugars present in the biofiber materials was determined using a total acid hydrolysis protocol, according to published procedures [20]. Analysis of concentrations of sugar monomers in hydrolysates was carried out using high-pressure anion exchange chromatography with pulsed amperometric detection (Dionex UK), with suitable reference monomer standards. The sugar concentrations of small samples of mixtures taken during enzyme digestion were also analyzed by ion chromatography. The yields achieved as a result of saccharification were presented as a percentage of the theoretical availability of the corresponding sugars from total hydrolysis. Sugar yields on a basis of total biomass weight were also calculated as appropriate.

2.6 Biofiber digestion experiments

As above, 20 kg portions of biofiber were premixed off-line with water to give a concentration of 25 wt% on solid, with a total volume estimated at 18 L. The prepared material was transferred to the commercial cooker/mixer, with mixing at 21 rpm to achieve stabilization at 50^{o}C, which was the optimum temperature for enzyme activity. The lid and seals were kept in place to avoid evaporation, with mixing stopped periodically allow measurement of pH through the sampling port. If necessary, quantities of 6M sulphuric acid were poured slowly into the bowl, under mixing conditions, to reduce the pH of the mixture to a target of pH 5, which was the optimum for enzyme activity. During initial investigations it was found that the pH of the biofiber tended to rise during mixing, which was believed to be due to a reaction of the added acid with calcium carbonate optical brightener present in the office paper fraction of the original MSW [21]. Sufficient mixing time was required to add the amount of acid needed to complete this reaction, typically around 1.5 hours, after which only minimal further additions were required to maintain the pH 5 target. In total, around 100 and 200 mls of 6M sulphuric acid were added respectively to stabilize the pH of the standard and paper-rich MHT-biofiber mixtures, which did not have significant effect on overall solids content.

After pH and temperature stabilization, a quantity of Cellic CTec-2 enzyme concentrate was added through the port in the lid, mixing at 21 rpm, to give a concentration of 5% on total dry weight of material. After 5 minutes the mixing was halted and small sample of the mixture was taken and immediately transferred to a freezer at -18°C, in order to halt enzyme activity, with power, temperature, speed and pH also recorded. Digestions were continued for durations or either 24 or 48 hours, with continued measurement of parameters and collection of samples at appropriate intervals, also continuing small additions of 6M acid if required to adjust the pH back to 5. In addition, as a simulation of a larger scale process, the mixing speed was incremented one or more times through each run, as the viscosity of the material reduced significantly as a result of digestion.

3. Theory

In the method outlined by Metzner and Otto it was first assumed that the shear rate of a mixing system $(\dot{\gamma}_e)$ is proportional to the stirrer rotational speed (N), in equation (1), where (k_m) is a proportionality constant dependent on the geometrical characteristics of the mixer [22].

$$(\dot{\gamma}_e) = k_m . N \qquad (1)$$

Also, the apparent viscosity (μ_a) is the constant of proportionality between shear rate $(\dot{\gamma}_e)$ and the shear stress (τ), in equation (2).

$$\mu_a = \tau \,/ (\dot{\gamma}_e) \qquad (2)$$

For Newtonian fluids a relationship exists between the dimensionless Reynolds Number (N_{re}), in equation (3) and Power Number (N_p), in equation (4), as shown in equation (5), where C is a geometrical constant [23].

$$N_{re} = \frac{D^2.N.\sigma}{\mu} \quad (3)$$

$$N_p = \frac{P}{\rho.N^3.D^5} \quad (4)$$

$$N_{re} \,.\, N_p = C \quad (5)$$

Following a previous approach, the expansion of equation (5) gives a relationship between apparent viscosity (μ_a) and measured power (P), in equation (6), where (D) is the diameter of the mixing vessel [24]. For a Newtonian fluid the apparent viscosity is considered to be independent of shear rate, so if the viscosity is known the use of this equation allows the mixer geometrical constant (C) to be established, which should in principle be constant at all mixer rotational speeds, applying to both Newtonian and non-Newtonian systems.

$$\mu_a = \frac{P}{D^3 N^2} . \frac{1}{C} \quad (6)$$

For a non-Newtonian fluid, the apparent viscosity is related to the shear rate via a power law relation, in equation (7), where K and n are the power law indices [25].

$$\tau \;=\; K.\dot{\gamma}_e{}^n \quad (7)$$

$$\log(\dot{\gamma}_e) = \frac{\log(\mu_a) - logK}{(n-1)} \quad (8)$$

The established geometrical constant C allows the apparent viscosity (μ_a) of a non-Newtonian fluid to be determined as a function of power, from equation (6). If equation (7) is reworked in logarithmic form, with known power law indices, as equation (8), then this relation can be used to establish the shear rate $(\dot{\gamma}_e)$, and hence the shear rate constant (k_m) in equation (1), from the known rotational speed (N). This then allows the shear rate to be determined for any fluid from the measured mixer rotational speed.

Therefore, with a knowledge of the appropriate geometrical constants C and k_m, the mixer can be used to determine both shear rate and viscosity of the fluid under examination. In addition, dimensionless indices including the Power Number and Reynolds Number can be found if the density of the fluid can be measured or estimated.

4. Results and Discussion

4.1 Rheological measurement of standard fluids

The viscosity of the GS standard measured using the rotational viscometer was constant over the full shear rate sweep range, in figure 3, as expected for Newtonian behavior, with a value of 67.4 Pa·s at 20°C, with minimal hysteresis between upward and downward sweep directions. The same figure confirmed the shear-thinning behavior of the CMC standard, where power law indices were determined as K=55.74 Pa·s^n and n=0.378, at 20°C, again with minimal hysteresis. For comparison, the cooker/mixer was used to measure the relationship between mixer rotation speed (N) and motor power (P) for both CMC and GS standard fluids, shown in figure 4a. In these experiments a hysteresis was observed between upward and downward rotational sweeps, believed to be partly due to the temporary entrainment of air bubbles in the fluids due to greater turbulence at increased speeds, as indicated by the visible increase in opacity. However, the greater power required for mixing GS at increased speeds was consistent with Newtonian behavior, where the reduced gradient for the CMC rotational sweep was consistent with shear thinning.

The viscosity of the GS standard was used to determine the geometry constant (C) for the pilot-scale mixer, from equation (6), shown graphically in figure 5. In principle this would be expected to be independent of rotational speed, but for this mixer arrangement it was found to fall with increasing speed, presumably as the circulation characteristics of the material changed with increasing centrifugal and other local speed dependent forces within the bowl. From observation, the GS material tended to climb up the walls of the bowl at higher speeds, with consequently less turn-over and lower contact with the fixed baffles. The power law indices for the standard CMC fluid were used to determine the apparent shear rate for the mixer at different rotational speeds, via equations (6) and (8), also shown in figure 5. This also revealed the change in behavior through the speed range, with the effective shear rate reaching a maximum and then reducing again, presumably due to the reduction in material contact with the baffles. However, the apparent positive behavior at lower speeds suggested a more stable mixing regime, up to around 0.67 s^{-1} (40 rpm). In this region the application of a single averaged shear rate constant (k_n) from equation (1) could be reasonable.

As a test of the stability of the mixing regime, the temperature dependence of viscosity of GS standard fluid was measured using the cooker/mixer at a constant rotational speed for 0.35 s^{-1} (21 rpm), which from the shear rate constant (k_p) was equivalent to a shear rate of 8.2 s^{-1}. Results were then compared with the same fluid measured using the rotational viscometer over a similar temperature range at a similar standard shear rate of 10 s^{-1}. The Arrhenius plots of log viscosity against reciprocal temperature in Kelvin are shown in figure 6, for both mixer and rheometer systems. The linearity of the data for the cooker/mixer was excellent, demonstrating the consistency of flow characteristics. The activation energies calculated for the cooker/mixer and rheometer were

84.0 and 95.9 kJmol^{-1} respectively, where the slight difference may be an indication of small changes in the turbulence patterns within the cooker/mixer as viscosity reduced at higher temperature.

4.3 Rheological measurements of wet biofiber

The lack of flow characteristics of the standard MSW biofiber at 25% solids meant that it was not possible to carry out rheological measurements using the rotational viscometer. The properties of the mixture were therefore investigated using the cooker/mixer, with power measurements recorded for both upward and downward speed increments, as shown in figure 4b. The geometry and shear rate constants determined from the rheology standards at each speed increment were applied to calculate the apparent viscosity of the biofiber in both sweep directions, shown in figure 7a. Severe shear-thinning behavior was observed with increase in effective shear rate, also shown in the figure, up to a rotational speed of around 0.67 s^{-1}. The corresponding flow curves for the biofiber are shown in figure 7b, for upward and downward sweeps, which were limited to the positive shear rate regime. At higher rotational speeds the biofiber mixture experienced the wall climbing effect which had also affected the standard fluids. The redistribution of material within the bowl at higher speeds was also presumed to be a cause of the marked hysteresis, where on the reversal of sweep direction the material was not able relax sufficiently quickly regain its original texture. The apparent viscosities derived from equation (6) of 100-60 Pa·s for the upward sweep, were consistent with that determined for similar biomass materials at similar solids contents, using various rheometer configurations [26]. In previous studies this consistency of biomass has been described as a Bingham Plastic, with a recognizable yield stress below which the constituent fibers exist in a pseudo solid network [27]

The Reynolds Numbers for the mixing process of the cooker/mixer were back-calculated for power data over the full speed range, shown in figure 8a. For the Newtonian glucose syrup this required only the use of the single experimental viscosity, from equation (3), which confirmed that mixing was within the laminar regime [20]. The individual apparent viscosities measured at every speed increment were used to obtain equivalent Reynolds Numbers for the wet biofiber, assuming a bulk density close to 1000 kg.m^{-3}. The trend was also found to be linear with respect to rotational speed, but with a constant offset which may be a result of a systematic discrepancy in the geometry constant (C), due to the differing flow characteristics of biofiber and glucose syrup in the mixer bowl. However, values were confirmed to be within the linear regime, which was consistent with the observed shearing/folding/turnover type mixing action [20]. The Power Number fell with increasing Reynolds Number, according to the diagram in figure 8b, which is again anticipated in the laminar regime.

4.4 Pilot-scale enzyme digestion of biofiber

4.4.1 Standard MSW biofiber

The data obtained from the digestion run for the standard biofiber at 25% solids is shown in figure 9, with combined units for the right-hand y-axis of mixer speed, % glucose yield and temperature. The enzyme was added at a time of 1.43 hours, as indicated in the figure, after the temperature and pH stabilization period. A small amount of glucose was detected in solution prior to enzyme addition, which was presumably liberated as a result of the mechanical thermal and mixing action during the original thermomechanical treatment. The run was continued for 48 hours, with glucose liberation shown to develop progressively over this time. In other studies, detailed kinetic analysis has been applied to understand the saccharification behavior of cellulosic biomass, accounting for complex substrate and enzyme dependent factors [28]. However, the limited number of datapoints collected by sampling in this pilot-scale configuration permitted only a simple first order model to be employed, according to equation (9), where C_∞ and C_t are glucose yields at time (t) and infinity, and (r) is a kinetic rate constant.

$$C_{t=}\ C_\infty(1-e^{-r.t}) \qquad (9)$$

Fitting of this equation to the experimental digestion curve gave a rate constant r = 0.05/hr, with a corresponding equilibrium glucose yield of 34% based on a total theoretical availability of glucose of 42 wt% of total solid biofiber. This corresponded to 143 mg/g on dry biomass. Although not shown, the digestion of xylose followed a very similar kinetic profile, with a slightly higher yield of 42% on a total theoretical availability of 4.9 wt% total solid, corresponding to 21 mg/g on dry biomass. The similar responses of the cellulose and hemicellulose polysaccharides are anticipated considering their close association within the biomass cell wall. The final glucose concentration in the mixture was around 50 g/L, which is considered insufficient to lead to enzyme inhibition. Therefore, the limited enzymatic yield suggests that at least some components of the biofiber are still recalcitrant, despite the MHT treatment, which is not severe enough to deconstruct the lignocellulosic structures of the cell wall [14]. The first order kinetic analysis accounts for the depletion of the more accessible, less recalcitrant cell wall polysaccharides through digestion, which leads to the reduction in observed rate.

During the initial stabilization time the apparent viscosity fell from around 200 to 80 Pa·s, as the temperature of the biofiber rose up to the set point of 50°C. The texture of the mixture changed visibly during this period, due to break up of larger fiber aggregates as a result of the shear action. Such changes in viscosity and texture would need to be accommodated in the design of a commercial digester, especially where very high viscosities might be experienced during initial the loading of the mixing vessel. On addition of enzyme a further dramatic fall in apparent viscosity was observed over the digestion period, which eventually reduced below the measurable range, where the measured power was no longer greater than the power under empty conditions. From a textural perspective the biofiber slurry took on fully fluid characteristics, becoming self-levelling and creating eddies around the moving stirrer blades. The Reynolds Number was calculated to be approaching the transitional regime, with a value around 2000 at the end of digestion. At a microscopic level there was evidence of a shortening of the length of the fibers constituting the biofiber material, which originated from the card and paper fractions, as shown in figure 10. At the start of digestion these wood and plant derived fibers were typically of several millimeters in length, whilst after 48 hours the fragments were of submillimeter dimensions, with a significant proportion in the micron range. The breakup of long fibers was considered to be chiefly responsible for the reduction in viscosity under digestion conditions, where the clashing and jamming of longer fibers inhibited the undigested material from undergoing fluid-like flow [29,30]. In addition, a proportion of fibrous polysaccharide material was dissolved during digestion, which from the analysis of initial and final sugar contents was around 16% of total dry mass . This led to relatively small reduction from 25 to 21% insoluble solids, which was insufficient in itself to account for the total observed fall in viscosity [31]. Other workers have investigated the influences of biomass particle size on biomass suspension rheology and subsequent enzyme digestion but have not considered the role of enzyme digestion directly on size and length reduction [32,33].

As explained, from figure 9, the stirrer speed was increased after the initial equilibration period and then incremented a further two times as the viscosity of the biofiber slurry reduced over time.
This approach was designed as a response to the dramatic changes in mixing characteristics during digestion, which was considered important to try and optimize mechanical action and flow behavior, moving from low to higher Reynolds number. On a larger scale such optimizations might be achieved by changes of mixer speed, or by use of more than one mixing vessel with differing paddle/propeller configurations and power output [34]. However, further work would be required to determine the

precise mixing regimes through the full viscosity range for highest digestion yields. The change in speed was accounted for in the viscosity and other rheological calculations, which led to small changes in apparent viscosity as would be expected from the shear thinning characteristics of the material.

4.4.2 Paper rich MSW biofiber

As in the previous protocol, the paper rich material was initially mixed without the presence of enzyme to allow full homogenization and stabilization at the desired temperature and pH. As before, the apparent viscosity reduced as the temperature increased over the equilibration period, in figure 11a, from an initial value of around 165 Pa·s, at 20°C, to around 100 Pa·s at 50°C. The mixing speed was then increased from 21 to 31 rpm, which resulted in a further fall in apparent viscosity, to around 62 Pa·s, as anticipated due to shear thinning. Enzyme concentrate was added at a time of 1.3 hours from the start of the experiment, again at a concentration of 5% on weight of dry material. From this point the apparent viscosity continued to fall smoothly and the concentration of glucose liberated as result of enzymatic hydrolysis was seen to progressively increase. However, a further increase in mixing speed to 40 rpm at 2.3 hours did not lead to a further fall in viscosity, which was presumed to be a consequence of the more Newtonian behavior of the fluid in this lower viscosity region. By the end of the 24-hour experiment period the viscosity has reduced significantly to around 1.2 Pa·s, from figure 11b, and displayed excellent flow and levelling characteristics, with no visible fibrous character.

From the total acid hydrolysis assay this biofiber feedstock represented a total glucose availability of 67 wt% on dry solid. The kinetic analysis by application of equation (9) indicated an ultimate glucose yield of 39%, slightly higher than the value for the standard biofiber, which was consistent with the greater content of refined paper, which would potentially be less recalcitrant and therefore lead to greater cellulose accessibility for enzyme digestion. The yield corresponded to 261mg/g on dry biomass. The rate constant from fitting of equation (9) was 0.31/hr, which was slightly lower than that measured for the standard biofiber, possibly a result of the lower enzyme to cellulose ratio.

5. Conclusions

Mechanical Heat Treatment using a rotating autoclave offers an attractive route for the better utilization of Municipal Solid Waste, through production and separation of a biofiber fraction containing a significant proportion of polysaccharides, including cellulose. This work has shown that MHT derived biofiber can be enzymatically digested using commercially available 50L cooker/mixer, which is a cost-effective platform for further scale-up. Analysis using data from standard fluids allowed generation of both rheological and engineering parameters over the range of mixing conditions found during digestion. A microscopy examination of the biofiber material showed that it consisted of many individual wood and other plant derived fibers, which entangle and so resist shear forces during mixing. Partial alignment of these fibers would be responsible for the shear-thinning behavior. The microscopy investigations also showed that fibers are repeatedly cut and reduced in length as a result of enzymatic action, which is responsible for the large fall in viscosity during the digestion process. Glucose yields of around 35-40% were determined for digestion of a biofiber derived from standard and also high paper MSW mixtures. These moderate yields point to the need for further optimization of the process to achieve commercial viability. The pilot scale system described in this work would be valuable in these endeavors.

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Figures

Figure 1. Schematic flow chart showing possible sequence including Mechanical Heat Treatment (MHT) for processing of municipal solid waste (MSW), with subsequent enzymatic hydrolysis of resulting biofiber

Figure 2. Schematic diagram of gate stirrer and baffle arrangement for pilot-scale cooker/mixer

Figure 3. Shear sweep curves for standard rheological fluids measured using the Rheolab rotational viscometer, at 20°C. GS=golden syrup, CMC=carboxymethylcellulose (4.7%). (■) up, (▲) down.

Figure 4. Rotational speed vs. active power relationships for materials in pilot-scale vertical mixer, at 20oC, (■) up, (▲) down. a: GS=golden syrup, CMC=carboxymethylcellulose (4.7%); b: standard MSW biofiber (25% solids).

Figure 5. Characteristics of pilot-scale mixer determined using standard fluids. (▲) geometry constant (C), (●) apparent shear rate.

Figure 6. Arrhenius plots of log(viscosity) against reciprocal temperature (Kelvin) for golden syrup. Measurement using the pilot-scale mixer at an apparent shear rate of 8.2 /s (▲), and the rotational viscometer at a shear rate of 10 /s (●).

Figure 7. Apparent viscosity of biofiber (25% wt on solid) derived from standard MSW, measured using the pilot-scale cooker/mixer at 20°C. a: vs. rotational speed b: vs. apparent shear rate. (●) upward speed ramp, (▲) downward speed ramp.

Figure 8. Dimensionless rheological indices measured using commercial cooker/mixer at 20°C. a: Reynolds Number vs rotational speed, b: Newton-Reynolds diagram; (▲) golden syrup standard fluid, (●), biofiber (25% wt on solid) derived from standard MSW.

Figure 9. Digestion of biofiber (25% wt on solid) derived from standard MSW, using pilot-scale cooker mixer. 5% Cellic CTec-2 enzyme on dry wt., with controlled acid addition to maintain pH 5. (●) apparent viscosity, (▲) temperature, (♦) glucose yield (% of theoretical), grey line = mixer rotational speed.

Figure 10. Transmitted light microscopy images of samples of standard MSW biofiber, taken at different times during digestion run using pilot-scale cooker/mixer.

Figure 11. Digestion of biofiber (25% wt on solid) derived from high paper MSW, using pilot-scale cooker mixer. 5% Cellic CTec-2 enzyme on dry wt., with controlled acid addition to maintain pH 5. (●) apparent viscosity, (▲) temperature, (♦) glucose yield (% of theoretical), grey line = mixer rotational speed. a: early time period b: full time period up to end of run at 24 hours.

References

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1 D. Watson, Municipal waste management in the United Kingdom, Copenhagen Resource Institute, http://www.cri.dk, working paper for the European Environment Agency (EEA) on waste implementation (2012)

2 B. Slater, M. Warhurst, Sorting Residual: Friends of the Earth briefing note (www.foe.co.uk) Trust company, (June 2008)

3 Department for Environmental Food and Rural Affairs (Defra); Science and Technology Select Committee, (2014)

4. A. Niziolek, O. Onel, F. Hasan, C. Floudas, Municipal solid waste to liquid transportation fuels – Part II: Process synthesis and global optimization strategies, Computers & Chemical Engineering 74 (2015) 184-203.

5. D.Tonini, T.Astrup, Life-cycle assessment of a waste refinery process for enzymatic treatment of municipal solid waste, Waste Management, 32(1) (2012) 165-176.

6. A. Umberto, Process and technological aspects of municipal solid waste gasification. A review, Waste Management, 32(4) (2012) 625-639.

7. A. Li, B. Antizar-Ladislao, M.Khraisheh, Bioconversion of municipal solid waste to glucose for bio-ethanol production, Bioprocess and Biosystems Engineering,30(3) (2007) 189–196.

8. X. Zhao, L. Zhang, D. Liu. Biomass recalcitrance: Part 1, Chemical compositions and physical structures affecting the enzymatic hydrolysis of lignocellulose, , Biofuels, Bioproducts and Biorefining, 6(4) (2012) 465-482

9. M. Ballesteros, F. Sáez, I. Ballesteros, P. Manzanares, M. Negro, J.Martínez, R. Castañeda, J. Dominguez, Ethanol Production from the Organic Fraction Obtained After Thermal Pretreatment of Municipal Solid Waste, Appl. Biochem. Biotechnol. 161 (2010) 423–431.

10. Mechanical Heat Treatment of Municipal Solid Waste, Enviros Consulting Limited on behalf of DEFRA as part of the New Technologies Supporter Programme (2007)

11. Mechanical Heat Treatment of Municipal Solid Waste, Frith Resource Management, report on waste management for the Department for Environment, Food & Rural Affairs (DEFRA), (2012).

12. V. Menon, M. Rao, Trends in bioconversion of lignocellulose: Biofuels, platform chemicals & biorefinery concept, Progress in Energy and Combustion Science, 38(4) (2012) 522-550.

13. L. Zhu, J. O'Dwyer, V. Chang, C. Granda, M. Holtzapple, Structural features affecting biomass enzymatic digestibility, Bioresource Technology, 99 (2008) 3817–3828.

14. N. Mosier, C. Wyman, B. Dale, R. Elander, Y. Lee, M. Holtzapple, M.Ladisch, Features of promising technologies for pretreatment of lignocellulosic biomass, Bioresource Technology, 96 (2005) 673–686.

15. Internal work, Wilson Biochemical Ltd

---

16. Department for Environmental Food and Rural Affairs (DEFRA), 2017

17. F. Meng, R. Ibbett, T. DeVrije, P. Metcalf, G. Tucker, J. McKechnie, Process simulation and life cycle assessment of converting autoclaved municipal solid waste into butanol and ethanol as transport fuels, Waste Management, 89 (2019) 177-189.

18. A. Dornau, J. Robson, G.Thomas, S. McQueen-Mason, Robust microorganisms for biofuel and chemical production from municipal solid waste. Microb. Cell. Fact., 19 (2020) 68-86.

19. A. Rodrigues, M. Haven, J. Lindedam, C. Felby, M. Gama, Celluclast and Cellic®CTec2: Saccharification/fermentation of wheatstraw, solid–liquid partition and potential of enzyme recycling byalkaline washing. Enzyme and Microbial Technology, 79 (2015) 70–77.

20. R. Ibbett, S. Gaddipati, S. Davies, S. Hill, G. Tucker, The mechanisms of hydrothermal deconstruction of lignocellulose: New insights from thermal–analytical and complementary studies, Bioresource Technology 102(19) (2011) 9272-9278.

21. X. Wang, A.Song, L. Li, X. Li, R. Zhang, J. Bao, Effect of calcium carbonate in waste office paper on enzymatic hydrolysis efficiency and enhancement procedures, Korean J. Chem. Eng., 28(2) (2011) 550-556.

22. P. Cullen, C O'Donnell. M. Houška, Rotational viscometry using complex geometries – a review, Journal of Texture Studies, 34(1) (2003) 1-20.

23. G. Tatterson, Scaleup and design of industrial mixing processes, (1994) McGraw-Hill, NY.

24 K. Takahashi, T. Yokota, H. Konno, Power consumption of helical ribbon agitators in highly viscous pseudoplastic liquids, Journal of Chemical Engineering of Japan, 17(6) (1984) 657-659.

25. R. Bird, W. Stewart, E Lightfoot, Chapter 9: Agitation, in Transport Phenomena, J. Wiley, New York (2007)

26. J. Knutsen, M Liberatore, Rheology of high-solids biomass slurries for biorefinery applications, J. Rheol. 53 (4) (2009) 877-892.

27. J. Stickel, J. Knutsen, M. Liberatore, W. Luu, D. Bousfield, D. Klingenberg, T. Thatcher, W. Root, M. Ehrhardt, T, Monz, Rheology measurements of a biomass slurry: an inter-laboratory study, Rheol. Acta 48 (2009) 1005–1015.

28. S. Harun, V. Balan, M. Takriff, O. Hassan, J. Jahim, B. Dale, Performance of AFEX™ pretreated rice straw as source of fermentable sugars: the influence of particle size, Biotechnology for Biofuels 6 (2013) 40.

29. D. Tatsumi, S. Ishioka, T. Matsumoto, Article Effect of Fiber Concentration and axial ratio on the rheological properties of cellulose fiber suspensions, Journal of Society of Rheology, Japan 30(1) (2002) 27-32.

30. B. Derakhshandeh, R. Kerekes, S. Hatzikiriakos, C. Bennington, Rheology of pulp fibre suspensions: A critical review, Chemical Engineering Science 66 (2011) 3460–347.

---

31. R. Kerekes, Rheology of fibre suspensions in papermaking: An overview of recent research, Nordic Pulp and Paper Research Journal 21(5) (2006) 598-612.

32. L. Tian, F. Shen, H, Yuan, D. Zou, Y. Liu, B. Zhu, X. Li, Reducing agitation energy-consumption by improving rheological properties of corn stover substrate in anaerobic digestion, Bioresource Technology 168 (2014) 86–91.

33. C. Dibble, T. Shatova, J. Jorgenson, J. Stickel, Particle Morphology Characterization and Manipulation in Biomass Slurries and the Effect on Rheological Properties and Enzymatic Conversion, Biotechnol. Prog. 27(6) (2011) 1751-1759.

34. D. Russ, J. Thomas, Q. Miller, R. Berson, Predicting Power for a Scaled-up Non-Newtonian Biomass Slurry. Chem. Eng. Technol., 38 (2015) 53-60.