Modified ADM1 for high-rate anaerobic co-digestion of thermally pre-treated brewery surplus yeast wastewater
Liam Pettigrew, Alexander Gutbrod, Herbert Domes, Frauke Groß, Juan M. Méndez-Contreras and Antonio Delgado

ABSTRACT
Co-digestion of surplus yeast with brewery wastewater is a potentially economical method for recovering energy, in the form of biogas, from this difficult to dispose of by-product. In this work a modified version of the ADM1 (Anaerobic Digestion Model No. 1) was calibrated for an anaerobic digester fed with thermally pre-treated brewery surplus wastewater. The model could predict changes to reactor methane production and reduction of biodegradable matter when fed with both pre-treated and untreated yeast surplus wastewater at varying loading rates. Model calibration focused on low temperature thermal pre-treatment as experiments into a combined thermal–alkaline pre-treatment did not show any significant improvements. A low temperature pre-treatment of 60°C for 30 minutes was sufficient for yeast inactivation and allowed for stable and more efficient operation of the high-rate anaerobic digester over a period of 232 days. The low temperature and time for pre-treatment also reduced the evaporation of easily biodegradable residual ethanol present in the influent, while still maintaining a low level of suspended matter. Inline measurements of gas composition, production and effluent chemical oxygen demand were sufficient for reliable model calibration of these same outputs. More detailed characterization of influent and effluent is required if organic acid concentrations for pH control are needed.

Key words | ADM1, brewery wastewater, co-digestion, pre-treatment, surplus yeast

INTRODUCTION
The beer brewing process produces many by-products that must be monitored and disposed of or reused correctly. Some of these by-products can be relatively easily disposed of or, as in the case of spent grains from mashing, sold on as feed for livestock. However, yeast surplus is a problem by-product for breweries, as although it can also be sold as a feed addition for livestock the value is low due to the need for a costly drying process (Kunze 2011). A large amount of wastewater produced by breweries must also be cost-effectively and safely treated so as to meet increasingly stricter discharge requirements (Simate et al. 2011). Although studies into reducing water consumption and therefore wastewater production have had success (Fillaudeau et al. 2006; Blomenhofer et al. 2013; Pettigrew et al. 2015), the brewing industry still discharges large volumes of highly polluting effluents every year (Enitan et al. 2015). This wastewater must be treated before being discharged into a municipal sewage system if costly fees are to be avoided. In Germany, brewery wastewater is required to have a chemical oxygen demand (COD) of under 110 mg/L. If the requirements are not met the brewery can face large fines (Abwasserverordnung – AbwV 2004). As the wastewater is already required to be treated, co-digestion of surplus yeast with the existing wastewater flows is a viable method for converting the low-value waste yeast into a larger volume of potential methane, which can be used as an alternative energy source in the brewery.

Despite both aerobic and anaerobic treatment methods being available for treatment of high strength wastewaters, an anaerobic treatment system, such as an upflow anaerobic sludge bed (UASB) reactor, is viewed to be the environmentally safer and more efficient method (Austermann-Haun & Seyfried 1994; Parawira et al. 2005; Brito et al. 2007). The expanded granulated sludge bed (EGSB) reactor is a type
of UASB that has higher upflow rates so as to induce granulation of biomass. The EGSB provides higher efficiency at higher loading rates than a standard UASB and is also a more robust system that can better handle fast changes or shocks to wastewater flow and concentration (Lettinga et al. 1997). A high-rate EGSB anaerobic digester has been found to be able to treat a concentrated brewery wastewater containing an organic loading of up to 30,000 mg/L with COD removal efficiencies of over 90%. Typical brewery effluent has a COD in the range of 2,000–6,000 mg/L (Driesen & Vereijken 2003), which can be increased by the addition of excess yeast biomass not already washed into the wastewater stream.

Practical and applied modelling of these high-rate anaerobic digestion systems is still developing and is becoming increasingly important as their advantages in certain industries become apparent. The IWA Anaerobic Digestion Model No. 1 (ADM1) aims to represent the complexity of many of the phenomena in the anaerobic process (Batstone et al. 2002). However, direct application for control purposes is difficult due to problems with identifying the influencing model parameters. Simpler models have been able to predict performance of UASB (Morel et al. 2006) and EGSB (López & Borzacconi 2011) reactors using online measurements and observer systems for kinetic constant estimation. The simpler models are easier to calibrate but do not properly represent the complexity of the actual processes taking place. Models using simplified kinetics also generally require that kinetic parameters be modified as the microorganisms evolve over time (López & Borzacconi 2011). The more complex ADM1 can still be used if enough data are available for proper model calibration and there is sufficient knowledge of certain process dynamics. Recent work investigating the modelling of starch industry wastewater treatment in a UASB found that a model calibrated from reactor steady state was able to predict changes in methane production at different loading rates and also in a separate reactor. Such prediction was possible with a fairly constant wastewater quality and proper fractionalization of influent substrate COD (Hinken et al. 2014). It has also been found that limited characterization of influent to just total carbon was sufficient to accurately predict gas production of a reactor treating brewery wastewater (Ramsay & Pllummanappallil 2005).

In practice the co-digestion of brewery yeast and wastewater in concentrations of up to 1.1 (v/v)% allowed for continued stable operation of a pilot-scale UASB. However, process failure occurred at concentrations over 2.8 (v/v)% or organic loading rates greater than 8 kgCOD/(m² d) due to an overload of suspended solids and their poor degradation (Zupančič et al. 2012). The effects of three pre-treatment techniques to increase the digestion rate and biogas production of an anaerobic co-digester treating brewery wastewater and surplus yeast were investigated in another study. The co-digestion influent consisted of brewery wastewater combined with surplus yeast from the brewing process. Mechanical pre-treatment consisted of exposing the wastewater to high shear rates by using a laboratory homogenizer for two 10 minute cycles of up to 24,000 rpm. Thermal pre-treatment was at 90 °C for 6 hours and chemical pre-treatment involved dosing of NaOH at up to 20 g/L. The study found that neither thermal, chemical nor mechanical pre-treatment of the mixed wastewater had any significant effect on the anaerobic digestion process by itself. In fact the organic portion of the wastewater was reduced during thermal pre-treatment due to evaporation of residual ethanol and only very low levels of cell lysis were observed from any of the treatment techniques. Longer term studies, greater than 70 days, were not undertaken to investigate the negative effects of wastewater and yeast on granular sludge development and reactor efficiency (Neira & Jeison 2010). Investigations into different waste streams, including spent grain from a brewery, found that a thermal pre-treatment step (170 °C for 30 minutes) increased methane generation in all cases. Although, it is noted that a substrate with an already high soluble fraction composed of high amounts of easily degradable sugars did not benefit greatly from a pre-treatment step (Cano et al. 2014).

The efficiency of low temperature (<100 °C) thermal pre-treatment on the solubilization of organic matter has also been tested using the example of poultry slaughterhouse sludge (Ruiz-Espinoza et al. 2012). In this study it was shown that a low temperature treatment method investigating treatment temperatures between 70 and 90 °C for between 30 and 90 minutes significantly reduced the required hydraulic retention time (HRT) for anaerobic digestion and increased both biogas and total methane production. However, the thermal pre-treatment of 70 °C for 30 minutes achieved only a negligible increase in soluble COD of 1.69%. The highest solubilization of 10.42% occurred at 90 °C for 90 minutes, which was the highest temperature and time for this investigation. Further investigations into the treatment of poultry slaughterhouse sludge also found that Salmonella spp., fecal coliforms and helminth ova present in the sludge were inactivated at temperatures above 80 °C when treated for longer than 2 hours (Atenodoro-Alonso et al. 2015). These works show that such technologies can be of benefit not just to industry but also to developing countries where
energy usage and the removal of pathogenic microorganisms is of upmost importance. Another study found that a combined thermo-chemical pre-treatment of dewatered pig manure produced noticeable enhancements to biogas production and methane content of the biogas at lower temperatures than only thermal pre-treatment. A maximum increase of 78% biogas and 60% methane production was realized with a thermo-chemical pre-treatment at 70 °C and 5% lime addition in the study (Rafique et al. 2010).

A study into the effect of thermal pre-treatment on waste activated sludge treated in a thermophilic anaerobic digester was investigated using a modified ADM1. The disintegration and hydrolysis processes were modified from first order kinetics to the Contois model, and the general Hill function was used to represent ammonia inhibition for acetoclastic methanogens. The Contois model has been found to represent a wide range of organic wastes accurately when compared with experimental data, where first order kinetics are not always applicable. The Hill function allows for a second phase of acetate production to be properly modelled, a phenomenon that cannot be simulated by the non-competitive function in the standard ADM1 model. The resulting modifications to the ADM1 model agreed well with data measured under different pre-treatment conditions and provided a better understanding of the acetate accumulation dynamics (Ramirez et al. 2009).

This work investigates the usefulness of a modified ADM1 for predicting the effects of low temperature pre-treatment on brewery surplus yeast wastewater with fluctuating high organic loading. The effect of thermal pre-treatment on the operation of a laboratory-scale high-rate EGSB anaerobic digester is analysed using the modified ADM1 and the suitability of a thermal–alkaline pre-treatment is also tested.

**MATERIALS AND METHODS**

**Brewery surplus yeast wastewater**

Surplus yeast from the brewery Kitzmann Bräu GmbH & Co. KG (Erlangen, Germany) with a COD of between 150,000 and 500,000 mg/L is used to produce a wastewater with a COD of between 4,000 and 15,000 mg/L. The surplus yeast is diluted with tap water to reach the targeted COD levels. A temperature of 4 °C is maintained in the storage container to inhibit further fermentation. The surplus yeast wastewater is produced in 100 L batches using yeast collected directly from the brewery. The typical characteristics of the brewery surplus yeast wastewater used and the minimum and maximum values over the course of the experiment are summarized in Table 1. This wastewater is fed batch where it is further diluted in the anaerobic digester for an initial reactor COD of between 2,000 and 8,000 mg/L.

**Thermal and thermal–alkaline pre-treatment**

The thermal–alkaline pre-treatment reactor is a continuously stirred tank reactor (CSTR) constructed from stainless steel. The thermal reactor is designed to treat approximately 13 L of wastewater per batch feed and can heat the contents up to a maximum temperature of 84 °C using both external and internal heating elements. Approximately 25 minutes is required to bring the wastewater to a maximum temperature of 84 °C. A custom software and hardware automation system allows for automatic filling and emptying of the reactor and exact temperature and heating times of the reactor contents. External and internal temperature sensors monitor reactor surface and wastewater temperatures to ensure a constant temperature throughout the wastewater volume being treated.

The pH is monitored using the Atlas Scientific pH Probe V2.0 with temperature compensation from Atlas Scientific LLC. Custom software retrieves data from the pH probe and uses this information for pH control with two peristaltic pumps connected to a 15% (m/v) HCl solution and a 15% (m/v) NaOH solution. The pH of the reactor is adjusted to the given set point once the target temperature of the treatment process has been reached. The pH of the wastewater is set to 7.2 after thermal chemical treatment is complete.

**Table 1 | Analysis of brewery surplus yeast wastewater feed undertaken during EGSB operation**

<table>
<thead>
<tr>
<th>Item</th>
<th>Unit</th>
<th>Influent (typical)</th>
<th>Min–Max</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Total COD</strong></td>
<td>mg COD/L</td>
<td>8,320 ± 135</td>
<td>3,180–15,800</td>
</tr>
<tr>
<td><strong>Soluble COD</strong></td>
<td>mg COD/L</td>
<td>4,660 ± 114</td>
<td>1,550–7,760</td>
</tr>
<tr>
<td><strong>Total solids</strong></td>
<td>mg TS/L</td>
<td>4,050 ± 165</td>
<td>2,200–6,000</td>
</tr>
<tr>
<td><strong>Volatile organic acids</strong></td>
<td>mg/L</td>
<td>1,460 ± 24</td>
<td>1,050–1,900</td>
</tr>
<tr>
<td><strong>Total N</strong></td>
<td>mg N/L</td>
<td>556 ± 9</td>
<td>350–750</td>
</tr>
<tr>
<td><strong>Soluble N</strong></td>
<td>mg N/L</td>
<td>106 ± 2</td>
<td>50–230</td>
</tr>
<tr>
<td><strong>Ammonium, NH₄⁺</strong></td>
<td>mg NH₄⁺/L</td>
<td>80 ± 2</td>
<td>60–120</td>
</tr>
<tr>
<td><strong>pH</strong></td>
<td>–</td>
<td>6.56 ± 0.1</td>
<td>5.5–7.2</td>
</tr>
</tbody>
</table>
Laboratory-scale EGSB reactor

The anaerobic digestion of the pre-treated wastewater is undertaken in a laboratory-scale EGSB sequencing batch reactor. The reactor holds 28 L of wastewater and maintains a temperature of 35 °C and a pH of 7.2. Feed sludge for the reactor was taken from the anaerobic digesters operating at the municipal wastewater treatment plant of Erlangen, Germany. The formation of granules was stimulated by circulating the wastewater in the reactor at a flow speed of 8.11 m/h. A start-up phase lasting 63 days allowed for granule formation and proper adaptation of the reactor to thermally pre-treated brewery yeast surplus wastewater. The EGSB was run as a sequencing batch reactor where 15 L of effluent was removed after allowing for the granules to settle and replaced with 15 L of influent taken from the thermal pre-treatment reactor.

Test CSTR

Brewery surplus yeast wastewater that has not been pre-treated either chemically or thermally was fed in parallel to a CSTR. The CSTR is a 2 L Erlenmeyer flask filled to 1.3 L with temperature maintained at 35 °C and pH at 7.2. A magnetic stirrer is set to 100 rpm to ensure complete mixing in the reactor. The CSTR is inoculated with granulated sludge taken from the EGSB reactor after 106 days of operation. The CSTR is also operated as a sequencing batch reactor where 600 mL batches are fed at the same intervals as the EGSB but with wastewater that has not been pre-treated.

Experimental analysis

Tests on different treatment times and pH were also undertaken in 250 mL Erlenmeyer flasks filled with 200 mL of treated and untreated wastewater and 10 mL of inoculum from the EGSB reactor. The flasks were sealed with aluminum foil and continuously stirred at 100 rpm in a warm water bath maintaining a temperature of 35 °C. The COD of the wastewater in the flasks was measured at the beginning of the experiment and after 5 days to determine the biological degradability of treated and untreated wastewater.

Initial experiments focused on a combined thermal–alkaline pre-treatment. Twenty-four flasks containing varying concentrations of brewery surplus yeast wastewater were prepared and pre-treated at differing pH levels and times between 41 and 50 minutes. A further 30 flasks were treated at times ranging from 51 to 60 minutes. The temperature was fixed at 84 °C for all experiments.

Further experiments focused on thermal pre-treatment at times ranging from 10 to 75 minutes at temperatures of 84 °C and 60 °C (yeast cells die at 55–60 °C). These experiments compared the biodegradability of the treated vs untreated wastewater in a CSTR and EGSB reactor.

The COD of the wastewater before and after pre-treatment, as well as during and after anaerobic digestion, was measured using a QuickCOD analyser from LAR Process Analysers AG (Berlin, Germany). The analyser implements a thermal combustion method that completely oxidizes the wastewater, which is followed by detection of the amount of oxygen consumed by the combustion. An inline continuous measurement system was developed that automatically sampled from the reactor every hour and measured the COD; the remaining sampled effluent was automatically returned to the reactor so as to maintain the liquid volume.

The volume of biogas produced by the EGSB reactor was measured inline using a custom tipping chamber volume counter. The gas bubbles through a water container and into the measurement chamber, which is filled by the rising gas bubbles. When the measurement chamber is filled, the buoyancy of the filled chamber causes it to tip and release the captured gas, allowing it to be refilled. This device is able to measure the amount of gas produced in 5 mL increments over a wide range of flow rates.

The composition of the produced biogas was measured inline using an SSM 6000 LT biogas analyser from Pronova Analysentechnik GmbH & Co KG (Berlin, Germany). The SSM 6000 is specially designed for the analysis of gas from biogas production plants. The device prepares the sample gas with filters and gas cooling to 5 °C for dehumidification. An infrared measuring process is used to detect methane (CH₄) and carbon dioxide (CO₂) with high accuracy. Hydrogen sulphide (H₂S) and oxygen (O₂) are detected using electrochemical sensors. The analyser is able to measure 0 to 100% CH₄ and CO₂, 0 to 25% O₂ and 0 to 1,000 ppm H₂S. Gas from the EGSB reactor was collected in a small container and periodically measured using a manually activated valve; this ensured that the biogas analyser was receiving enough feed gas and was not creating a vacuum in the small laboratory-scale reactor. Methane production by the EGSB was calculated by combining the gas composition measurements with the gas production rate. This value combined with the inline and offline COD measurements was used for model calibration and validation.

Model implementation

The ADM1 model implemented is based on that produced for the Benchmark Simulation Model No. 2 (BSM2).
open-source model is programmed in Java and can handle dynamic inputs as well as time-discrete and event-driven control actions. The stiffness problem inherent in the original ADM1 model is addressed by using the BSM2 implementation. The standard ADM1 model is considered very stiff due to time constants from different processes within the system ranging from fractions of a second to months. The BSM2 implementation omits the fastest states by reformulating them to be instantaneous. Therefore, the implementation becomes a differential algebraic equation system that can simulate the total process much faster than a standard implementation (Rosen et al. 2006).

A Dormand-Prince 8(5,3) integrator is instantiated inside a simulation function of the model class with pre-defined maximum and minimum step sizes for model solving. A step handler records model output at every step. Multiple event handlers can also be attached to the integrator before beginning the simulation to automatically access output values at pre-defined set points.

The modified BSM2 implementation used for simulation, modelling and analysis of the experimental system in this study also contains a number of other modifications (Rosen et al. 2006; Ramirez et al. 2009; Batstone et al. 2015). These modifications are designed to address a major drawback of the ADM1, which is that a detailed characterization of the influent is often required for its correct implementation. Such detailed analysis of the influent wastewater characteristics can from a practical viewpoint be difficult to achieve (Huete et al. 2006; Kleerebezem & van Loosdrecht 2006b). Therefore, so as to simplify the characterization of the wastewater influent the composite material variable is removed and decay products are directly mapped into biodegradable and inert organics. Disintegration parameters are no longer needed with inerts, carbohydrates, proteins and lipids becoming the primary input to the model. Due to composite material no longer being available, only hydrolysis is coupled to the growth of hydrolytic bacteria and a separate disintegration step is completely removed.

So that the hydrolysis steps of the anaerobic digester are better able to account for slowly degradable materials the Contois model is used to replace the first order kinetics typically applied to model the hydrolysis of particulate organic material. The Contois model has been found to give a better representation of experimental results from a wider range of organic wastes (Vavilin et al. 2008). This implementation has been shown to better represent the impact of thermal pre-treatment on influent biodegradability when compared to the standard ADM1 (Ramirez et al. 2009).

The non-competitive function for modelling of free ammonia inhibition is also replaced with a Hill function to represent acetate degradation and production effects more accurately.

The liquid–gas transfer coefficient value is divided into three separate kinetic coefficients for the different gases being modelled, CH4, CO2 and H2, as described in Ramirez et al. (2009). This modification ensured that diffusivity values for the different gases were able to be taken into account rather than one overall liquid–gas transfer coefficient being identical for all gases. In this case the universal coefficient is replaced by that for CO2 and the kinetic coefficients for CH4 and H2 are calculated using the known diffusivities of the gases in regard to the calibrated CO2 coefficient.

**Model calibration**

The kinetic parameters for thermally pre-treated brewery surplus yeast wastewater digestion and biogas methane production in an EGSB reactor are estimated through fitting of the model equations to the measured data. Latin hypercube sampling (LHS) and sensitivity analysis are used to assist in model parameter calibration (Marino et al. 2008; Girault et al. 2011).

LHS was used to sample from a large range of parameters and variables before narrowing down those that had the greatest sensitivity. LHS allows an un-biased estimate of the average model output, with the advantage that fewer samples are required when compared to normal random sampling for the same accuracy. The default values from the BSM2 implementation and the work of Ramirez et al. 2009 were used in a reference configuration with a range of ±20% being explored for each variable. Samples are taken from an interval in a given sample range using a uniform probability density function.

The root mean squared error (RMSE) of the model when compared with inline and offline COD measurements and the inline methane measurements was used to investigate the impact of varying the sensitive input factors on the model output. LHS was again used here to test a wide range of values for the selected parameters. A second iterative step search with a much finer resolution and tighter range was used for further parameter optimization to obtain the best fit. These selected parameters were calibrated for the EGSB reactor using different time periods and a separate CSTR for validation as described by Girault et al. 2011.

It is assumed that all of the biomass and solids are retained in the EGSB reactor. Therefore, the model needs to be adjusted to account for the fact that the solid retention
time is higher than the HRT. This is considered by recycling a given fraction of the solids and biomass from the effluent back into the reactor after each batch so as to maintain a realistic biomass concentration in the reactor (Kleerebezem & van Loosdrecht 2006a; Antonopoulou et al. 2012).

The influent wastewater characterization for implementation into the modified ADM1 is calculated using periodic measurements and assumptions on typical elemental composition of yeast biomass, which is assumed to contain 50% protein, 35% carbohydrates and 5% lipids (Pacheco et al. 1997). Particulate inerts represent the non-degradable fraction of the total influent COD.

The wastewater composition and the effects of a low temperature thermal pre-treatment are investigated using a CSTR running in parallel to the EGSB reactor. Kinetic parameters in both reactors were calibrated for a period of the experimental phase with constant and varying retention times; parameters were then held constant during further experimental observations to confirm the model as valid. A final test period involving feeding of untreated wastewater to the EGSB is implemented to further validate the calibrated model.

RESULTS AND DISCUSSION

Thermal alkaline pre-treatment

Combining thermal and alkaline pre-treatments is expected to increase the rate of COD reduction during anaerobic digestion so that a higher percentage of the initial wastewater COD is removed in a given period and a higher rate of methane production is realized. Greater conversion of inerts into biodegradable compounds should also increase the total COD reduction percentage and methane produced. Therefore, initial experiments focused on a combined pre-treatment with temperature at 84°C, pre-treatment time at 60 minutes and pH between 7 and 11 (Figure 1). Experiments were repeated during different brewing periods to simulate differing yeast surplus concentration from the brewery; this introduced a 5–15% variation in COD reduction for each pH level tested. However, it was generally observed that higher pH levels had little to no effect on the level of COD reduction when compared to just low temperature pre-treatment. Increasing the pH and bringing it back down to 7.2 did introduce extra buffering capacity to the wastewater and negated the requirement for pH control during the anaerobic digestion process. However, the total amount of acid and base solution required for the alkaline pre-treatment process was significantly more than that required to simply maintain pH in the anaerobic digester.

Thermal pre-treatment

Further tests were conducted on wastewater that only had thermal pre-treatment without any pH control. These tests compared COD reduction on wastewaters that were thermally pre-treated versus the same wastewater without any pre-treatment (Figure 2). The results again varied due to changing wastewater concentration from different brewing periods.
periods but the pre-treated wastewater generally achieved a slightly better reduction in COD after 5 days when compared to the untreated wastewater. In these tests the temperature was again held constant at 84 °C while the treatment time was varied. The reactor required 24 minutes to reach the target temperature of 84 °C, meaning a total pre-treatment time of 34 minutes for 10 minutes of treatment.

Although thermal pre-treatment did show a slight improvement in COD reduction for a given wastewater it also caused more residual ethanol to be evaporated, decreasing the potential total methane production. Figure 3 shows how COD, representing the potential for methane production, is further decreased at a longer pre-treatment time and higher temperature due to ethanol evaporation. The per cent of COD that was lost during pre-treatment at higher temperatures and longer pre-treatment times negated any direct advantage to total methane production, confirming the results of previous studies. Therefore, further investigation focused on the effect a very low temperature pre-treatment has on process stability over longer periods.

Anaerobic digestion for the initial thermal and thermal alkaline pre-treatment tests was undertaken in continuously stirred Erlenmeyer flasks. Using the results from these experiments an EGSB reactor was brought into operation and further experiments conducted for model calibration and analysis. To ensure optimal conditions during the start-up phase a pre-treatment time of 75 minutes and maximum temperature of 84 °C were implemented. During normal operation of the EGSB a pre-treatment time of 30 minutes and temperature of 60 °C was found to be the best compromise between COD reduction improvement, potential methane production and total energy required by the thermal reactor. Due to hydrolysis effects of pre-treatment being minimal at such low temperature, model calibration focused on the effects that yeast inactivation and the reduction in suspended, colloidal matter have on methane production and COD reduction in the EGSB.

COD reduction rate in an EGSB reactor and model calibration

COD and total biogas production were measured inline from a 28 L EGSB reactor fed with brewery surplus yeast wastewater that was thermally pre-treated at low temperature (<100 °C). An inline continuous measurement regime was initiated after 134 days of operation to assist with model calibration. At 100 days the temperature and time of the thermal pre-treatment stage were reduced from 84 °C for 75 minutes to 60 °C for 30 minutes. This was to ensure yeast inactivation, reduce energy usage and reduce evaporation of residual ethanol.

Initial measurements found the EGSB reactor required 5 days to bring the reactor with a starting COD of 2,370 mg/L to under 500 mg/L. Final COD was 468 mg/L after 3 days. In 3 days 30.5 L of biogas was produced with a methane content of 81%, giving 24.7 L of methane. After 5 days the reactor was refed with 15 L of brewery surplus yeast wastewater as methane production and COD reduction rates plateaued. A series of continuous inline measurement regimes of COD were conducted between 134 to 165 days of operation. Data used to calibrate a modified version of the ADM1 were taken from 106 to 138 days. The calibration of kinetic parameters that influenced the COD degradation and methane production of the EGSB reactor was undertaken using a combination of LHS and local sensitivity analysis. As the yeast wastewater composition was considered to be fairly close to constant for the pre-treated influent with just the concentrations and loading rates varying, the focus was on reactor kinetics. The yield of product on substrate in the model was adjusted for the pre-treated feed wastewater to $f_{\text{ch}, xc} = 0.01$, $f_{\text{ch}, xc} = 0.4$, $f_{\text{pr}, xc} = 0.5$, $f_{\text{ch}, xc} = 0.09$, where $f_{xc}$ represents the particulate fraction of inerts ($f_{\text{ch}, xc}$), carbohydrates ($f_{\text{ch}, xc}$), proteins ($f_{\text{pr}, xc}$) and lipids ($f_{\text{li}, xc}$) in the wastewater composite respectively. Tests were conducted on the addition of soluble products to the model feed with acetate assumed to be the main volatile fatty acid. However, as the pH of the reactor was controlled and due to the focus
being on total COD reduction and methane production, this addition was found to have little effect on the chosen model outputs for this system. Also, as hydrolysis was considered negligible during the low temperature pre-treatment and so as to remove unnecessary complexity to the characterization of the model influent, soluble products were not included in the model feed. This simplification is important for the modelling of full-scale plants in small to medium sized breweries, where only the process efficiency is important and elaborate measurements, such as those required for individual fatty acids, are not economical. A model that can accurately predict the gas production of a plant is useful as it provides a direct indication of the process efficiency. More detailed characterization of the feed would be required if pH and caustic addition rates for pH control are of importance.

Sensitivity analysis found the specific uptake rates of carbohydrates, proteins, lipids and acetate to have the most effect on the model output. LHS was used to explore a wide range of values for these parameters. An RMSE of both COD and methane production model outputs compared to experimental data chose the best range for each parameter. A second manual calibration step was applied iteratively within the optimal range to get the best fit between measured and simulated values. Table 2 shows the default kinetic parameters used for BSM2 and Ramirez et al. 2009 compared to those used for modelling the laboratory EGSB reactor in this study, where $k_m$ represents the maximum uptake rates for carbohydrates ($k_{m,\text{ch}}$), proteins ($k_{m,\text{pr}}$), lipids ($k_{m,\text{li}}$) and acetate ($k_{m,\text{ac}}$), and $K_{S,\text{ac}}$ represents the half-saturation value for acetate. The liquid–gas transfer coefficient for carbon dioxide ($K_{L,aCO_2}$) also needs to be properly calibrated for the reactor to predict gas production volumes accurately. Calibration of the model for this period gave $K_{L,aCO_2} = 10.0$.

Figure 4 shows the effluent COD and methane production of the EGSB reactor over a 28 day period with four batch feedings and the implementation of the continuous inline measurement regime. The reactor was fed with 13 L of brewery surplus yeast wastewater every 7 days before a 2 day inline COD measurement phase. The wastewater was pre-treated at 60°C for 30 minutes before each batch feeding. Samples of reactor effluent were taken once daily and the COD measured. Experimental values for gas composition were compared with a daily moving average taken from the model outputs. This approximated the mixing effect of inline gas measurements taken periodically from a separate collecting container. The methane gas production rate was calculated from the average gas compositions collected at each sampling time and the total volume gas produced. An error of ±10% is seen between experimental and simulation results for final methane production when using this method. Gas losses during sampling from the reactor and small calibration errors in the gas counter at the lower gas flow rates found after the first few days of digestion can also contribute to errors in the volume and composition measurements. The average methane content over the calibration period was 73% (±5%) with carbon dioxide concentrations averaging 24% (±7%) with O₂ leakages accounting for 1% (±1%). No H₂S was detected in the gas during this study.

### Comparison of CSTR and EGSB in modified ADM1

A comparison was made with a CSTR running in parallel to the EGSB reactor. The CSTR was batch fed at the same intervals as the EGSB but with wastewater that had not been pre-treated. Three weeks of data taken from the CSTR were used to calibrate a separate model, where the uptake rate of acetate ($k_{m,\text{ac}}$) needed to be adjusted from 1.7 to 1.0 and the fraction of non-biodegradable particulate inerts in the feed increased from 0.01 to 0.09. The remaining biodegradable substrate composition remained the same for both reactors.

Figure 5 shows the effluent COD in mg/L for the calibrated models and the measured data from the CSTR during two measurement routines after 7 days of operation and after 21 days of operation. It is compared with the EGSB treating the same wastewater after running already for 106 days; the CSTR was inoculated with biomass from the EGSB on day 106. After 56 days of operation the CSTR was not operating effectively, removing only 48% of influent COD over 7 days and producing 0.06 L of methane per gram of COD. The calibrated model was no longer able to predict COD removal or gas production rates for the CSTR after this period. Meanwhile, the EGSB with low temperature pre-treated wastewater was achieving 91% COD reduction on the same wastewater and producing 0.31 L of methane per gram of COD. The calibrated

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**Table 2** | Calibrated parameters for EGSB treating thermally pre-treated brewery surplus yeast wastewater using a modified ADM1

<table>
<thead>
<tr>
<th>$k_m$ (mg COD/(mg COD d))</th>
<th>Default (BSM2 &amp; Ramirez et al. 2009)</th>
<th>Calibrated (thermal pre-treatment)</th>
</tr>
</thead>
<tbody>
<tr>
<td>$k_{m,\text{ch}}$</td>
<td>10.0</td>
<td>20.0</td>
</tr>
<tr>
<td>$k_{m,\text{pr}}$</td>
<td>10.0</td>
<td>20.0</td>
</tr>
<tr>
<td>$k_{m,\text{li}}$</td>
<td>10.0</td>
<td>20.0</td>
</tr>
<tr>
<td>$k_{m,\text{ac}}$</td>
<td>8.0</td>
<td>1.7</td>
</tr>
<tr>
<td>$K_{S,\text{ac}}$</td>
<td>0.15</td>
<td>0.8</td>
</tr>
</tbody>
</table>
Figure 4 | Modified ADM1 model fitted to the experimental data for methane production and COD reduction by a high-rate EGSB reactor treating batch-fed thermally pre-treated brewery surplus yeast wastewater at 60 °C for 30 minutes (circles and triangles: experimental data, lines: modified ADM1).

Figure 5 | Modified ADM1 model fitted to experimental data for EGSB fed with thermally pre-treated (60 °C for 30 minutes) brewery surplus yeast wastewater (solid line: modified ADM1, dots: experimental data) and wastewater with no pre-treatment in a CSTR inoculated with granulated sludge from the EGSB on day 106 (dashed line: modified ADM1, triangles: experimental data).
modified ADM1 was able to continuously predict COD and methane production by the EGSB reactor treating varying influent loading and retention times over 165 days of operation (Figure 6). The inline COD measurement system introduced disturbances to the inline gas measurements over longer periods, so was only used at every third batch feeding for closer monitoring of the process COD reduction and better model comparison. A problem with the return valve from the COD analyser occurred during days 152 to 159 causing discrepancies in the measured effluent COD and gas volume and composition. The reactor remained in operation for a total of 232 days but the COD was only measured periodically from the feed wastewater after 165 days of operation.

Final validation of the model occurred after 232 days of operation. The reactor had been fed with thermally pre-treated (60°C for 30 minutes) brewery surplus yeast wastewater at varying loading rates up until this period. The reactor was then fed four times with untreated wastewater over a 1 week period before monitoring the COD reduction and methane production over 7 days. The experimental results were then compared to the pre-calibrated model for untreated wastewater in the CSTR. Figure 7 shows experimental results and model prediction after feeding with and without thermal pre-treatment. The previously calibrated model parameters are also shown. Despite using the CSTR for calibration of the model when fed with untreated wastewater the adjusted parameters fit well with experimental results from the EGSB. It is therefore assumed that the inoculation of the CSTR with granulated sludge from the EGSB and the shorter testing period maintained the reactor kinetics of the EGSB and model calibration was required solely due to the untreated wastewater.

The model predicts an increased uptake of acetate after thermal pre-treatment, which agrees with the reduction in inhibiting suspended material in the feed. Suspended particles and colloidal matter have been found to reduce the specific methanogenic activity of granular sludge in high-rate reactors. The reduction in the inert fraction of the biomass suggests the inactivation of yeast, and breaking down of colloidal matter in the feed provides a greater portion of biodegradable matter to the anaerobic process. Despite the advantage of using thermal pre-treatment for increased biogas production and longer term process stability, such a system would still require some form of tertiary treatment to further reduce the COD, nitrogen and phosphorous concentrations to acceptable levels.

CONCLUSIONS

This study shows that a modified ADM1 is able to predict COD removal and potential methane production in a high-rate anaerobic digester treating a brewery yeast surplus wastewater
using inline measurements and a simplified characterization of the wastewater feed. After calibration the model was also able to predict the effect of a low temperature thermal pre-treatment on reactor efficiency. Using this model for analysis of a laboratory-scale plant it was found that a low temperature thermal pre-treatment of brewery surplus yeast wastewater at 60 °C for 30 minutes allowed for stable and more efficient operation of an EGSB under varying loading conditions. The low temperature and time reduced the evaporation of residual biodegradable organic matter present in the influent and ensured inactivation of the yeast, while maintaining a low level of particulate inerts for a stable granular sludge. This finding provides an economical way for breweries to gain value from the otherwise difficult to dispose of yeast surplus. The developed model also provides a way to predict the potential benefits of such a system in a brewery, using only total COD and gas production measurements. A more detailed prediction of changes to organic acid concentrations and required caustic additions for pH control needs a more extensive analysis of reactor influent and effluent.

The complete source code for Java implementation of the ADM1 with modifications used in this study can be found at: https://github.com/liampetti/jADM1.

**ACKNOWLEDGEMENTS**

The authors are grateful for the financial support from the ‘Bundesministerium für Bildung und Forschung (BMBF)’ funding program for ‘Internationalisierung von Wissenschaft und Forschung von Richtlinien zur Förderung der Wissenschaftlich-Technologischen Zusammenarbeit (WTZ) mit Mexiko’ (funding code: 01DN15001). Special thanks to Benjamin Kloos, Stefan Herz and Kitzmann Bräu GmbH & Co. KG for providing assistance and raw materials for these experiments. Special thanks also to Dr Ulf Jeppsson, Dr Christian Rosen and Dr Darko Vrecko for use of their source code for the ADM1, developed at Lund University, Sweden.

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First received 28 November 2016; accepted in revised form 5 April 2017. Available online 18 April 2017.