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Anaerobic Digestion of Whole-Crop Winter Wheat Silage for Renewable Energy Production

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ABSTRACT: With biogas production expanding across Europe in response to renewable energy incentives, a wider variety of crops need to be considered as feedstock. Maize, the most commonly used crop at present, is not ideal in cooler wetter regions where higher energy yields per hectare might be achieved with other cereals. Winter wheat is a possible candidate because, under these conditions, it has a good biomass yield, can be ensiled and used as whole crop material. The results showed that when harvested at the medium milk stage the specific methane yield was $0.32 \text{ m}^3 \text{ CH}_4 \text{ kg}^{-1} \text{ VS added}$, equal to 73% of the measured calorific value. Using crop yield figures for the north of England a net energy yield of $146\text{-}155 \text{ GJ ha}^{-1} \text{ year}^{-1}$ could be achieved after taking into account both direct and indirect energy consumption in cultivation, processing through anaerobic digestion, and spreading digestate back to land. The process showed some limitations, however: the relatively low density of the substrate made it difficult to mix the digester; there was a build-up of soluble chemical oxygen demand (COD) which represented a loss in methane potential, and may also have led to bio-foaming. The high nitrogen content of the wheat initially caused problems but these could be overcome by acclimatisation. A combination of these factors is likely to limit the loading that can be applied to the digester when using winter wheat as a substrate.

1. INTRODUCTION

There is increasing interest in the production of biofuel using whole plant material, in which both the cellulose and hemicellulose fractions are biochemically converted to the fuel product.¹ The production of methane through the anaerobic digestion process demonstrates this principle and has been widely adopted in Germany and Austria for biofuel production from whole crop maize², often co-digested with animal slurry³. Conventionally grown maize can achieve a net energy production of 141 GJ ha⁻¹ year⁻¹, assuming a biomass yield of 40 tonnes ha⁻¹ year⁻¹ with a total solids content of ~30% and taking into account direct and indirect energy inputs in cultivation and harvesting.⁴ Although maize is an ideal crop for central Europe where yields are particularly high, it may not be suited to other regions that experience wetter, cooler conditions, in which cereals such as wheat and barley give better yields.^{5,6}

The energy potential of whole crop materials has been studied in biochemical methane potential (BMP) tests, including different growth stages of maize, sunflower, triticale and winter rye² and of winter wheat⁷. In testing for methane potential it is also important to consider the effect that storage may have on the crop and its methane yield. In practice harvested crops must be stored, and to achieve this they must either be dried in a hay-making process or made into silage by a combination of microbially-induced anaerobic conditions and acidity. Silage treatment is the most commonly used process for preservation of material harvested as a green 'whole crop' for forage⁸, although other methods such as alkaline treatment may also be considered⁹.

Since energy crops have mainly been digested as co-substrates with animal slurry^{3, 10, 11}, there are relatively few studies using them as mono-substrates in long term trials with continuous or semi-continuous feeding. In the case of wheat, there are no reported

studies of the methane production potential in semi-continuous fed digesters to determine the optimum loading rate and operating parameters. The objective of the current work was thus to establish the specific and volumetric methane yields and the operational stability of anaerobic digestion of winter wheat as a sole substrate, without addition of water, at different organic loading rates and associated retention times.

2. MATERIALS AND METHODS

Eight 5-litre digesters each with a working volume of 4 litres were used. These were constructed of uPVC tube with gas-tight top and bottom plates. The top plate was fitted with a gas outlet, a feed port sealed with a rubber bung, and a draught tube liquid seal through which an asymmetric bar stirrer was inserted with a 40 rpm motor mounted directly on the top plate. Temperature was maintained at $35\text{ }^{\circ}\text{C}\pm 0.5$ by water circulating through an external heating coil. During semi-continuous operation digestate was removed through an outlet port in the base plate and feed added via the top plate. Gas production was measured using tipping-bucket gas counters¹² with continuous datalogging. Calibration of gas counters was checked weekly by collecting the gas in a Tedlar bag (SKC Ltd, Blandford Forum, UK): the volume was then measured accurately by weighing the water displaced when discharged into a weight-type gasometer. All gas volumes reported are corrected to standard temperature and pressure of 0°C , 101.325 kPa in accordance with Walker et al.¹²

The substrate used was a variety of winter wheat (*Triticum aestivum* L.) harvested on 24 July at the medium milk harvest stage (moisture content 63.4 %) and preserved after collection with a silage treatment (Pioneer Hybrids 11A44 high dry matter Buchnerii inoculant) applied in accordance with the supplier's instructions. After

collection from the farm on 28 February, the substrate was stored in 1 kg batches in sealed polythene bags at -20 °C. Substrate was defrosted as required and milled to a particle size of 0.5-1.5 cm before digestion, to ensure homogeneity in laboratory-scale operation.

The digesters were initially filled with inoculum collected from an anaerobic digester treating municipal wastewater biosolids (Millbrook, Southampton, UK). Before use the inoculum was sieved through a 1 mm mesh to remove large particles and grit. The inoculum had a total solids (TS) content of $29.1 \pm 0.4 \text{ g kg}^{-1}$ and volatile solids (VS) content of $20.6 \pm 0.4 \text{ g kg}^{-1}$.

The digesters were filled with 4 kg of sieved inoculum then left for 24 hours to allow consumption of residual organic matter. The digesters were then fed daily with a wet weight of wheat calculated to provide the desired organic loading rate. No water was added, in order to maintain a 'natural' retention time based on the substrate properties only. An amount of digestate was removed three times per week based on an estimated mass balance taking into account sampling and gas production. The digester was weighed each week and any necessary correction needed to maintain a constant weight was made by adjusting the mass of digestate removed over the following week. The digesters were initially fed at organic loading rates (OLR) of ~2, 3, 4, and 5 $\text{g VS}_{\text{added}} \text{ l}^{-1} \text{ day}^{-1}$ and the operational conditions used in the trial are given in Table 1. At the start of the trial each digester received 4 ml of a trace element solution with the following composition: $\text{FeCl}_2 \cdot 4\text{H}_2\text{O}$ 2 g l^{-1} , $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$ 2 g l^{-1} , $\text{MnCl}_2 \cdot 4 \text{H}_2\text{O}$ 0.5 g l^{-1} , $\text{CuCl}_2 \cdot 2 \text{H}_2\text{O}$ 38 mg l^{-1} , ZnCl_2 50 mg l^{-1} , H_3BO_3 50 mg l^{-1} , $(\text{NH}_4)_6\text{Mo}_7\text{O}_{24} \cdot 4\text{H}_2\text{O}$ 50 mg l^{-1} , $\text{Na}_2\text{SeO}_3 \cdot 5\text{H}_2\text{O}$ 194 mg l^{-1} , $\text{AlCl}_3 \cdot 6\text{H}_2\text{O}$ 90 mg l^{-1} , $\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$ 50 mg l^{-1} , EDTA 1 g l^{-1} and resazurin 200 mg l^{-1} .¹³

Samples of digestate were analysed for pH, alkalinity, TS and VS content, total Kjeldahl nitrogen (TKN), total ammoniacal nitrogen (TAN) and VFA concentration. Gas volumes were recorded daily and gas composition was determined by gas chromatography twice per week.

2.1. Analytical methods. Total and volatile solids were measured using Standard Method 2540 G.¹⁴ Alkalinity was measured by titration with 0.25 N H₂SO₄ to endpoints of pH 5.75 and 4.3, to allow calculation of partial alkalinity (to pH 5.75), total alkalinity (to pH 4.3), and intermediate alkalinity (between pH 5.75 and 4.3)¹⁵. Total Kjeldahl Nitrogen (TKN) was determined using reflux digestion and steam distillation and digestate TAN was measured by steam distillation, in both cases according to the equipment manufacturer's instructions (Foss Ltd, Warrington, UK). Volatile fatty acids (VFA) were quantified in a Shimadzu GC-2010 gas chromatograph (Shimadzu, Milton Keynes, UK), using a flame ionization detector and a capillary column type SGE BP-21. Biogas composition was analysed using a Varian CP 3800 gas chromatograph (GC) with a gas sampling loop, with argon as the carrier gas at a flow of 50 ml min⁻¹. The GC was fitted with a Haysep C column and a molecular sieve 13 x (80-100 mesh) operating at a temperature of 50 °C. The GC was calibrated using a standard gas containing 35% CO₂ and 65% CH₄ (BOC, Guildford, UK).

Further characterisation was carried out on samples prepared by air drying to constant weight and then milled to a particle size ≤0.5 mm in a micro hammer mill (Glen Creston Ltd, Standmore Mill, UK). Fibre composition, expressed as Neutral Detergent Fibre (NDF), Acid Detergent Fibre (ADF) and Acid Detergent Lignin (ADL), was measured using the FibreCapTM 2021/2023 system (Foss Analytical, Warrington, UK) following the method given by Kitcherside *et al.*¹⁶. Elemental Analysis (C, H, N) was carried out using a Flash EA 1112 machine (Thermo Finnigan, Hemel Hempsted,

UK) following the manufacturer's recommended procedure with L-Aspartic Acid, Atropine and Nicotinamide as standards. Phosphorus (P) was determined using the ascorbic acid spectrophotometry method 4500-PE¹⁴, with measurements taken at 880 nm using a Cecil 3000 Series Spectrophotometer (Cecil Instruments, Cambridge, UK). An acid extract of the air-dried material was microwave digested with nitric acid (Microwave Accelerated Reaction System, Model MARS X^R, XP-1500 Plus, CEM Corporation). The extract was filtered and diluted to 50 ml with deionised water (Milli-Q Gradient, Millipore, Watford, UK) and Cd, Cr, Cu, K, Ni, Pb, and Zn determined using a flame atomic absorption spectrometer (Spectr AA-200, Varian, USA) according to the manufacturer's procedures and against appropriate stock standards (Sigma Aldrich Co, Gillingham, UK; Fisher Scientific, Loughborough, UK).

2.1.1. Solids destruction and energy values. VS destruction rates were calculated based on a mass balance of solids in the influent and effluent, but without taking into account changes in storage within the digester. Before steady state conditions are established, these values are best described as an apparent VS destruction. For this purpose it was assumed that the wet weight of digestate removed was equal to the wet weight of feedstock added, minus the weight of biogas removed. The weight of biogas removed was estimated from the weekly average volume and gas composition in terms of % CH₄ and CO₂, ignoring water vapour and other gases.

The Buswell equation¹⁷ was used to calculate the theoretical methane yield of the wheat samples based on elemental composition, with O estimated by assuming C+H+O+N = 99.5% on a VS basis. Theoretical CV was calculated using the Du Long equation according to the method in Combustion File 24¹⁸, and a higher heat value for methane of 39.84 MJ STP m⁻³.

3. RESULTS

3.1. Feedstock Characteristics. The characteristics of the ensiled wheat feedstock are given in Table 2. The pH was 4.2 as a result of lactic fermentation during the silage storage. The TKN was 6.4 g N kg^{-1} wet weight (WW), TAN was $1.3 \pm 0.0 \text{ g N kg}^{-1}$ WW and phosphorus $0.74 \pm 0.04 \text{ g P kg}^{-1}$ WW. The moisture content was 63.4 %WW, lignin content was relatively low at 8.9 %TS, and the carbon to nitrogen (C/TKN) ratio was 25. Further characterisation of the wheat used (identified as Wheat A) and determination of its Biochemical Methane Potential (BMP) was carried out by Rincón *et al.*^{7,9}

3.2. Digestion trials. Digesters R1 and R2 (OLR $2.1 \text{ g VS l}^{-1} \text{ day}^{-1}$) were successfully operated over the full experimental period of 420 days, equivalent to around 2.5 times the 'natural' retention time. Digesters R3 and R4 (OLR $3.1 \text{ g VS l}^{-1} \text{ day}^{-1}$) operated smoothly until day 114 when the gas venting line in R4 blocked due to foaming, causing a loss of $\sim 1.6 \text{ kg}$ of digestate. Feeding of R4 was continued at the same OLR until day 420 (around 3.8 retention times) but maintaining the reduced volume, with a corresponding increase in digester headspace. On day 288 a similar but even more extensive loss occurred in R3 and feeding of this digester was stopped. Digesters R5 and R6 (OLR $4 \text{ g VS l}^{-1} \text{ day}^{-1}$) ran for 70-80 days (~ 1.2 retention times) before signs of failure became evident and feeding was stopped. It was not possible to operate digesters R7 and R8 successfully at the highest OLR of $5 \text{ g VS}_{\text{added}} \text{ l}^{-1} \text{ day}^{-1}$. Winter wheat is a lightweight substrate and the volume of daily feed corresponding to the 60 g WW d^{-1} required by R7 and R8 was very large. This led to problems in stirring, accompanied by entrainment of biogas and blockage of gas lines. It was only possible to

run these digesters for a period of 26 days and no consistent analytical or monitoring results were obtained.

3.2.1. pH and alkalinity. The pH at the start of the trial was 7.90 and showed a slight initial decrease to between 7.50-7.70 from day 16 to day 120 in all digesters (Figure 1a). After this the pH rose in digesters R1-R4 and fluctuated around 8.20-8.40 till the end of the run, except for a brief fall around day 223 to pH 8.00. For R5 and R6 (OLR 4 g VS l⁻¹ day⁻¹) pH values remained similar to those in the other digesters until day 50 then fell sharply to 6.0 and 5.7 by day 84 and 72 respectively, at which point methanogenesis was inhibited.

Figure 1b shows the alkalinity in digesters R1-4. At an OLR of 2.1 g VS l⁻¹ day⁻¹ the partial alkalinity (PA), which indicates the bicarbonate buffering available in the digester, rose from 4.0 g CaCO₃ l⁻¹ to 9.25 for R1 and to 8.75 g l⁻¹ for R2 by day 150, and appeared to stabilise at around 12.5-13.0 g l⁻¹ in both digesters by day 350. Total alkalinity (TA), which includes both bicarbonate and VFA buffering¹⁵, also increased from 6.0 g CaCO₃ l⁻¹ to 12.5 and 11.25 g l⁻¹ for R1 and R2 respectively in the first 150 days, stabilising around 17.0 g l⁻¹. The intermediate to partial alkalinity ratio (IA/PA) (Figure 1d) rose to around 0.6 between day 131-170 in R1, with a similar but slightly delayed peak of around 0.55 between day 200-226 in R2. As the intermediate alkalinity (IA) reflects the VFA buffering, this ratio provides a very sensitive indicator of digestion stability. The IA/PA ratio for the last 100 days of operation averaged 0.31 in R1 and 0.37 in R2, close to the classic value for stable operation¹⁵. In digesters R3 and R4 at the OLR of 3.1 g VS l⁻¹ day⁻¹ a similar pattern was observed but with a slightly higher TA during the initial period. Stable values of both PA and TA were observed over the final 50 and 150 days of operation in R3 and R4, with IA/PA ratios of 0.61 and 0.41 respectively.

In R5 and R6 (OLR 4 g VS l⁻¹ d⁻¹) PA increased to 7.0 g l⁻¹ after 28 days, and then fell steadily to final values of 2.99 and 2.67 g l⁻¹ (Figure 1c). TA remained constant at around 10 g l⁻¹ from day 28 on, with an accompanying rise in intermediate alkalinity. This resulted in increases in the IA/PA ratio to 2.63 and 2.94 on days 85 and 60 in R5 and R6 respectively (Figure 1d), due to rising VFA concentrations that ultimately reduced the pH to less than 6, resulting in digester failure. While this failure occurred slightly earlier and more rapidly in R6, the two reactors showed similar behaviour.

3.2.2. Ammoniacal and Kjeldahl Nitrogen. The measured TKN concentration in the substrate was 6.4 g kg⁻¹ WW, but the expected concentration in the digestate is higher due to the breakdown of solids. The feedstock VS concentration was 347 g VS kg⁻¹ WW. Assuming 75% VS destruction the residual quantity of digestate from 1 kg feedstock is equal to (1000 - 0.75 x 347) = 740 g WW, and the predicted TKN concentration under steady-state conditions is thus 6.4 * 1000/740 = 8.6 g TKN kg⁻¹ WW, which corresponded closely to the final measured value in R4 (Figure 2a). TKN and TAN concentrations in all digesters were modelled on a simple mass balance basis, assuming digestate concentrations of 8.6 g TKN kg⁻¹ WW and 4.75 g TAN kg⁻¹ WW respectively. It can be seen that both R1-2 and R3-4 were close to steady state concentrations by the end of trial (Figure 2b and c). The correlation coefficient between measured and modelled values for TAN was R² = 0.98 (all measurements, n = 152); the value for TKN was slightly lower at R² = 0.78 for all digesters (n = 62) and 0.93 for R3 and 4 (n = 24) (Figure 2d). The goodness of fit of this simple model suggests that there is a fairly rapid breakdown of incoming nitrogen-containing material which releases ~55% of the measured TKN as ammoniacal nitrogen within a short period. This high TAN concentration contributes to the high alkalinity noted and therefore provides buffering able to protect against accumulations of VFA.

3.2.3. *Solids*. Figure 3a shows the evolution of digestate TS content over time for all digesters. The rate of increase from initial values of around 34 g TS kg⁻¹ WW again reflects the OLR in each case. Values in R2 and R4 had equalised by around day 350, while R1 appeared to be lagging slightly behind R2 but reached a similar concentration of 140 g TS g⁻¹ WW by the end of the experimental period. From day 119 TS concentrations in R3 were consistently higher than those in R4 by around 15 g TS kg⁻¹ WW, while in the last 50 days before feeding ceased there was a further increase in R3 to around 147 g TS kg⁻¹ WW, possibly associated with the failure, and equivalent to the final concentration in R1, R2 and R4. VS concentrations (Figure 3b) showed a closely similar pattern to TS. Apparent VS destruction rates are shown in Figure 3c and appeared to be stabilising at around 75% in R1, R2 and R4 towards the end of the experimental period, confirming the values based on digestate TKN: the higher solids concentration in R4 before failure is reflected by the earlier onset of reduced VS destruction. TS, VS and associated apparent removal rates in R5 and R6 are shown in Figure 3d and indicate a slightly lower rate of acclimation

3.2.4. *VFA and SCOD*. VFA concentrations in R1 and R2 remained at fairly low values generally < 200 mg l⁻¹ for over 120 days, after which there was a sharp increase in acetic acid accompanied by smaller increases in propionic and iso-valeric concentrations (Figure 4a and b). The reactors appeared to overcome this accumulation after a further 50-60 days when VFA concentrations started to fall. Acetic acid did not return to the previous low concentration, however, but fluctuated between ~500-1250 mg l⁻¹ for the rest of the experimental period. A similar pattern was observed in R3 and R4 but with the increase in acetic acid starting from day ~50 and peaking close to 6000 mg l⁻¹ around day 112 in both digesters. Increases in propionic and iso-valeric acid were also seen (Figure 4c and d). Again there was a recovery to a residual concentration of

acetic acid similar to that in R1 and 2. In R5 and 6, acetic acid accumulation began even earlier at around day 38, and reached concentrations of $\sim 13000 \text{ mg l}^{-1}$ by around day 80 (Figure 4e and f). This concentration was sufficient to overcome the digester buffering capacity, leading to the fall in pH and increase in IA/PA noted above, and to failure of digestion.

The increase in VFA occurred earlier in the higher loaded reactors, but did not directly correlate to HRT. The sudden onset of VFA accumulation after a period of relatively stable operation can be indicative of accumulation of some component inhibitory to part of the microbial population, or of the washout of an essential element that may impair enzyme function, in both cases interrupting the flow of carbon through to methane. As the acetic acid peak decreased without any further build-up of VFA, it is possible that there was a change in the structure of the methanogenic population: similar acetic acid peaks have been observed in other studies associated with a shift in dominance from acetoclastic to hydrogenotrophic methanogens.¹⁹ This shift can be associated with an increase in digestate TAN concentration, which is known to be more toxic to the acetoclastic population.^{20, 21} Ammonia toxicity depends on a number of factors, including pH and temperature which determine the equilibrium between free ammonia and dissociated ionic ammonium. TAN concentrations at the onset of VFA accumulation were around 3000, 2300 and 2400 mg l^{-1} in R1-2, R3-4 and R5-6 respectively: free ammonia concentrations are highly sensitive to pH but values at this time were below 300 mg l^{-1} in all digesters. As TAN concentrations increase the acetoclastic population is gradually lost and hydrogenotrophic activity takes over, with acetic acid converted to CO_2 via the reverse Wood-Ljungdahl pathway.^{21, 22} This would explain the decrease in the acetic acid peak and the continued functioning of digesters R1-4 at TAN concentrations approaching 4500 mg l^{-1} . The higher loading on R5 and 6

gave the reactors relatively little time to adapt to these changing conditions, and a longer acclimation period may have allowed successful operation at the OLR of 4 g VS $\text{l}^{-1} \text{ day}^{-1}$.

SCOD accumulated through the experimental period in all digesters. The majority of this could not be accounted for by accumulation of VFA up to heptanoic acid (C7), as SCOD concentrations appeared to stabilise at around 60 g l^{-1} in R1 and 2 by the end of the run. One possible explanation for the SCOD is from the build-up of soluble microbial products: these are associated with long solids retention times, and may account for the foaming observed.^{23, 24} SCOD can also result from the solubilisation and non-degradation of organic material present in the substrate, such as lignin. If the lignin present in the feedstock was released from solid state through the breakdown of degradable fibre it could account for up to 65 g SCOD l^{-1} of digestate, based on a theoretical SCOD for lignin of 1.85 g g^{-1} .²⁵

3.2.5. Methane production. Specific and volumetric methane productions are shown in Figure 5. Initially there was some fluctuation in specific biogas and methane yields reflecting the changing reactor conditions, in particular the observed peaks in VFA concentration. In the latter part of the study from day ~250 onwards the specific methane yields in R1-2 and R4 were closely similar at 0.320 $\text{l CH}_4 \text{ g}^{-1} \text{ VS}_{\text{added}}$; R3 appeared to be recovering around day 200 but the specific methane yield then fell slightly, corresponding to the reduced solids destruction in the period before failure. Specific methane yield based on the volatile solids destruction in R1-2 and R4 was ~0.43 $\text{l CH}_4 \text{ g}^{-1} \text{ VS destroyed}$, slightly greater than the theoretical value for cellulose. The average methane concentration was 53%. The volumetric methane yields reflected the loading rates, with R3 and 4 achieving a value of around 1.8 $\text{l CH}_4 \text{ l}^{-1} \text{ reactor day}^{-1}$.

Table 3 summarises some key energy production parameters. The theoretical methane yield calculated from the Buswell equation¹⁷ was $0.451 \text{ l CH}_4 \text{ g}^{-1} \text{ VS}$ respectively: the measured value corresponds to about 71% of this, reflecting the VS destruction of about 75%. The theoretical and measured calorific values were in reasonably good agreement, confirming the elemental analysis results. The recovery of energy as methane corresponded to 73.3% and 68.7% of the measured and theoretical calorific values, respectively. The specific methane yield in semi-continuous digestion was about 12% less than the BMP value of $0.36 \text{ l CH}_4 \text{ g}^{-1} \text{ VS}$ as determined by Rincón et al.⁷ for the same batch of material. This difference is greater than expected given the long retention times, and it is possible that some of the methane potential was present in the accumulated SCOD which at steady-state conditions had reached concentrations of $\sim 60 \text{ g l}^{-1}$. The amount of SCOD removed in the digestate each day would have a theoretical methane yield of $0.046 \text{ l g}^{-1} \text{ VS}_{\text{added}}$, which if added to the actual specific methane yield gives a total of $0.366 \text{ l CH}_4 \text{ g}^{-1} \text{ VS}_{\text{added}}$, very close to the BMP value. This may favour soluble microbial products (SMP) rather than lignin as the source of the undegraded SCOD, as the SMP may not form or may be successfully broken down in the batch test.

Whole crop winter wheat is ideal for growing in cooler and wetter climates. With a biomass yield of around $40 \text{ tonnes wet weight ha}^{-1} \text{ year}^{-1}$ ⁹ and a specific methane yield of $0.320 \text{ l CH}_4 \text{ g}^{-1} \text{ VS}_{\text{added}}$, the gross energy yield from anaerobic digestion of the current material based on a lower heat value for methane of 35.8 MJ m^{-3} is thus around $160 \text{ GJ ha}^{-1} \text{ year}^{-1}$. Using the methods described in Rincón et al.⁹ the total input energy for crop production can be estimated as 13.7 GJ ha^{-1} with mineral fertilisers or 4.7 GJ ha^{-1} if cattle slurry is used as fertiliser, giving net energy yields of around 146 or 155 $\text{GJ ha}^{-1} \text{ year}^{-1}$. There may however be some disadvantages in using winter wheat as an

energy crop for anaerobic digestion. These are related to its high nitrogen content which may cause instability during the acclimatisation period. More problematic are the difficulties in processing the material due to its physical characteristics and tendency to bio-foaming, which may ultimately limit the loading that can be applied in practice.

4. CONCLUSIONS

Semi-continuous anaerobic digestion of winter wheat showed high volatile solids destruction, an important property for an arable energy crop, and a biogas methane content typical of cellulosic crop materials. The substrate TKN and the accumulation of TAN in the digesters indicated that whole crop wheat has a higher protein content than maize, which is more commonly used as an energy crop for biogas production. This high nitrogen content caused some temporary digester instability, as the TAN concentration rose above the inhibitory threshold for acetoclastic methanogenesis: the volatile fatty acid accumulation observed was probably due to a shift in the methanogenic population from acetoclastic to hydrogenotrophic. Gross and net energy yields indicated that, where annual per hectare yields of wheat are higher than can be achieved with other cereal crops for climatic or geographical reasons, it may be a suitable choice for energy production as a whole crop material. The material is more difficult to work with than some alternative crops, however, as its relatively low density and tendency to bio-foaming can lead to problems in reactor operation and mixing. At the long retention times applied there was also accumulation of SCOD, representing a loss in substrate specific methane yield.

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Table 1. OLRs and HRTs studied

Digesters	OLR	Feedstock added		Retention Time (day)
	(g VS l ⁻¹ day ⁻¹)	(g VS day ⁻¹)	(g WW day ⁻¹)	
R1 and R2	2.1	8.4	24	166
R3 and R4	3.1	12.5	36	111
R5 and R6	4	16.7	48	83
R7 and R8	5	20.9	60	66

Table 2. Substrate characteristics

	Unit	Winter wheat^a
Treatment		Silage
pH ^b		4.2
TKN	g N kg ⁻¹ WW	6.4
TAN	g N kg ⁻¹ WW	1.3
TS	g kg ⁻¹ WW	363
VS	g kg ⁻¹ WW	347
Moisture	% WW	63.7
CV	MJ kg ⁻¹ VS	17.0
P	g kg ⁻¹ WW	0.74
Fibre (H+C+L)	% TS	40.0
Fibre (C+L)	% TS	23.8
Fibre (L)	% TS	8.9
K	g kg ⁻¹ WW	4.88
Cd	µg g ⁻¹ TS	0.40
Cr	µg g ⁻¹ TS	104
Cu	µg g ⁻¹ TS	37.9
Ni	µg g ⁻¹ TS	35.6
Pb	µg g ⁻¹ TS	2.21
Zn	µg g ⁻¹ TS	172
C	% VS	46.7
H	% VS	6.61

^a based on Rincón et al.^{7,9} (Wheat A), apart from Fibre content (measured)

^b 1:10 weight:weight in deionised water

Table 3. Energy values for semi-continuous digestion of winter wheat

	Unit	Parameter
CH ₄ yield in BMP ^a	l g ⁻¹ VS _{added}	0.360±0.03
CH ₄ yield in semi-continuous digestion	l g ⁻¹ VS _{added}	0.320
	l g ⁻¹ VS _{destroyed}	0.430
Substrate destruction (semi-continuous)	%	75
Empirical formula		C _{29.5} H _{49.7} O _{21.3} N _{1.0}
Theoretical CH ₄ yield (Buswell)	l g ⁻¹ VS	0.451
Theoretical methane content (Buswell)	%	51.8
Average measured methane content	%	53.0
Calculated CV (Du Long equation)	MJ kg ⁻¹ VS	18.4
Measured CV	MJ kg ⁻¹ VS	17.0
Energy recovered as CH ₄ (semi-continuous)	MJ kg ⁻¹ VS	12.5
Recovery of measured CV as CH ₄	%	73.3
Recovery of calculated CV as CH ₄	%	67.8

^a Rincón et al.⁷

Figure captions

Figure 1. (1a) pH for R1-6, (1b), alkalinity for R1-4, (1c) alkalinity for R5-6 and (d) IA/PA ratio for R5-6 during the experimental period.

Figure 2. (2a) TKN and modelled TKN nitrogen for R3-4, (2b) measured and modelled TAN for R1-2, (2c) measured and modelled TAN for R3-4 and (2d) measured and modelled TAN for R5-6.

Figure 3. Digestate solids concentration and apparent solids destruction during the experimental period. (3a) Total Solids (TS) for R1-6, (3b) Volatile Solids (VS) for (R1-6), (3c) Volatile Solids Removed for R1-4 and (3d) Total Solids and Solids Removed for R5-6.

Figure 4. VFA profiles during the experimental period: (4a) R1, (4b) R2, (4c) R3, (4d) R5 and (4e) R6 (Note different axis scales for R1-4 and R5-6).

Figure 5. (5a) Specific methane yield for R1-2, (5b) volumetric biogas production for R1-2, (5c) specific methane yield for R3-4, (5d) volumetric biogas production for R3-4, (5e) specific methane yield for R5-6, (5f) volumetric biogas production for R5-6 during the experimental period (rolling 7-day average).

Figure 1

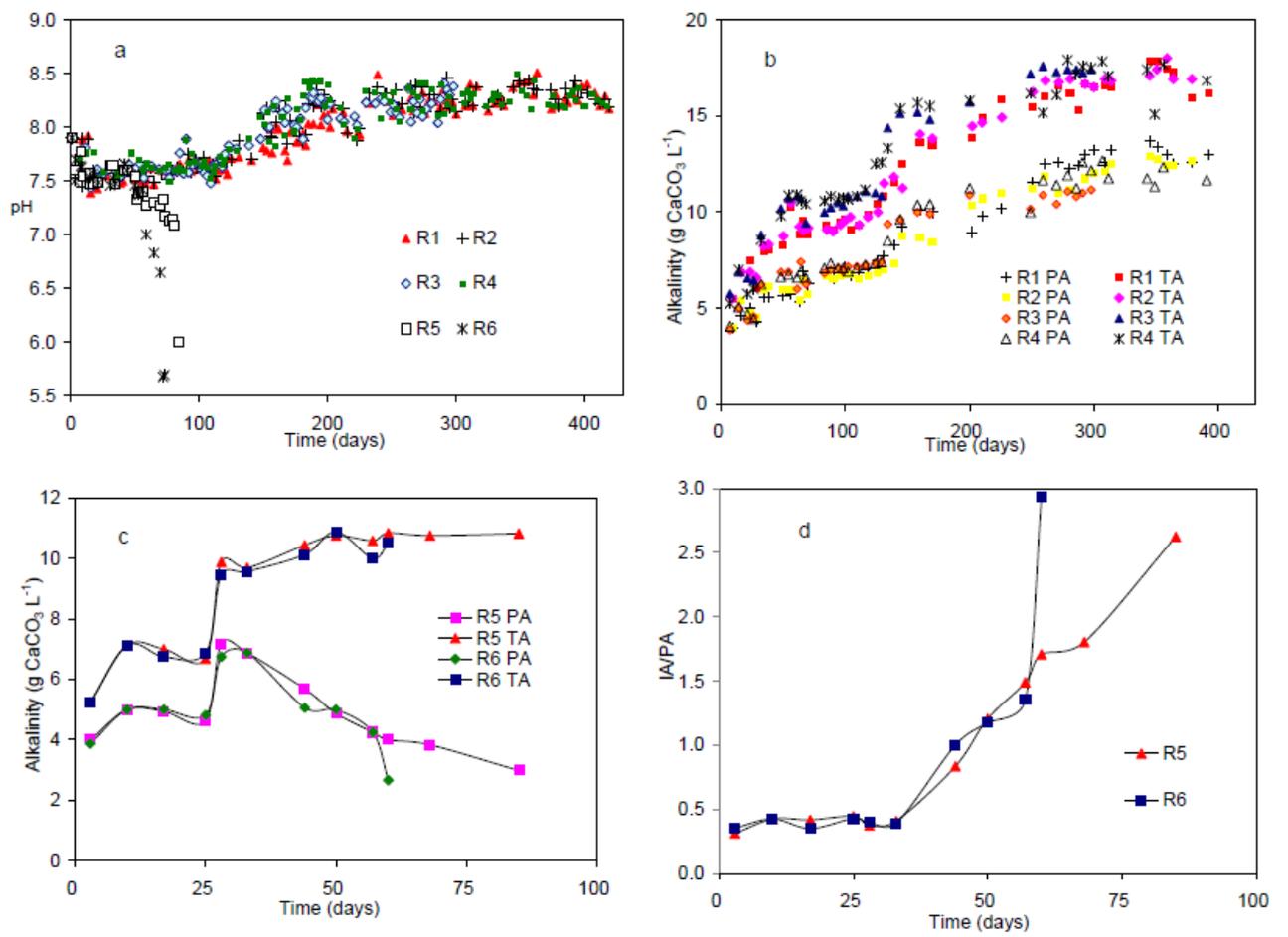


Figure 2

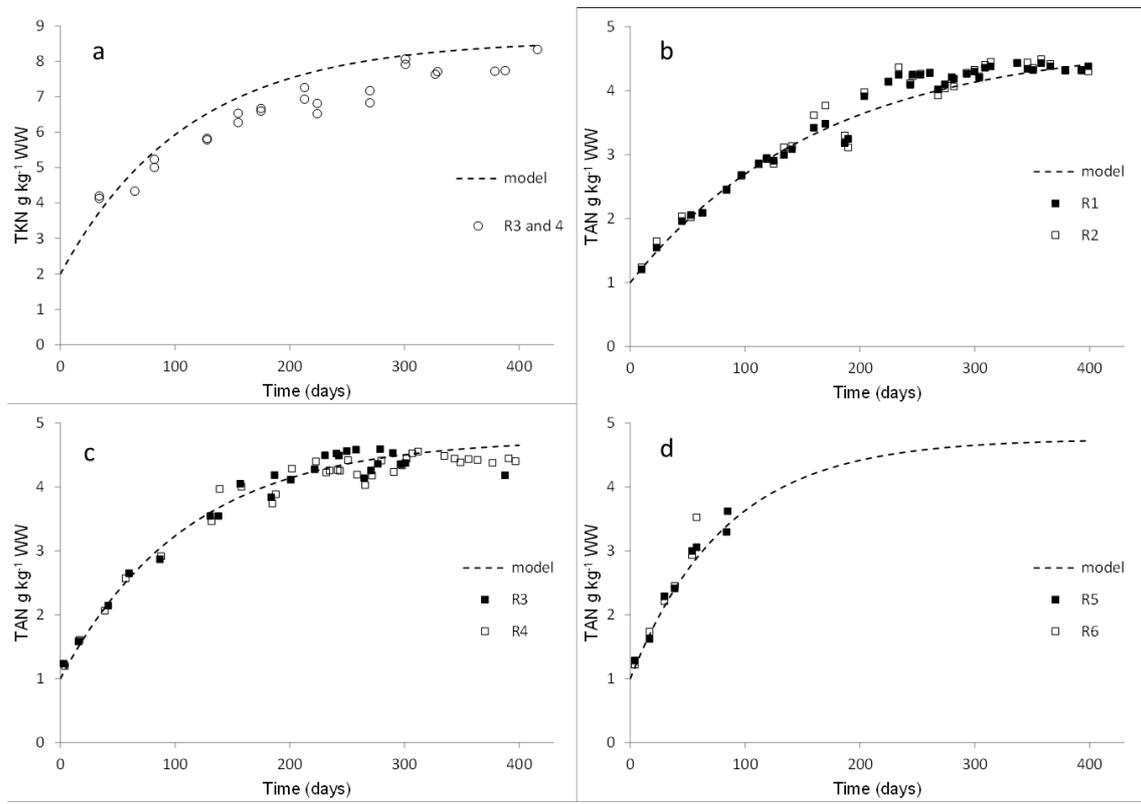


Figure 3

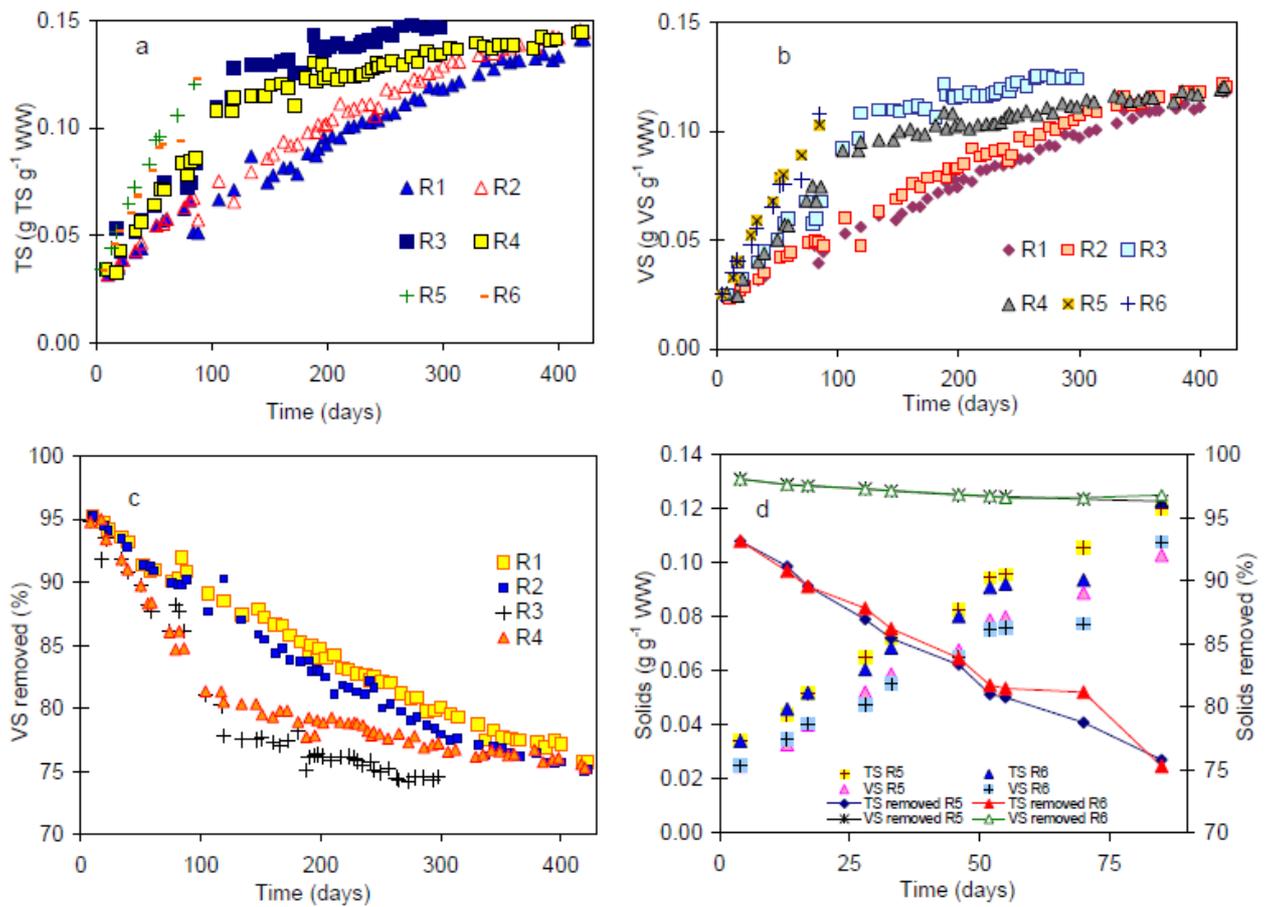


Figure 4

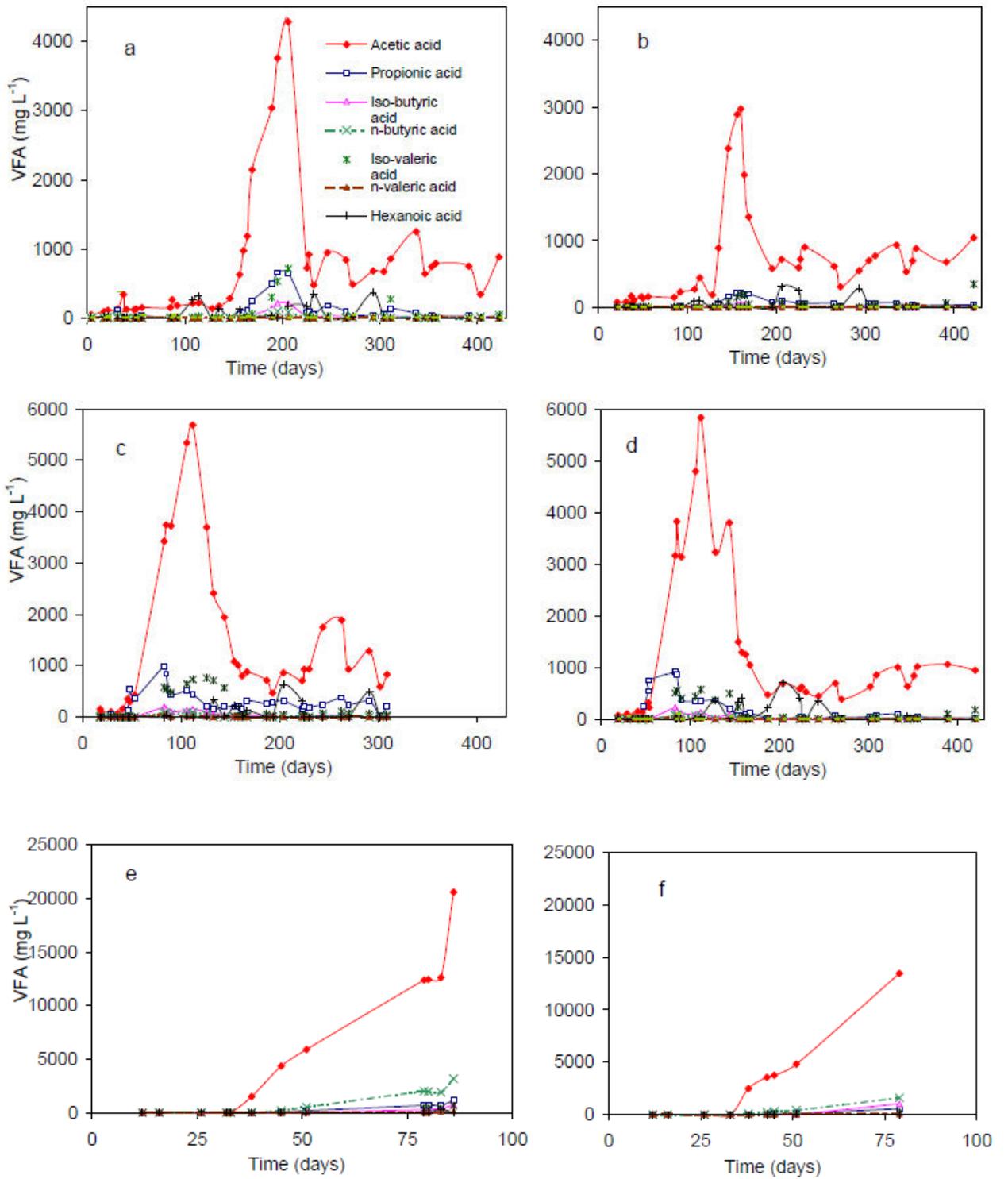


Figure 5

