Anaerobic digestion of starch-polyvinyl alcohol biopolymer packaging: biodegradability and environmental impact assessment

M. Guo [a, 1], A.P. Trzcinski [b, 2], D.C. Stuckey [b], R. J. Murphy [a,*]

a. Department of Biology, Imperial College of Science and Technology and Medicine, London SW7 2AZ, UK

b. Department of Chemical Engineering, Imperial College of Science and Technology and Medicine, London SW7 2AZ, UK

E-mail address: miao.guo06@imperial.ac.uk, antoine.trzcinski@manchester.ac.uk, d.stuckey@imperial.ac.uk, r.murphy@imperial.ac.uk

** Correspondence author: Tel:+44 2075945389. Fax: +44 (0) 2075842056*

1. Tel:+44 (0)7726479669

2. Tel: +44 (0)7826814053

Abstract

The digestibility of a starch-polyvinyl alcohol (PVOH) biopolymer insulated cardboard coolbox was investigated under a defined anaerobic digestion (AD) system with key parameters characterized. Laboratory results were combined with industrial operational data to develop a site-specific life cycle assessment (LCA) model. Inoculated with active bacterial trophic groups, the anaerobic biodegradability of three starch-PVOH biopolymers achieved 58-62%. The LCA modelling showed that the environmental burdens of the starch-PVOH biopolymer packaging under AD conditions on acidification, eutrophication, global warming and photochemical oxidation potential were dominated by atmospheric emissions released from substrate degradation and fuel combustion, whereas energy consumption and infrastructure requirements were the causes of abiotic depletion, ozone depletion and toxic impacts.

Nevertheless, for this bio-packaging, AD of the starch-PVOH biopolymer combined with recycling of the cardboard emerged as the environmentally superior option and optimization of the energy utilization system could bring further environmental benefits to the AD process.

Key words: Starch-PVOH biopolymer; Anaerobic digestion; Life Cycle Assessment.

Abbreviations

AD, anaerobic digestion; BFMSW, biodegradable fraction of municipal solid waste; BMP, biochemical methane potential; CHP, combine heat and power system; COD, chemical oxygen demand; CV, coefficient of variation (%); GC, gas chromatograph; GWP100, global warming potential for 100-year time horizon; ICP-OES, Inductive Coupled Plasma-Optical Emission Spectrometer; LCA, life cycle assessment; LCIA, life cycle impact assessment; MSBF, maize starch-based foam; NF, nitrogen to protein conversion factor ; ODP, ozone depletion potential; POCP, photochemical oxidation potential; PSBF, potato starch-based foam; PVOH, polyvinyl alcohol; SD, standard deviation; TN, total nitrogen; TS, total solids; TSS, the total suspended solid; VFAs, volatile fatty acids; VS, volatile solids; VSS, volatile suspended solid; WBF, wheat-based foam.

1. Introduction

Starch, composed of repeating D-glucopyranosyl units, has been recognized as one of the most promising natural feedstocks to substitute for petrochemical plastics in a variety of applications (Shogren et al., 2002). The biodegradability of starch together

with its low cost and wide availability offers several advantages (Russo et al., 2009), but its applications are limited by poor mechanical strength, hydrophilic characteristics and susceptibility to microbial attack. These can be managed by blending starch with other synthetic polymers (Follain et al., 2005). Amongst the starch-based composites, starch/PVOH blends have attracted great interest since the 1980s because of their excellent compatibility and processability, and the improved properties of the blends (Follain et al., 2005, Russo et al., 2009). Starch/PVOH blends have developed rapidly in the last decades and are widely applied as packaging or agricultural mulch film. For instance, the starch/PVOH loosefills have been commercialized under the Mater-Bi® trademark since the 1990's (Composto, 2000), and nowadays approximately 25,000 tonnes of starch-PVOH loosefills are estimated to be consumed annually worldwide (data from Greenlight Products Ltd). The increasing consumption of starch/PVOH based products brings concern about their waste treatment. Some research has been carried out on the biodegradability of PVOH and PVOH/starch blends under various environmental conditions including anaerobic digestion (Matsumura et al., 1993, Chiellini et al., 2003, Russo et al., 2009).

PVOH is different from starch, which can be easily metabolized by a wide range of micro-organisms, since it can only be assimilated by specific microbial strains (Chiellini et al., 2003, Kawai and Hu, 2009, Russo et al., 2009). Generally, the catabolic pathway of PVOH consists of two steps - oxidation of the hydroxyl group and cleavage of the C-C linkage (Finch, 1992, Kawai and Hu, 2009). It was found that the rate of PVOH biodegradation under AD was mainly dependent on the polymer's molecular weight and the inoculum. Matsumura et al. (1993) tested PVOH with molecular weights of 14,000 and 2,000. They found that the low molecular weight polymer tended to biodegrade rapidly and that river sediments gave higher

degradation rates than activated sludge. In contrast to the high biodegradability reported by Matsumura et al. (1993) for PVOH in activated sludge (above 40% in 125 days), PVOH was found to degrade to a minor extent in sludge (below 12% in 77 days) (Chiellini et al., 2003).

Limited studies have been conducted on the anaerobic digestibility of PVOH/starch blends. The degradation of varying starch/PVOH blends was studied by Russo et al. (2009) who concluded that after 900 hours of digestion PVOH was the predominant residue, and that the PVOH inhibited the degradation of the starch. In contrast, high degradation rates of PVOH under anaerobic conditions (66% in 22 days) have been found with PVOH/starch blends (Liu et al., 2009). Liu et al. (2009) concluded that PVOH degradation was suppressed by high glucose concentrations as starch started degrading before PVOH.

However, some key parameters such as inoculum activity, and substrate to inoculum ratio have not been documented clearly in many previous AD studies, and this affects the repeatability and comparability of literature results (Angelidaki et al., 2008). In addition, limited research has been carried out on a LCA of AD. Amongst those limited LCAs, most have focused on waste water treatment. Only a few LCA studies on AD examine the biodegradable fraction of municipal solid waste (BFMSW) (Sonesson et al., 2000, Eriksson et al., 2005), and moreover, serious data gaps for AD emerged after reviewing the literature. There is currently no LCA on AD of starch/PVOH foam packaging.

The current study aims to present the biodegradation results for three starch/PVOH based biopolymers in a transparent manner, i.e. under a defined anaerobic digestion

system with key parameters specified. In addition, another objective of this research was to combine laboratory results with industrial data to develop a site-specific LCA inventory for the AD processes, and to identify the key contributions to environmental impact associated with use of AD for the waste management of starch/PVOH biopolymer packaging.

2. Materials and methodologies

2.1 Experimental methods

2.1.1 Materials

Three starch/PVOH biopolymer foams (provided by Greenlight Products Ltd) were investigated - a wheat based foam (WBF), a potato starch-based foam (PSBF) and a maize starch-based foam (MSBF). The other main component of a biopolymer-insulated coolbox - the corrugated cardboard (provided by Hydropac Ltd) was also analyzed.

2.1.2 Biochemical methane potential (BMP) test

The BMP assay was conducted according to the techniques developed by Owen et al. (1979) and Angelidaki et al (2008), and was run in 165 mL serum bottles fitted with leak proof Teflon seals and against controls of inoculum without substrate. In each bottle, a total liquid volume of 100 mL was added, including media, inoculum and substrates. The inocula were collected from the commercial AD plant in the UK which is operated as a mesophilic, wet (< 15% dry solid), continuous-feeding two-

stage AD system. The final concentrations of inocula in the serum bottles were 2 g volatile suspended solid (VSS) L^{-1}.

To determine the inoculum activity, the protocol proposed by Angelidaki et al (2008) was applied. Model substrates chosen to determine hydrolytic, acidogenic, acetogenic and methanogenic activities were amorphous cellulose (1g L^{-1}), glucose (1g L^{-1}), a mixture of propionic and butyric acid (0.5 g L^{-1} for each acid), and acetic acid (1g L^{-1}) respectively.

The BMP assays for different substrates were conducted in four replicates (triplicate for biogas analysis and one for volatile fatty acids analysis) at an approximate 1:1 ratio of inoculum VSS to substrate chemical oxygen demand (COD). All the serum bottles were incubated at 37ºC and shaken at 200 rpm in a Gallenkamp Orbital Incubator and the total digestion duration was 115 days. 1 ml headspace gas and 2 ml liquid samples were collected from serum bottles using plastic syringes (Terumo) to determine the composition of biogas and concentration of volatile fatty acids (VFAs), respectively.

2.1.3 Analytical methods

The total suspended solid (TSS), and VSS of the inoculum were assayed according to Standard Methods (APHA, 1999). The biogas compositions were determined on a gas chromatograph (GC) (Shimadzu GC-14A) equipped with a thermal conductivity detector (TCD) and Porapak N column (1500 × 6.35 mm). The temperature of the column, TCD and injection port were set at 28°C, 38°C and 128°C, respectively.

Calibration gases were accurate to 5%, and the coefficient of variation (CV) for 10 identical samples was 2%.

VFAs were measured using a Shimadzu GC-2014 fitted with a flame-ionised detector and a SGE capillary column (BP21, 12m x 53mm ID with film thickness 0.5μm). The carrier gas was helium at a flow rate of 102.5 ml min^{-1}; temperature for the injector, and detector were constant at 200°C, and 250°C, respectively; the initial temperature for the column was 80°C, then increasing by 10°C min^{-1} to 160°C after which the temperature was held for 1 min. The concentrations for acetic, propionic, n-butyric, iso-butyric, n-valeric, iso-valeric and n-caproic acids were analyzed and the CV for ten identical samples was 6.6 %.

The PVOH and wheat protein left in the serum bottle after the BMP tests were also measured. The PVOH was determined by a colorimetric method based on formation of a PVOH-iodine-boric acid blue complex (Finch, 1992). 0.15 ml of sample was treated with 0.75 ml of 4% boric acid solution and 0.15 ml of iodine solution (containing 0.05 M iodine and 0.15 M potassium iodine) in turn and mixed well after each addition. The final solution was diluted to 2.5 ml and kept at 25ºC for 15 min and then its absorbance measured at 690 nm on a UV/VIS scanning spectrophotometer (Shimadzu UV-2101PC). All the samples were prepared within a concentration range of 0-20 mg PVOH L^{-1} which behave according to Beer's law (Finch, 1992).

To determine wheat protein degradation during the digestion period, 1 ml liquid samples were collected from serum bottles using a plastic syringe and filtered through a 0.22 μm filter (VWR) to remove cellular proteins (Aquino and Stuckey, 2003).

Wheat protein degradation was estimated by the difference of total protein content in a bottle fed with WBF (extracellular protein and wheat protein residue were present) and in the PSBF/MSBF/blank bottle, where only secreted extracellular proteins but no wheat proteins were present. The soluble protein content was determined by the modified Lowry assay developed by Peterson (1977) (Protein Assay Kit, Sigma product codes TP0300 and L3540). The samples were analyzed on a UV/VIS scanning spectrophotometer (Shimadzu UV-2101 PC) at a wavelength of 750 nm (Peterson, 1977). Bovine serum albumin was used as a standard for calibration. The detection limit was 5 mg L^{-1}, and the CV for ten identical samples was within 6.6%.

The composition analyses were carried out to characterize the materials studied, which included total solids (TS), volatile solids (VS), elements N and S, carbohydrates and lignin content. The derived data were used in the LCA model. The TS and VS were assayed according to Standard Methods (APHA, 1999). The chemical oxygen demand (COD) was measured based on the standard closed reflux colorimetric method (APHA, 1999). The analysis of total nitrogen (TN) was conducted according to the persulphate digestion method (Hach TN kit). The TN contents were determined on a Shimadzu UV/VIS scanning spectrophotometer (Model UV-2101PC) at 410 nm, with ammonium chloride as a standard. The detection limits were 10-150 mg N L^{-1}, and the CV for ten identical samples was 11%. The protein content of the biopolymers was estimated by the TN/protein conversion method, i.e. the protein concentration was obtained by multiplying its TN by a nitrogen to protein conversion factor (NF), which was calculated from the amino acids composition (Mosse, 1990). A NF of 5.52, which is specific for wheat flour (Mariotti et al., 2008) was used in calculations.

The carbohydrate and lignin content in cardboard was analyzed according to standard methods developed by National Renewable Laboratory (NREL) (Sluiter et al., 2008). The acid soluble lignin was determined on the UV-VIS spectrophotometer (LightwaveII, Biochrom Ltd) at 330 nm. The carbohydrate composition was analyzed on high-performance liquid chromatography (Agilent Technologies 1200 series) with a Bio-Rad Aminex HPX-87H column at 50 ºC with water as the mobile phase at a flow rate of 0.6 ml min^{-1}. All samples were analysed in five replicates; filter paper (> 98% cellulose) and sugar monomers were used as internal standards to control for the sugar recovery rate in the hydrolysis.

The total S elements were extracted using a three-step sequential microwave digestion (by HNO_3, H_2O_2 and HCl) method developed by Kalra et al. (1989), and analyzed on an Inductive Coupled Plasma-Optical Emission Spectrometer (ICP-OES) (Perkin Elmer Optima 7300DV). Argon was used as both carrier and purge gas. The detection limit for S was 30 µg L^{-1}. $NaSO_4$ standards were used for calibration and the recovery rate of S and matrix interferences were tested for by spiking the samples and blanks with $NaSO_4$.

2.1.4 Statistical methods

A non-parametric test method - the one-tailed Mann-Whitney test was performed on each set of BMP results for different substrates to determine the substrate(s) with the greatest anaerobic biodegradability over the digestion period. All the data were analyzed in Matlab (R2007b) at a significance level of $\alpha = 0.05$.

2.2. Characterization of the inocula and materials

2.2.1 Activity of the inocula

The characterized inoculum activities expressed as conversion efficiency are presented in Fig. 1, where the theoretical CH_4 was calculated based on 1g COD biodegraded producing 395 mL CH_4 at 35°C and one atmosphere (Speece, 1996). Approximately 247 ± 1.2 ml CH_4 g^{-1} COD and 237.3 ± 5.6 ml CH_4 g^{-1} COD were produced from digesting glucose and cellulose, respectively, which corresponds to 62.5 ± 0.3 % and 60.1 ± 1.4% conversion efficiency. A high utilization of VFAs was achieved: nearly 100% of the theoretical methane potential of propionic/butyric acid and 89.9 ± 2.6 % for acetic acid conversion. The different conversion efficiencies between model substrates were mainly due to the different cell biomass yields of the bacterial trophic groups: much higher cell biomass yields were found for acidogens than for acetogens and aceticlastic methanogens (Pavlostathis and Giraldo-Gomez, 1991). Besides a satisfactory conversion efficiency, the inoculum in the present study had a specific aceticlastic activity of 45-70 mL CH_4/g VSS/day, which indicated an active population of aceticlastic methanogens according to the protocol (minimum 39.5 ml CH_4/g VSS/day) proposed by Angelidaki et al. (2008).

The apparent reduction in conversion efficiencies in Fig 1 for the longer digestion periods (e.g. 60 and 115 days) is because the results are derived after subtraction of the gas produced in 'blank' bottles from that produced in the test sample bottles. These blank bottles are used to provide an estimate of methane yield due to cell lysis for each unit of inoculum. The blank bottles represent the autolysis phenomenon due to starvation (absence of a carbon source), whereas the 'test' substrate BMP sample bottles normally do not experience this stress when a biodegradable substrate is

present. Thus, this diminishing curve of conversion efficiencies at the longer incubation times is a characteristic of the autolysis occurring in blank bottles. However, this characteristic of the BMP method does not affect the subsequent analysis and modelling as the ultimate biogas production (within the first 55 days) is the value actually used to characterise the activity of the inoculum.

Overall, these assays confirmed that highly active bacterial and archaeal trophic groups were present in the inoculum, supporting the likely presence of balanced microbial populations with good inherent abilities to undertake degradation of bio-packaging materials.

2.2.2 Materials compositions

The contents of wheat flour, potato starch and maize starch in each biopolymer foam, varied but was between 85-90% of the foam mass, with the PVOH content being about 10%. The laboratory-determined material compositions are given in Table 1.

2.2.2.1 Total sulphur content

For blanks and samples spiked with $NaSO_4$, the recovery rate of $NaSO_4$ varied between 100.6 % and 105.4%. S contents measured via the SI 180.669 nm emission line of ICP-OES are considered as reliable (Grosser et al., 2009) and are given in Table 1.

2.2.2.2 Carbohydrate content

All carbohydrate contents were corrected for the recovery rates for sugar monomer standards or filter paper. It was assumed that 100% of the polymeric sugars contained in cardboard were hydrolyzed to sugar monomers.

Hemicelluloses accounted for 18.86 % of the mass of dry cardboard, which included xylan (10.04%), mannan (6.09%) galactan (2.34%), arabinan (0.39%). Based on the overall compositional analysis of the cardboard (see Table 1), it was estimated that the carbon sequestered from the atmosphere from wood growth was 45.84% on a dry basis, equivalent to 1.68 kg CO_2 kg^{-1} dry cardboard. The C content in the polymeric sugars was calculated from their molar mass. As the raw wood logs and sawmill residues used for cardboard paper making are primarily derived from softwood (FEFCO, 2006), a typical C content of softwood lignin (62.2% on a dry basis) from the Phyllis database (ECN, 2007) was used in the calculations.

2.3. LCA modelling

The LCA approach was applied to evaluate the 'cradle-to-grave' environmental profiles of a biopolymer insulated coolbox disposed of via AD, and compared the environmental performance of various components of the coolbox (i.e. WBF/PSBF/MSBF/cardboard) at the AD stage. The product system modelled and the system boundaries are shown in Fig. 2 for the WBF coolbox as an example. The system and boundaries were similar for two other alternative products insulated with PSBF or MSBF. The functional unit was defined as '*a single 8.5 litre capacity corrugated box insulated with WBF/PSBF/MSBF to maintain a temperature below 5^{o}C for 24 hours for the transport of temperature-sensitive contents*'. In the LCA model, the economic allocation approach (except for CO_2 sequestration) was adopted

for most of the stages where multiple-products occurred; an 'avoided burdens' approach was applied in the cases where energy related co-products occurred (e.g. electricity from combine heat and power system (CHP)) or closed-loop recycling occurred. A carbon counting approach following the carbon stoichiometry was used to 'track' the carbon flows during the life cycle of the biopolymer-insulated coolbox (Guo, 2010).

The LCA inventory was developed by using primary data collected from industrial sources combined with the results from the laboratory experiments supplemented with secondary data from publicly available sources and the Ecoinvent database (v2.0) (Guo, 2010). The production data for wheat flour including the wheat farming and milling processes were derived from Heygates Ltd. A computer simulation of the field emissions (e.g. N_2O, NH_3, NO_3^- etc) was run using the process-oriented model Denitrification-Decomposition (DNDC) (Guo, 2010). The input-output data for PVOH production were based on a theoretical model and expert estimations (Guo, 2010). The cardboard box manufacturing was modelled according to the European average process (FEFCO, 2006) and data supplied by Box Factory. Data for the production of starch/PVOH biopolymers were provided by Greenlight Product Ltd. The scenario for production and usage of a biopolymer insulated coolbox was based on laboratory results and commercial trial data provided by Brunel University and Hydropac Ltd. The inventories for the AD scenario were primarily derived from industrial data and laboratory experimental results, except for the infrastructure inputs where the WRATE database was used (EnvironmentAgency, 2009).

3. Results and iscussion

3.1 BMP assay

3.1.1 Biogas production and material biodegradability

The cumulative CH_4 production at an I/S ratio of 1 is given in Fig. 3. No lag phase was observed for almost all the substrates except cardboard, which only showed a 1-day lag phase. The methane content in the headspace was similar for all the substrates investigated, and reached 45% CH_4 and 53-55% CO_2 at the end of the test.

As shown in Fig. 3, within the first 10 days a rapid digestion was observed for all substrates, especially the biodegradable foams; cumulative CH_4 production from foam digestion increased substantially over the first 5-6 days followed by a plateau period. The CH_4 yield from the digestion of cardboard rose gradually after 10 days. There was a small but statistically greater cumulative CH_4 yield from WBF than PSBF and MSBF during the first 5-day incubation period, after which no difference in cumulative CH_4 yield was found between the different biodegradable foams. ~~According to statistical analysis ($\alpha = 0.05$), the digestibility of WBF was significantly greater than PSBF and MSBF within the first 5-day incubation period during which the cumulative CH_4 yield from WBF reached 249.9 ± 6.2 ml g^{-1} VS.~~ This was probably due to the starch and protein contained in the wheat flour component of WBF providing both C and N nutrients for microorganisms, whereas only a C-source was supplied in PSBF and MSBF. The C:N ratio of WBF (34.2) is close to the optimum range for an AD substrate (20-30) suggested by Monson et al. (2007). As expected, the cardboard had the slowest degradation rate in comparison with the foams. This can be explained by the impeded access to cellulose by the complex three-dimensional structures formed between cellulose, hemicellulose, and the lignin component being somewhat recalcitrant to biodegradation in the AD system.

WBF gave the highest ultimate CH_4 yield (293.7 ± 6.7 ml g^{-1} VS fed), followed by MSBF (280.9 ± 6.8 ml g^{-1} VS fed), cardboard (272.8 ± 7.9 ml g^{-1} VS fed) and PSBF (264.1 ± 12.9 ml g^{-1} VS fed). The final conversion efficiency of WBF at 61.9 ± 1.4% was slightly higher than PSBF (58.3 ± 2.9%) and MSBF (57.8 ± 1.4%). Thus, over 55% biodegradability is reachable for all the substrates tested. Moreover, the methane yields of approximately 260 to 290 ml g-1 VS fed obtained for the foams were considerably greater than for OFMSW which are typically around 200 ml g^{-1} VS (Owens and Chynoweth, 1993).

3.1.2 Process indicator - VFAs

No significant quantities of VFAs were detected after the first 12-day incubation period (see Fig. 4). The dominant VFAs in the digestion of WBF, PSBF and MSBF were acetic, propionic and butyric acids which is consistent with findings of Russo et al. (2009). In contrast to the foams, acetic and propionic acid were the most prevalent VFAs from cardboard, while n-butyric acid only accounted for a small proportion.

Comparing patterns of acetic acid and CH_4, it was found that the timing of the acetic acid peak (day 2/3 for WBF/PSBF/MSBF and day 4 for cardboard) coincided with the occurrence of maximum specific methane production rate (not shown here) and the plateau period i.e. zero acetic acid production at day 6 and day 9 for foams and cardboard respectively, matched well with the CH_4 production curves. This demonstrated that the various trophic groups involved in AD were well balanced so that the build up of VFAs was avoided.

3.1.3 PVOH and protein assay

After 115-days of incubation 17.4% ± 1.1% of the initial PVOH remained in the WBF bottle, but only 8.1 ± 1.7% and 3.6 ± 0.8% of the input PVOH remained in bottles fed with MSBF and PSBF respectively. This finding gives an approximation of PVOH degradation in the presence of inocula collected from the AD plant. The extensive biodegradation of PVOH (greater than 80%) can partly be explained by the highly active inocula, but may also be attributable to the relatively low molecular weight of the PVOH-2488 component in the foams. Generally, PVOH with low molecular weight is considered to be more rapidly degradable than higher molecular weight variants (Matsumura et al., 1993, Chiellini et al., 2003).

Soluble microbial products (including extracellular protein) may be produced by cells in response to stress conditions e.g. limitation of nutrients (Aquino and Stuckey, 2003). However, in the current study, no significant difference was found in the soluble protein content of control bottles without feeding and in sample bottles fed with MSBF/PSBF. This may be attributable to long digestion periods which led to nutrient deficiency occurring in sample bottles. Total protein present in control bottles and the MSBF/PSBF sample bottles ranged between 3.34 - 3.54 mg, which is equivalent to a range of 0.0167-0.0177 mg protein mg^{-1} VSS. This result is similar to the findings in previous studies (Aquino and Stuckey, 2003). In comparison with the blank bottles and sample bottles fed with MSBF and PSBF, only slightly higher protein contents were found in WBF sample bottles (4.1 ± 0.16 mg protein per bottle), which may be caused by the small fraction of wheat protein remaining as residues (approximately 3.2-3.5% of the initial wheat protein), or higher extracellular protein produced during metabolism of WBF. It is not possible to separate the influence of

these two factors on protein content results, however, they demonstrate that most of the initial wheat protein was degraded.

3.1.4 C element flow

The calculated C balances from the laboratory work are presented in Table 2. 68 - 75% of the total C contained in foams was released as biogas; assuming that all gasified C was of biogenic and not from the PVOH, approx 82.8% - 86.9% of the C sequestered from the atmosphere, and contained in the foams, was converted to CO_2 or CH_4. C present in the PVOH residue in the liquid phase only made up a small fraction of the total C. The rest of the C could be partially utilized by microorganisms for cell synthesis, but a fraction of the C could also be present in the liquid phase as molecules produced from PVOH degradation. In the case of cardboard, it was estimated that approx 62% of the total C was gasified, representing about 75% of the C contained in cellulose and hemi-cellulose released as biogas (lignin was assumed to be non-biodegradable in AD). Therefore, a high gasification efficiency of degradable C was achieved for all the substrates during this study.

As expected, the composition of biogas observed in the laboratory (53 - 55% CO_2 and 45% CH_4) differed somewhat from the gas composition from BFMSW degradation reported at the commercial AD plant (32-35% CO_2 and 65% CH_4) Therefore, it was assumed that under industrial-scale digestion conditions, higher conversion efficiencies of C from CO_2/$C_2H_4O_2$ to CH_4 were achievable from foam/cardboard digestion and the typical biogas composition at the AD plant was used in LCA model.

3.2. LCA model

3.2.1 Inventory analysis

Based on the laboratory and industrial data collected from the AD plant and the assumption that lab-derived data on digestibility and ultimate biogas yields represent the behaviour of the materials digested in the industrial plant, the inventories for the AD scenarios treating WBF, PSBF are MSBF products are given in Table 3. There are uncertainties in these inventories as the different digestion conditions between commercial AD systems and lab-scale tests could lead to different digestion 'performance', which should be explored in further research.

85 - 90% of the ultimate theoretical methane production for foams and cardboard was achieved within 5 days and 17 days, respectively. An additional one day needed for the hydrolysis step was taken into account so 6 and 18 days were assumed as representative operational times for foam and cardboard degradation, respectively. On average it takes 25 days to digest BFMSW, and therefore the energy consumed for AD of the foams and cardboard accounting for their various digestibilities was estimated based on the assumption that the same amount of electrical and thermal energy is used per unit of BFMSW per day.

A baseline scenario reflecting current technology of the AD plant was developed where the thermal energy generated was unused and 100% of the renewable electricity exported. Electrical energy for operation of the AD plant was imported from the national grid and the heat requirement supplied form diesel fuel, although an optimized AD process can be expected in the near future. Therefore, an AD best

scenario with an improved efficient energy utilization system was also modelled. In this scenario, heat from the CHP was assumed to be the main thermal energy source; diesel was assumed as a supplementary source to provide any extra heat demand; only surplus electricity after satisfying the energy requirement for the AD plant operation was assumed to be exported. As shown in Table 3, in this scenario the renewable energy recovered from biopolymers can meet the heat demand for the AD process (surplus renewable thermal energy was assumed to be wasted); but in the case of cardboard, supplementary diesel heat input is required.

Modelled emissions from the AD plant for the baseline scenario are given in Table 4. Based on the results reported by Dewil et al. (2008), it was assumed that only 0.02% of S was emitted as H_2S in biogas, while the remaining S was retained in the sludge as an insoluble iron sulphide complex after the $FeCl_3$ desulphurization treatment. N_2O emission was considered to be negligible following the Intergovermental Panel on Climate Change (IPCC) guidelines (IPCC, 2006). Released NH_3 was estimated according to an on-line model (Alleman, 1998), which was based on the pH and temperature dependent relationship between NH_4^+ and free NH_3.

Overall, three gas emission sources were considered: 1) the oxidized gases released from a CHP system where complete biogas combustion was assumed; 2) the fugitive gases i.e. the unintentional leakage escaping from open reactors during operation/maintenance where good practice was assumed (unintentional CH_4 emissions are flared thus uncontrolled CH_4 emissions are close to zero) (IPCC, 2006); 3) emissions from diesel combustion, where the IPCC Tier 1 approach (2006) and EMEP-EEA Tier 1 approach (2009) were applied to calculate potential emissions.

Besides gas phase C emissions, the remaining C including un-degraded or partially digested fractions together with other elements, e.g. mineralized N or insoluble S, are contained in the digestate. As presented in Table 3, approx 0.10 - 0.17 kg digestate was estimated to be produced per kg foam or cardboard, which is very close to the data reported by the AD plant (on average 0.18 kg digestate kg^{-1} feedstock). Here, only 'functional' components contained in the digestate and effective for land reclamation were taken into account, (including organic content and nutrients) and so the 'functional equivalent' quantity (dry basis) of compost produced from a generic composting process (Ecoinvent v2.04) was allocated as an 'avoided burden' to the AD system.

3.2.2 Life cycle impact assessment (LCIA) results

The LCIA profiles for AD baseline scenarios of the coolboxes insulated by WBF, PSBF and MSBF are given in Fig. 5. In most impact categories, much higher environmental impacts occurred at the end of life of the cardboard than the foams.

Generally, the main contributors to the impacts of AD baseline scenarios on acidification, eutrophication, global warming potential (for 100-year time horizon, GWP 100) and photochemical oxidation potential (POCP) were the gases produced either by diesel production and combustion, or from biodegradation of the cardboard and foam. Diesel fuel caused 70-95% of the impact score in acidification, eutrophication and POCP mainly due to the NO_x and SO_x emitted directly from its combustion. About 75% of the positive GWP100 score (GHG emission) for the cardboard and 50% of the positive GWP100 score for foams arose from the release of

CO_2 during combustion of the biogas in the CHP system (this ignores the 'negative' GWP100 component below the line from CO_2 sequestration during plant growth).

As shown in Fig. 5A, the inclusion of infrastructure and energy inputs in the AD baseline scenarios dominated environmental burdens in the abiotic depletion, ozone depletion potential (ODP) and toxicity impact categories. About 50-85% of the positive toxicity impact scores and 20-40% of positive abiotic depletion and 15-30% of positive ODP impact scores were attributed to infrastructure (this ignores the negative scores below the line from electrical energy substitution).The toxic impacts were mainly caused by the emissions from steel production, e.g. mercury, chromium, arsenic released to atmosphere, and the metallic ions emitted to water (nickel, vanadium); whilst both steel and bitumen production (oil resource depletion as well as $CBrF_3$ released from oil production) were dominant contributors to ODP burdens and resource depletion. In addition, energy consumed in the AD scenario, especially diesel, not only accounted for approx 15-50% of the positive toxicity impacts, but also dominated ODP impacts and abiotic depletion (65-85%) due to crude oil depletion and the emissions from crude oil production (e.g.. PAH, barite, barium, $CBrF_3$.), and atmospheric pollutants released from fuel combustion during diesel refining (e.g.. vanadium, mercury).

The products generated from AD process, including electricity and digestate, brought environmental credits to the LCIA profiles of foams and cardboard by energy substitution or avoidance of compost. However, the benefits of energy recovery from cardboard digestion offsetting operational demands of the AD process were not as high as for the foams due to the lower biodegradability of the cardboard.

As illustrated in Fig. 5B, the environmental profiles of a WBF coolbox are dominated by the production process in most impact categories except for GWP100 where the end-of-life contributed 50-70% of the positive impact scores. Results for the AD 'best' scenarios suggested that optimisation of energy utilisation in the AD system could bring up to 26% saving in the whole life cycle environmental impact of the WBF coolbox system. Comparison between different waste management options further indicated that recycling rather than AD was a better option for the cardboard component. Similar results to these were also found in the cases with PSBF or MSBF. Thus, the integration of recycling and AD offers the environmentally optimal choice for coolboxes insulated with starch-PVOH based biopolymers.

4. Conclusions

With highly active inocula, 58-62% biodegradation of starch-PVOH based biopolymers are achievable under AD conditions. WBF gave slightly higher CH_4 yield (294 mL g^{-1} VS), followed by MSBF (281 mL g^{-1} VS) and PSBF (264 mL g^{-1} VS). The major contributors to environmental burdens were identified as energy inputs and atmospheric emissions during the AD process, although optimization of the energy utilization system could bring significant environmental benefits to the AD process. Mechanical and biological treatment (AD of the biopolymer plus recycling of the cardboard) emerged as an environmentally superior choice compared with pure AD for the starch-PVOH biopolymer-insulated coolbox.

5. Acknowledgements

This study is based on research financially supported by the UK Department of Trade and Industry through the Technology Programme. We would like to thank all the participants in the consortium project led by Greenlight Products Ltd and Brunel University.

References

Alleman, J. E., 1998. Free Ammonia-Nitrogen Calculator & Information. Purdue University

Angelidaki, I., Alves, M., Bolzonella, D., Borzacconim, L., Guwy, A. J., Kalyuzhnyi, S., Jenicek, P., Campos, L. & van Lier, J. B., 2008. Defining the biomethane potential (BMP) of solid organic wastes: a proposed protocol for batch assays. *5th International Symposium of anaerobic digestion of solid waste and energy crops.* Hammamet, Tunisia.

APHA, 1999. *Standard Methods for the Examination of Water and Wastewater*, American Public Health Association, Washington D.C.

Aquino, S. F. & Stuckey, D. C., 2003. Production of soluble microbial products (SMP) in anaerobic chemostats under nutrient deficiency. *Journal of Environmental Engineering-Asce,* 129**,** 1007-1014.

Chiellini, E., Corti, A., D'Antone, S. & Solaro, R., 2003. Biodegradation of poly (vinyl alcohol) based materials. *Progress in Polymer Science,* 28**,** 963-1014.

Composto, 2000. Life cycle assessment of Mater-Bi and EPS loose fills. . Study prepared by COMPOSTO for Novamont, Novara, Italy

Dewil, R., Baeyens, J., Roels, J. & Van de Steene, B., 2008. Distribution of sulphur compounds in sewage sludge treatment. *Environmental Engineering Science,* 25**,** 879-886.

DTI, 2007. Energy and commodity balances, conversion factors and calorific values. DTI.

ECN, 2007. Phyllis, database for biomass and waste,. Energy research Centre of the Netherlands

EEA, 2009. The EMEP/EEA Air Pollutant Emission Inventory Guidebook-2009. IN PROJECTIONS, U. E. T. F. O. E. I. A. (Ed.), European Environment Agency.

EnvironmentAgency, 2009. Waste and Resources Assessment Tool for the Environment (WRATE).

Eriksson, O., Reich, M. C., Frostell, B., Bjorklund, A., Assefa, G., Sundqvist, J. O., Granath, J., Baky, A. & Thyselius, L., 2005. Municipal solid waste management from a systems perspective. *Journal of Cleaner Production,* 13**,** 241-252.

FEFCO, G. E., 2006. European Database for Corrugated Board Life Cycle Studies. IN EUROPEAN FEDERATION OF CORRUGATED BOARD MANUFACTURERS, EUROPEAN ASSOCIATION OF MAKERS OF CORRUGATED BASE PAPERS & ORGANISATION, E. C. (Eds.).

Finch, C. A., 1992. *Polyvinyl Alcohol-developments,* John Wiley&Sons Ltd.

Follain, N., Joly, C., Dole, P. & Bliard, C., 2005. Properties of starch based blends. Part 2. Influence of poly vinyl alcohol addition and photocrosslinking on starch based materials mechanical properties. *Carbohydrate Polymers,* 60**,** 185-192.

Grosser, Z. A., Davidowski, L. J. & Wee, P., 2009. The Analysis of Biodiesel for Inorganic Contaminants including Sulfur by ICP-OES.

Guo, M., 2010. Life Cycle Assessment (LCA) of Light-weight Eco-composites. London, Imperial College London.

IPCC, 2006. 2006 IPCC Guidelines for National Greenhouse Gas Inventories, Prepared by the National Greenhouse Gas Inventories Programme, Eggleston H.S., Buendia L., Miwa K., Ngara T. and Tanabe K. (eds). IN CHANGE, I. P. O. C. (Ed.), IGES, Japan.

Kalra, Y. P., Maynard, D. G. & Radford, F. G., 1989. Microwave Digestion of Tree Foliage for Multi-Element Analysis. *Canadian Journal of Forest Research-Revue Canadienne De Recherche Forestiere,* 19**,** 981-985.

Kawai, F. & Hu, X. P., 2009. Biochemistry of microbial polyvinyl alcohol degradation. *Applied Microbiology and Biotechnology,* 84**,** 227-237.

Liu, R. R., Chen, J. H. & Tian, Q., 2009. Pilot Study on Anaerobic Biodegradability of PVA 1799. IN LUO, Q. & LUO, Q. (Eds.) *2nd International Workshop on Knowledge Discovery Data Mining.* Moscow, RUSSIA, World Acad Union-World Acad Press.

Mariotti, F., Tome, D. & Mirand, P. P., 2008. Converting nitrogen into protein - beyond 6.25 and Jones' factors. *Critical Reviews in Food Science and Nutrition,* 48**,** 177-184.

Matsumura, S., Kurita, H. & Shimokobe, H., 1993. Anaerobic Biodegradability of Polyvinyl-Alcohol. *Biotechnology Letters,* 15**,** 749-754.

Monson, K. D., Esteves, S. R., Guwy, A. J. & Dinsdale, R. M., 2007. Anaerobic Digestion of Biodegradable Municipal Solid Wastes A Review. Univerisity of Glamorgan.

Mosse, J., 1990. Nitrogen to Protein Conversion Factor for 10 Cereals and 6 Legumes or Oilseeds - a Reappraisal of Its Definition and Determination - Variation According to Species and to Seed Protein-Content. *Journal of Agricultural and Food Chemistry,* 38**,** 18-24.

Owen, W. F., Stuckey, D. C., Healy, J. B., Young, L. Y. & McCarty, P. L., 1979. Bioassay for Monitoring Biochemical Methane Potential and Anaerobic Toxicity. *Water Research,* 13**,** 485-492.

Owens, J. M. & Chynoweth, D. P., 1993. Biochemical Methane Potential of Municipal Solid-Waste (Msw) Components. *Water Science and Technology,* 27**,** 1-14.

Pavlostathis, S. G. & Giraldo-Gomez, E., 1991. Kinetics of Anaerobic Treatment. *Water Science and Technology,* 24**,** 35-59.

Peterson, G. L., 1977. Simplification of Protein Assay Method of Lowry Et Al - Which Is More Generally Applicable. *Analytical Biochemistry,* 83**,** 346-356.

Russo, M. A. L., O'Sullivan, C., Rounsefell, B., Halley, P. J., Truss, R. & Clarke, W. P., 2009. The anaerobic degradability of thermoplastic starch: Polyvinyl alcohol blends: Potential biodegradable food packaging materials. *Bioresource Technology,* 100**,** 1705-1710.

Shogren, R. L., Lawton, J. W. & Tiefenbacher, K. F., 2002. Baked starch foams: starch modifications and additives improve process parameters, structure and properties. *Industrial Crops and Products,* 16**,** 69-79.

Sluiter, A., Hames, B., Ruiz, R., Scarlata, C., Sluiter, J., Templeton, D. & Crocker, D., 2008. Determination of Structural Carbohydrates and Lignin in Biomass Laboratory Analytical Procedure. National Renewable Energy Laboratory.

Sonesson, U., Bjorklund, A., Carlsson, M. & Dalemo, M., 2000. Environmental and economic analysis of management systems for biodegradable waste. *Resources Conservation and Recycling*, 28**,** 29-53.

Speece, R. E., 1996. *Anaerobic Biotechnology for Industrial Wastewaters*, Archae Press, Nashville, Tennessee, USA.

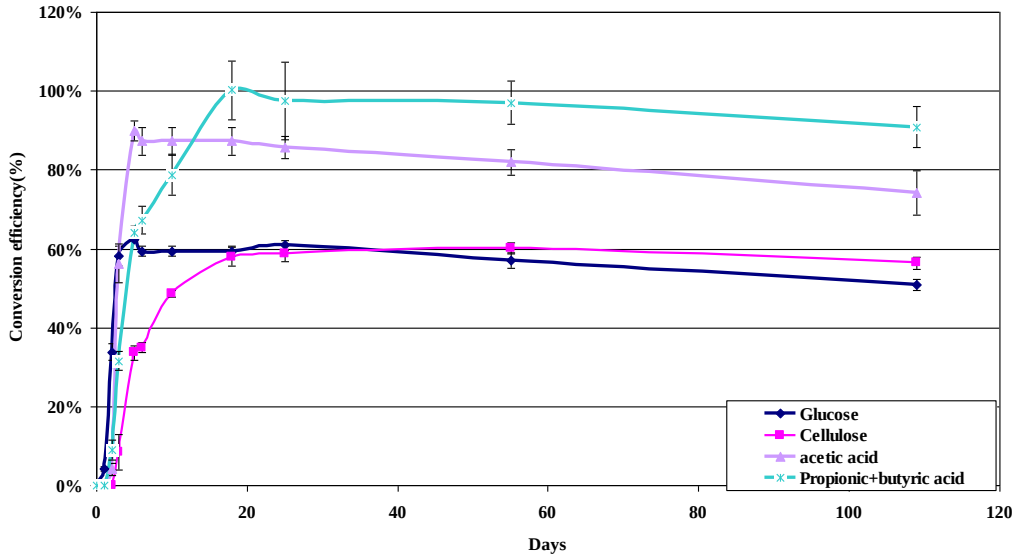

Fig. 1 Conversion efficiency (measured CH_4/theoretical CH_4) of synthetic substrates by various trophic groups of the inoculum used in this study

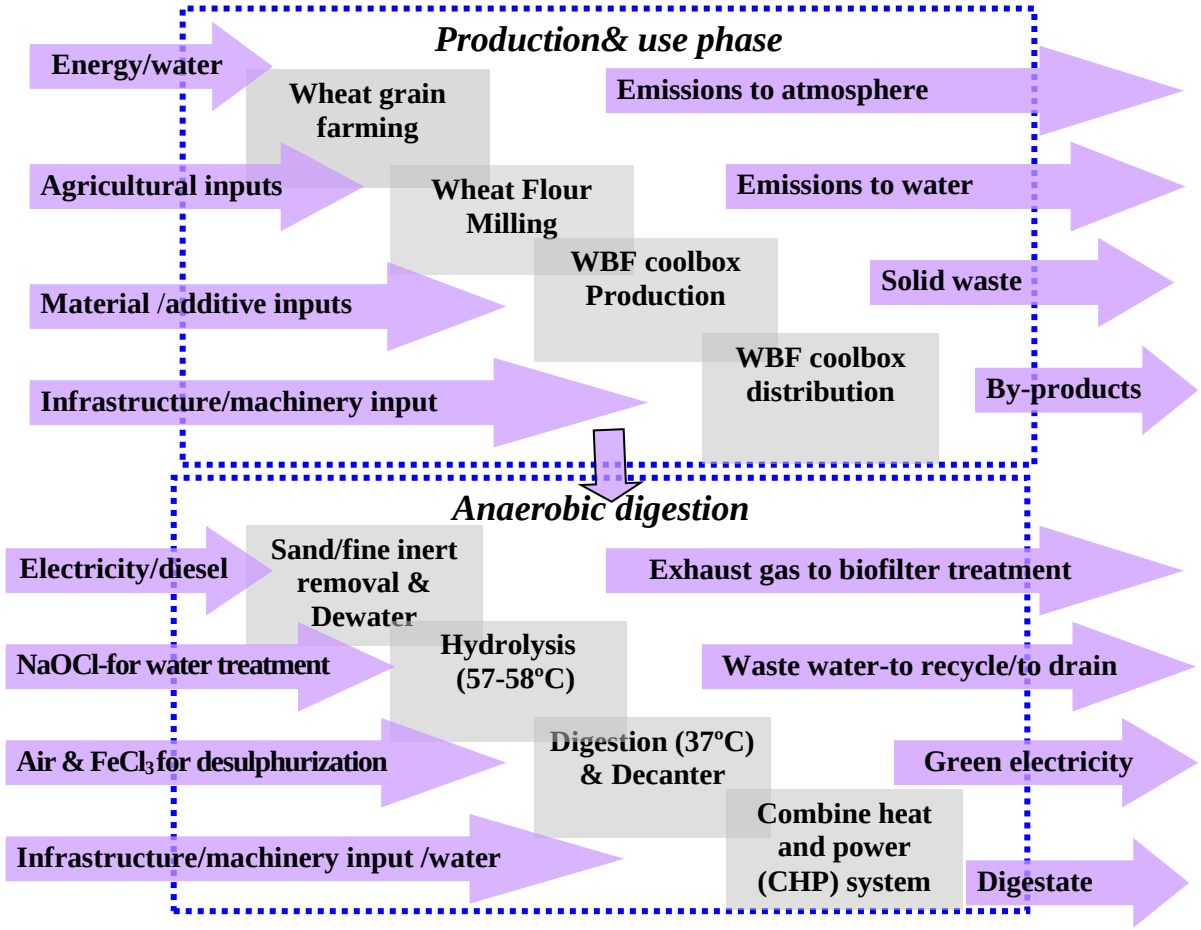

Fig. 2 Product system and system boundary for WBF coolbox

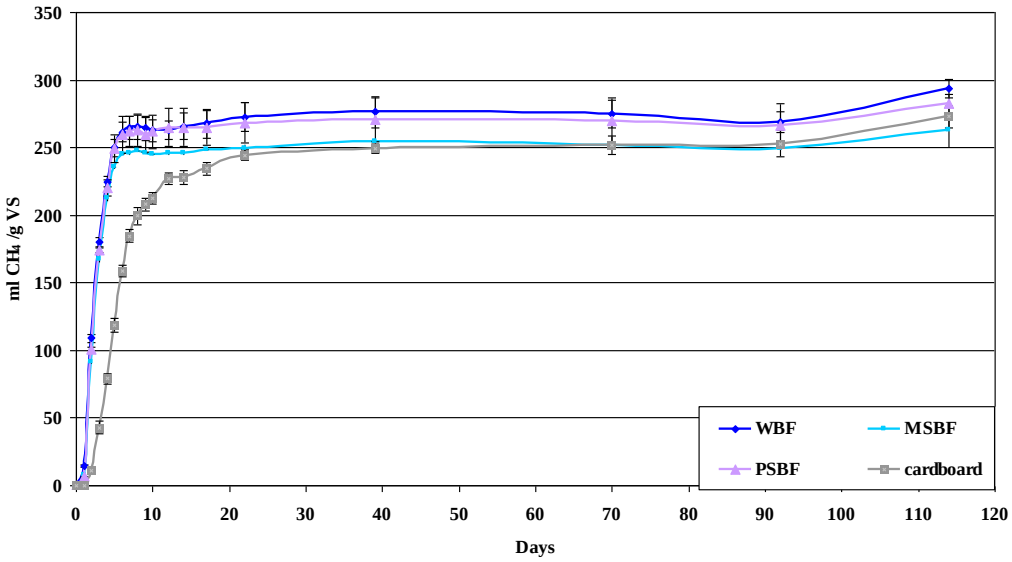

Fig. 3 Evolution of cumulative methane yield with time during BMP assay of biopolymer and cardboard at an I/S ratio=1 (Error bar shows SD)

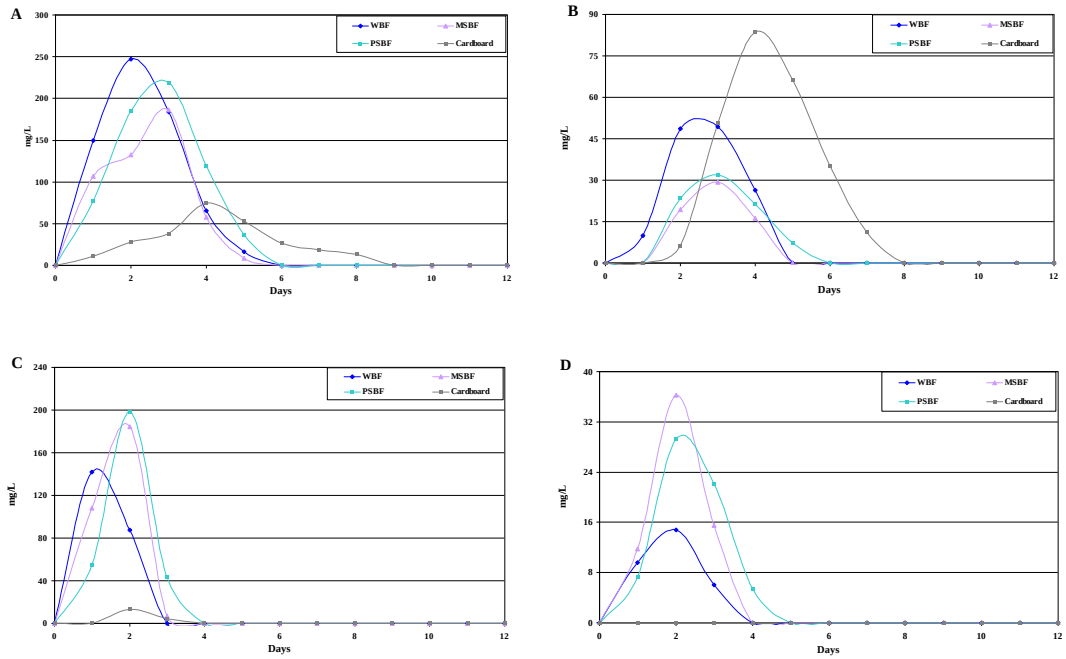

Fig. 4. Evolution with time of the VFA concentrations during the BMP assays on biopolymers and cardboard (A: acetic acid, B: propionic acid, C: n-butyric acid, D: iso-butyric acid).

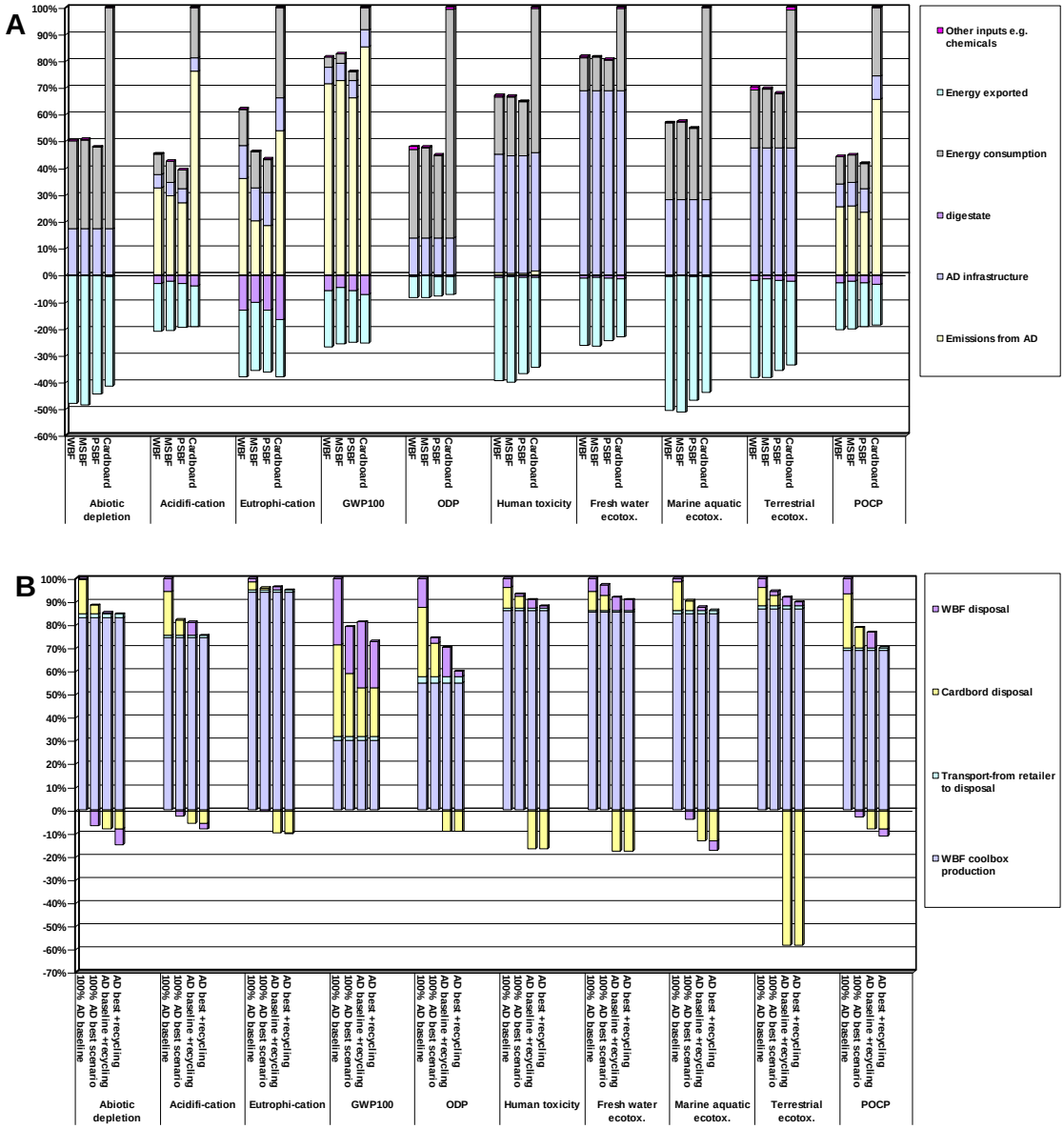

Fig. 5. The characterized LCIA profiles. A: AD process in baseline scenario (unit: per kg substrate). B: life cycle of WBF coolbox (unit: per coolbox)

Table 1 Physical and chemical properties of materials (SD is indicated in brackets).

	WBF	PSBF	MSBF	Cardboard
TS (%)	93.30 (0.77)	92.72 (0.26)	93.18 (0.19)	95.79 (0.32)
VS (% of TS)	99.10 (0.24)	99.55 (0.06)	99.87 (0.12)	89.46 (0.04)
COD (mgO_2/g TS)	1188 (173)	1167 (252)	1253 (449)	1133 (137)
Total N (mg/g TS)	13.72 (1.52)	0	0	2.23 (0.05)
Protein (mg/g TS)	75.73	0	0	0
Total S (mg/g TS)	0.94 (0.03)	0	0	0.93 (0.02)
Cellulose (mg/g TS)	NA	NA	NA	658.41 (9.63)
Hemicellulose (mg/g TS)	NA	NA	NA	188.64 (6.39)
Acid-soluble lignin (mg/g TS)	NA	NA	NA	17.44 (2.23)
Acid-insoluble lignin (mg/g TS)	NA	NA	NA	112.6 (8.35)

Notes: *NA=not available*

Table 2 Carbon balance in anaerobic digestion (SD is indicated in brackets).

	WBF	PSBF	MSBF	Cardboard
C mass flow (g g^{-1} TS)				
Total C	0.469	0.461	0.457	0.458
Biogenic C	0.389	0.382	0.399	0.458[a]
CH_4 yield as C [b]	0.157 (0.004)	0.141 (0.007)	0.151 (0.004)	0.131 (0.004)
CO_2 yield as C [b]	0.182 (0.01)	0.174 (0.003)	0.194 (0.011)	0.153 (0.004)
C balance (% total C)				
CH_4	33.36% (0.76%)	30.70% (1.50%)	33.03% (0.80%)	28.63% (0.83%)
CO_2	38.73% (2.09%)	37.87% (0.73%)	42.39% (2.37%)	33.39% (0.83%)
PVOH residue	2.97% (0.19%)	0.61% (0.14%)	1.03% (0.20%)	---

Notes:

a. Amongst biogenic C contained in cardboard 0.378gC g^{-1} TS is derived from cellulose and hemi-cellulose

b. Density of CH_4=0.717 g L^{-1}; Density of CO_2=1.977 g L^{-1}

Table 3 LCA inventory for AD scenarios of WBF/PSBF/MSBF products

	WBF	PSBF	MSBF	cardboard
AD baseline scenario input (Unit: per kg received waste)				
Electricity for ball mill (kwh)	2.00E-02	2.00E-02	2.00E-02	2.00E-02
Electricity for AD (kwh)	2.68E-02	2.49E-02	2.73E-02	6.95E-02
Fresh water (m^3)	1.67E-03	1.67E-03	1.67E-03	1.67E-03
Recycled process water (m^3)	1.67E-03	1.67E-03	1.67E-03	1.67E-03
$FeCl_3$ (kg)	5.17E-04	0	0	4.46E-04
NaOCl (kg)	5.02E-05	5.02E-05	5.02E-05	5.02E-05
Air flow (m^3)	7.10E-02	0	0	6.13E-02
Diesel (MJ) [a]	3.70E+00	3.43E+00	3.76E+00	9.57E+00
AD baseline scenario output (Unit: per kg received waste)				
Digestate cake (kg)	1.36E-01	1.34E-01	1.05E-01	1.70E-01
Gasified C (kg) [b]	3.16E-01	2.93E-01	3.21E-01	2.72E-01
Total biogas (m^3) [b]	5.86E-01	5.44E-01	5.96E-01	5.06E-01
Bio-electricity-generated (kwh) [c]	7.12E-01	6.60E-01	7.24E-01	6.14E-01
Bio-heat generated (MJ)[d]	6.29E+00	5.84E+00	6.40E+00	5.43E+00
Waste water (m^3)	1.67E-03	1.67E-03	1.67E-03	1.67E-03
AD best scenario energy balance (Unit: per kg received waste)				
Electricity exported (kwh)	6.85E-01	6.36E-01	6.97E-01	5.45E-01
Renewable-heat input (MJ)	3.70E+00	3.43E+00	3.76E+00	9.57E+00
Diesel consumed (MJ) [a]	0	0	0	9.53E-02
Transportation (Unit: per kg received waste)				
Waste (from Ballmill to AD plant) (kgkm)	4.99E+00	4.99E+00	4.99E+00	4.99E+00
$FeCl_3$ (kgkm)	4.59E-02	0	0	3.96E-02
NaClO (kgkm)	8.15E-03	8.15E-03	8.15E-03	8.15E-03
Digestate -to landfill (kgkm)	7.47E+00	7.39E+00	5.76E+00	9.35E+00

Notes:

a. Diesel density=0.85 kg L^{-1}; net calorific value=43.4MJ/kg (DTI, 2007)

b. Laboratory data; gasified C include CH_4-C and CO_2-C

c. Estimated from the average electrical conversion efficiency in AD plant (1.2 kwh/m^3 biogas)

d. Net calorific value of biogas was assumed as 21.48 KJ L^{-1} and the 50% of the energy contained in biogas was converted to thermal energy (Monson et al., 2007)

Table 4 Modelled emissions from AD of bio-based foams and cardboard in AD baseline scenario

	WBF	PSBF	MSBF	cardboard
Emissions from biogas combustion [a] (kg emission kg $^{-1}$ received waste)				
CO_2	1.16E+00	1.07E+00	1.18E+00	9.99E-01
NOx as NO_2	5.48E-04	0	0	9.16E-05
SO_2	3.50E-07	0	0	3.59E-07
Emissions from diesel combustion [b] (kg emission kg $^{-1}$ received waste)				
CO_2	2.74E-01	2.54E-01	2.79E-01	7.09E-01
CH_4	1.11E-05	1.03E-05	1.13E-05	2.87E-05
N_2O	2.22E-06	2.06E-06	2.26E-06	5.74E-06
NO_x	6.65E-04	6.17E-04	6.77E-04	1.72E-03
CO	5.55E-05	5.15E-05	5.64E-05	1.44E-04
NMVOC	2.96E-06	2.74E-06	3.01E-06	7.66E-06
SO_x [c]	1.70E-03	1.58E-03	1.73E-03	4.40E-03
TSP	1.11E-05	1.03E-05	1.13E-05	2.87E-05
PM 10 [d]	7.39E-06	6.86E-06	7.52E-06	1.91E-05
PM 2.5 [d]	3.70E-06	3.43E-06	3.76E-06	9.57E-06

Notes:

a. Complete combustion assumed

b. Tier 1 approach applied (IPCC, 2006, EEA, 2009)

c. The majority of SOx is SO_2 (EEA, 2009)

d. PM 10 and PM 2.5 represent particulate matters with aerodynamic diameter less than $10\mu m$ and particulate matters with diameter less than $2.5\mu m$ respectively