Bioresource Technology 101 (2010) 3388–3393

Contents lists available at ScienceDirect

Bioresource Technology

journal homepage: www.elsevier.com/locate/biortech

Slaughterhouse fatty waste saponification to increase biogas yield

A. Battimelli [a,*], M. Torrijos [a], R. Moletta [b], J.P. Delgenès [a]

[a] INRA, UR050, Laboratoire de Biotechnologie de l'Environnement, Avenue des Etangs, Narbonne F-11100, France
[b] Optimisation Lab of Environmental Conception and Engineering, Savoie University, Le Bourget Du Lac F-73376, France

ARTICLE INFO

Article history:
Received 9 September 2009
Received in revised form 2 December 2009
Accepted 10 December 2009
Available online 13 January 2010

Keywords:
Anaerobic digestion
Lipid
Long-chain fatty acid
Thermochemical pretreatment

ABSTRACT

A thermochemical pretreatment, i.e. saponification, was optimised in order to improve anaerobic biodegradation of slaughterhouse wastes such as aeroflotation grease and flesh fats from cattle carcass. Anaerobic digestion of raw wastes, as well as of wastes saponified at different temperatures (60 °C, 120 °C and 150 °C) was conducted in fed-batch reactors under mesophilic condition and the effect of different saponification temperatures on anaerobic biodegradation and on the long-chain fatty acids (LCFAs) relative composition was assessed. Even after increasing loads over a long period of time, raw fatty wastes were biodegraded slowly and the biogas potentials were lower than those of theoretical estimations. In contrast, pretreated wastes exhibited improved batch biodegradation, indicating a better initial bio-availability, particularly obvious for carcass wastes. However, LCFA relative composition was not significantly altered by the pretreatment. Consequently, the enhanced biodegradation should be attributed to an increased initial bio-availability of fatty wastes without any modification of their long chain structure which remained slowly biodegradable. Finally, saponification at 120 °C achieved best performances during anaerobic digestion of slaughterhouse wastes.

1. Introduction

Food-processing industries such as slaughterhouse are facing more stringent European regulation (2002) concerning wastes and by-products. As already reported by Battimelli et al. (2009), this led to a drastic limitation of their management options (reuse, transformation and disposal ways) and incineration became one of the main and sole solutions for the disposal of fatty wastes, resulting in increasing costs. As methanisation leads to the reduction of organic matter content and to the production of a biogas mainly constituted of methane which is a renewable source of energy, it could become a suitable alternative to waste incineration. During anaerobic digestion, lipids are hydrolysed by extracellular lipases, then long-chain fatty acids (LCFAs) and glycerol, a well known easily biodegradable product, are released into the liquid phase. In anaerobic conditions, biomass is producing volatile fatty acids (VFAs) which are then converted into biogas. In addition, as reported by Li et al. (2002), LCFAs are first adsorbed onto the micro-organisms surface, then transferred into the microbial cells and finally degraded via beta-oxidation This last step leads to the production of acetate and hydrogen which are then converted into a biogas mainly composed of CH_4 and CO_2.

Moreover, anaerobic digestion of pure fats is inconvenient because they are insoluble, less dense than water and slowly biodegradable. The limiting step of this process is assumed to be the physical mass transfer from solid to liquid phase, but also the biological step of LCFA degradation. In addition, some long-chain fatty acids are believed to inhibit certain methanogenic micro-organisms, as reported by Rinzema et al. (1994). The batch study carried out by Cirne et al. (2007) showed that the inhibition caused by lipid concentration was linked to their slow hydrolysis rate but that it was also reversible. A way to limit the inhibition is to perform grease co-digestion with other wastes such as waste activated sludge as described by Davidsson et al. (2008) and Luostarinen et al. (2009).

Saponification is the hydrolysis reaction between a lipid and an alkali, resulting in LCFA salt production and glycerol release. Few studies concerning the thermochemical pretreatment of fatty waste prior to anaerobic digestion have been performed. Mouneimne at al. (2003) only studied fatty waste saponification for the enhancement of VFA production.

The conversion of lipids and free LCFA constituting insoluble fat, oil and grease wastes into soluble soaps could improve the contact between the substrate and micro-organisms, thereby enhancing their anaerobic biodegradability. Preliminary batch biodegradations were assessed by Battimelli et al. (2009) on slaughterhouse wastes, both in the solid and suspension form, with and without pretreatment. Wastes pretreated at 60 °C were initially biodegraded more rapidly than raw wastes in batch experiments, but some

* Corresponding author.
E-mail addresses: battimel@supagro.inra.fr (A. Battimelli), torrijos@supagro.inra.fr (M. Torrijos), Rene.Moletta@univ-savoie.fr (R. Moletta), delgenes@supagro.inra.fr (J.P. Delgenès).

0960-8524/$ - see front matter © 2009 Elsevier Ltd. All rights reserved.
doi:10.1016/j.biortech.2009.12.043

Table 1
Slaughterhouse waste characteristics.

		Aeroflotation fats	Flesh fat from cattle carcass
Aspect	–	High load suspension, brown, viscous, contains hair and flesh	White, solid, granular after sieving (5 mm)
Total COD	(g/g)	0.41	1.68
HEM	(%)	15	100
TS; VS	(g/kg)	155; 138	935; 934
Organic fraction	VS/TS	89%	100%

slowly biodegradable compounds remained. A higher temperature of pretreatment will improve the hydrolysis rate and then could enhance the biodegradability of fatty wastes.

Thus, the aim of the present study was to confirm the anaerobic biodegradability of slaughterhouse fatty wastes using fed-batch reactors over a long period of time and also to analyse the impact of high pretreatment temperatures.

2. Methods

2.1. Substrates

Fatty samples were collected in French slaughterhouses and sample characteristics are given in Table 1, describing visual aspect, total Chemical Oxygen Demand (COD), Hexane Extractible Matter (HEM), Total Solids (TS), Volatile Solids (VS) and the relative organic fraction. Prior to storage at −20 °C, samples were homogenised. A light mixing was performed on aeroflotation waste, and flesh fats were sieved at 5 mm, which led to the removal of the fat-containing membranes. Ethanol was used for biomass activity and co-substrate test at 95% v/v concentration.

2.2. Pretreatment conditions

Saponification pretreatment was performed at 60, 120 and 150 °C for 3 h with mixing at 250 rpm. The alkali used for soap production was sodium hydroxide at 50 wt% concentration. The alkali dose was adjusted so that it would be equivalent to 0.156 g NaOH/g VS, determined in order to have an excess amount of OH^-. Hydroxyl amount corresponded to the stoichiometric amount needed for a theoretical waste constituted of solely palmitic acid (one of the lightest LCFA found in slaughterhouse fatty wastes). At the end of soap production, pH was measured in order to check the presence of alkali in excess.

2.3. Anaerobic digestion

Experiments were performed using eight 5-L glass reactors. Mesophilic anaerobic sludge was sampled from pilot reactors treating winery effluent. Biodegradation was carried out under constant stirring and mesophilic conditions were maintained at 35 °C using water jacket. Biogas production was continuously measured using a mass flowmeter. Gas flowrate and pH data were acquired every 2 min by a computer and all biogas volumes were calculated under standard conditions of temperature and pressure (STP).

Three successive steps were followed for biodegradation tests:

- initial sludge starvation for removal of residual biodegradable COD,
- ethanol injections (10 mL) for determination of sludge activity for an easily biodegradable compound,
- increasing successive fatty waste additions (from 1 to 5.3 g COD/L) for determination of biodegradability and maximum organic load. After a 4-h settlement period, the same volume of supernatant that was added at the beginning of the run was withdrawn from the bioreactor. This step, besides maintaining a constant the volume in the reactor, avoided biomass washout.

Biogas potential, expressed as mL/g VS, was determined for both types of raw waste and for each pretreated waste.

Theoretical biogas potential was calculated using the equation given by Buswell and Neave (1930) as reported in Angelidaki and Sanders (2004).

$$C_nH_aO_b + \left(n - \frac{a}{4} - \frac{b}{2}\right)H_2O \rightarrow \left(\frac{n}{2} + \frac{a}{8} - \frac{b}{4}\right)CH_4 + \left(\frac{n}{2} - \frac{a}{8} + \frac{b}{4}\right)CO_2. \quad (1)$$

To solve this equation, it is required to know the organic matter composition, while assuming that the organic matter is completely converted into biogas. The ratio between experimental and theoretical biogas production results in the equivalent degradation of fatty wastes. Knowing the fatty waste concentration (g COD/g VSS), the reactor volume, the duration of biodegradation and the experimental biogas production, the equivalent degraded load can be expressed as g VSS/(L.d).

2.4. Analysis

Fatty wastes were conditioned prior to analysis following the protocol of Bridoux et al. (1994). Analytical measurements, i.e. COD, TS, VS, pH and alkalinity, followed the standard methods from American Public Health Association (1992). Soluble fraction was obtained after centrifugation (15,000 rpm, 15 min, 5 °C) and filtration at 0.45 μm. Hexane Extractable Matter (HEM) measurements were performed in accordance with the method described by Canler et al. (2001), three consecutive extractions were required to get a steady value. Fatty waste hydrolysis rate was estimated by pH measurements.

LCFA chromatographic measurements were performed using GC-FID. The column used was a CP-Select CB for FAME fused silica WCOT (VARIAN), 50 m length, 0.25 mm internal diameter, film thick 0.25 μm. Oven temperature was set to 185 °C for 40 min, then 15 °C/min until 250 °C and 250 °C for 10.7 min. Injection was performed by split 1:100, 1 μL, at 250 °C for 55 min. Detection was done by FID at 250 °C and the gas phase consisted of helium at 1.2 mL/min flow rate. Samples were prepared according to the following procedure: initial Ter Butyl Methyl Ether (TBME) solubilisation after sulphuric acid hydrolysis; filtration (0.45 μm) of TBME extracts; and extract transesterification using 0.5 M Tri Methyl Sulfonium Hydroxide (TMSH) in ethanol at the proportion of 160 μL extract for 40 μL TMSH.

3. Results and discussion

3.1. Theoretical biogas potentials

LCFA composition. The aim of the chromatographic characterisation of lipids was first to determine the waste composition in order