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Biogas production from thermophilic anaerobic digestion of kraft pulp mill sludge

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ABSTRACT

Primary and secondary sludges originating from kraft pulp mill effluent treatment plants represent an environmental challenge. Their final disposal mainly includes landfill or burning in the mill's biomass boiler. Seeking energy self-sufficiency and better environmental outcomes, the pulp industry is looking to develop new waste management strategies. Biogas production is a millennial technology already applied in many fields, but still behind in terms of pulp and paper mill sludges. Due to the high moisture content of sludge, anaerobic digestion shows great potential. This paper aimed to study biogas production using kraft pulp mill primary and secondary sludges under thermophilic conditions, coupling laboratory experiments with mathematical modeling. Methane production was estimated through the Biochemical Methane Potential (BMP). The Process Simulation Model developed by Rajendran et al. [1] was calibrated for kraft pulp mill sludge based on the BMP results. Cumulative methane production from the secondary sludge reached 46.9 NmL CH_4/g VS in 30 days. In addition, the Rajendran et al. [1] model was shown to be suitable for simulating the methane yield from bleached kraft pulp mill secondary sludge after minor adjustments. The energy balance showed that the anaerobic digestion process under thermophilic condition for kraft pulp mill secondary sludge still is not feasible on large scale, since the heat produced by biogas was smaller than the heat demanded for heating the reactors.

1. Introduction

Brazil is the second largest manufacturer of bleached kraft pulp in the world, with almost 15 Mt produced in 2015 [2]. Bleached kraft pulping is the most utilized production process worldwide, generating effluent with high organic content. The most applied effluent treatment process is the activated sludge treatment system, which generates about 14–140 kg of sludge per ton of pulp [3]. Currently, several mills dewater and dispose of their sludge in landfills; however, sludge dewatering and final disposal may comprise more than half of the total operating costs of effluent treatment [4]. Therefore, sludge handling represents an important issue that must be tackled by the industry.

The kraft pulping process involves high-energy demands. Although the mill generates part of its own energy by burning the high organic load black liquor and wooden biomass, it still relies on additional electricity and fossil fuel sources [5] and [6]. Due to an energy price increase, the pulp industry has been driven to

Abbreviations: ADM1, Anaerobic Digestion Model No 1; ADt, Air-Dried ton; ANOVA, Analysis of Variance; BMP, Biochemical Methane Potential; COD, Chemical Oxygen Demand; CSTR, Continuously Stirred Tank Reactor; DHFORM, Standard Heat of Formation (ideal gas at 25 °C); FF, 2-Furfuraldehyde; F/I, Food/Inoculum ratio; GC, Gas Chromatograph; HAc, Acetic acid; HMF, 5-Hydroxymethyl-2-furfuraldehyde; HPLC, High Performance Liquid Chromatography; HRT, Hydraulic Retention Time; IWA, International Water Association; LCFA, Long-Chain Fatty Acids; MIX, Mixture between PS and SS in a 2.5:1 ratio, in TS basis; NmL, Normal milliliter (0 °C and 1 atm); P, Cumulative methane yield; P_0, Maximum methane yield; PS, Primary Sludge; PSM, Process Simulation Model; R_m, Maximum methane production rate; SS, Secondary Sludge; t, incubation time; TCD, Thermal Conductivity Detector; TMP, Theoretical Methane Potential; TS, Total Solids; UASB, Upflow Anaerobic Sludge Blanket); VS, Volatile Solids; w.b, wet basis; λ, lag phase.

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optimize its energy efficiency and self-sufficiency. One attractive industrial opportunity is to produce energy from sludge. Recent studies have proven the technical feasibility of digesting pulp mill sludges for biogas production [7–11]. Nevertheless, little attention has been given to this process at the industrial level [9].

Modeling has been applied to overcome limitations in predicting biogas production in large scale anaerobic digestion plants. Mathematical models of anaerobic digestion began to be developed over 50 years ago; nevertheless, they are still not well assimilated by engineers or operators. This might be due to (i) a wide variety of anaerobic digestion models, and (ii) their specificity for a determined feedstock [12]. In addition, the development of modeling is further hampered by complex microorganism metabolism [13].

In 2002, the first comprehensive anaerobic digestion model, ADM1, was developed by the IWA Anaerobic Digestion Modeling Task Group. The ADM1 considers the disintegration and hydrolysis, acidogenesis, acetogenesis and methanogenesis steps. Extracellular biochemical reactions follow the first order rate kinetics, and intra-cellular biochemical reactions follow Monod's equation. The model also considers inhibition by pH, hydrogen, free ammonia and growth limitation, when inorganic nitrogen is limited [12].

ADM1 brought important contributions to anaerobic digestion, although it has limitations and is difficult to use [14]. Rajendran et al. [1] developed a process simulation model (PSM), using a simpler interface, that can be run in the software Aspen Plus® (Advanced System for Process Engineering). The PSM was based on previous anaerobic digestion models, such as the ADM1 [12], Angelidaki et al. [15], Angelidaki et al. [16], and Serrano [17].

The PSM uses the NRTL (Non-Random Two-Liquid Model) as the property method and considers two reactors: (a) a stoichiometry reactor, where the hydrolysis reactions occur; and (b) a continuously stirred tank reactor (CSTR), where the acidogenesis, acetogenesis and methanogenesis take place [1]. The input parameters include mass flow, hydraulic retention time, and substrate composition [1]. The reactor's volume is calculated based on interactions and an initial value is estimated by the user. The model calculates the final volume based on the Broyden mass balance convergence.

The main objective of this study was to estimate the potential energy production from kraft pulp mill primary and secondary sludges and their mixture using the software Aspen Plus® based on Rajendran et al. [1] model. The specific objectives were to (i) adjust the model using the results from the kraft pulp mill anaerobic digestion batch assays; (ii) estimate the energy recovery potential from biogas; (iii) determine the best sludge composition; and (iv) verify the influence of nitrogen addition in the methane yield.

2. Material and methods

The research was carried out in four phases. Phase 1 consisted of characterizing the substrates (primary and secondary sludges); Phase 2 consisted of carrying out anaerobic digestion batch assays; Phase 3 aimed to adjust the Rajendran et al. anaerobic digestion model [1] using the results from Phase 2. Phase 4 comprised of a simplified energy balance of the anaerobic digestion process. Phase 5 included sensitivity analyses to estimate the methane production from different sludge compositions and nitrogen content.

2.1. Material sampling

Primary sludge (PS) and secondary sludge (SS) were sampled from the effluent treatment plant of a bleached kraft pulp mill, located in Brazil. The mill uses eucalyptus as raw material for pulp production (about 1 Mt of air-dried pulp a year). The effluent treatment process consists of a primary clarifier followed by a conventional activated sludge. Approximately 40 kg (dry basis) of primary sludge and 15 kg (dry basis) of bio-sludge are generated per air-dried ton of pulp (ADt). The primary sludge was sampled after a screw-press and the secondary bio-sludge after a belt-press dewatering process. The samples were stored in a freezer, with a temperature below 0 °C until use.

The inoculum was collected from a mesophilic UASB (upflow anaerobic sludge blanket) reactor, located at the Arrudas Wastewater Treatment Facility, in Brazil. Manure was collected at the Animal Science Department of the Universidade Federal de Vicosa, Brazil and used as nitrogen source in the batch assays.

2.2. Material characterization

Primary and secondary sludges were characterized for total solids (TS), volatile solids (VS), and oil/grease according to APHA [18]; ashes were determined according to TAPPI [19]; pH according to EPA [20]; cellulose, hemicellulose, lignin as described by Baêta et al. [21]; protein according to Kyllönen et al. [22]; chemical oxygen demand (COD) according to Ferreira [23]; elemental composition (C, N, H, S, O) according to the analyst's manual of TruSpec Micro CHN, TruSpec O and TruSpec S (LECO). The theoretical methane potential (TMP) of the PS and SS was calculated using the Buswell equation described by Pellera and Gidarakos [24]. Inocula was characterized for TS, VS, ash, pH and elemental composition according to the methods previously described.

For cellulose, hemicellulose, lignin, oil and grease and protein characterization, sludges were first dried in an oven at 65 °C, and sieved (40–60 mesh). Oil and grease followed the procedures described by APHA [18], method 5520 D, but without prior acidification, since the objective was to determine the raw sludge characterization without any pre-treatment. Protein determination was based on the total nitrogen content of the sample, considering a factor of 6.25 [22]. Although the total nitrogen expresses amines, nucleic acids and non-protein amino acids, among others, as well as protein compounds, the proteins have a constant nitrogen percentage. In addition, pulp and paper mill wastewaters have very low ammonium content [8].

2.3. BMP assays

The Biochemical Methane Potential (BMP) assays were carried out in bottles of 275 mL in triplicate. The inoculum was prepared by mixing 50% of UASB enriched with macro- and micronutrients and 50% of manure, in VS basis. The inoculum was incubated at 55 °C three days prior to the assays for acclimatization and reduction of endogenous methane production. A sample of the acclimatized inoculum was incubated at 35 °C to verify if there was still methane production in the mesophilic state, even after the pre-incubation period in a thermophilic state.

Three substrates were tested: primary sludge, secondary sludge, and the mixture between them in a 2.5:1 ratio (TS basis). This ratio was chosen based on the sludge generation of a typical bleached kraft pulp mill. The food to inoculum (F/I) ratio was 2 g $VS_{substrate}$/g $VS_{inoculum}$. Since substrate and inoculum pHs were already nearly neutral, no pH adjustment was necessary. Assays containing only inoculum were used as blanks. Methane produced from the blank assays was subtracted from each sample assay. The prepared BMP assays were closed with butyl rubber stopper and aluminum seal

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