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Research paper

Evaluation of the correlations between biodegradability of lignocellulosic feedstocks in anaerobic digestion process and their biochemical characteristics

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ABSTRACT

Biochemical composition and reactivity are key factors controlling the biodegradability of lignocellulosic residues. In the present study, 14 lignocellulosic substrates including 6 agricultural and 8 forest residues were analyzed for 9 biochemical characteristics, including BioMethane Potential (BMP), Biological Oxygen Demand (BOD), Enzymatic Cellulose Degradation tests (ECD), Van Soest and NREL fractionation methods. The data obtained were exploited by principal component analysis (PCA) and other statistical methods to investigate the possible correlations between the parameters. The study showed that the contents in particular lignin or in non-extractible residues (RES) were the characteristics which influenced most the anaerobic biodegradability (BMP), while the influence of the soluble fraction was quite low. BMP was well correlated with the ratio of the contents in non-lignin over lignin fractions and the cellulose to lignin ratio. Regarding agricultural residues, BMP was better correlated with lignin content than with RES content. Agricultural and forest residues exhibited distinct characteristics of aerobic and anaerobic biodegradability. Good correlation was observed between ECD and lignin content. Finally, it was also observed that Van Soest's and NREL methods did not provide the same results in terms of biochemical composition.

1. Introduction

Energy recovery from lignocellulosic biomass is one of the major options to reduce greenhouse gases emissions and the depletion of fossil fuels without causing direct competition with food products. Several processes are possible to meet this objective. Microbial Anaerobic Digestion (AD) into methane is one of the most attractive approaches as compared to typical pathways to biodiesel or ethanol. It is known that are in AD processes biopolymers are converted into simple compounds and finally into methane and carbon dioxide through the activity of the different types of anaerobic micro-organisms. To date, AD has essentially been developed for the treatment of animal manure, municipal solid waste, sewage sludge and energy crops. Yet, large amounts of lignocellulosic biomass such as crop residues and forest residues remain available in Europe and other countries as a potential resource to increase the production of renewable fuels [1,2,3].

Due to the diversity of vegetable species and growth conditions however, the biochemical composition of biomass substrates is quite variable both qualitatively and quantitatively [4]. Lignocellulosic biomass is mainly composed of cellulose, hemicelluloses and lignin, with cellulose being the most abundant natural carbohydrate polymer. The variability in biochemical composition and structural characteristics, along with other parameters, make quite variable and not easily predictable the potential production of methane by biological anaerobic digestion of these substrates. Therefore, detailed analyses of feedstocks are required to estimate the anaerobic biodegradability of lignocellulosic biomass. Several methods of chemical characterization are available, such as elemental analysis biochemical fiber analysis, enzymatic hydrolyses and experimental evaluations of biodegradability. Several studies have already investigated for various biomasses the relationships between biodegradability and some biochemical characteristics of the substrates, including proteins, lipids, carbohydrates and fibers contents [5–15]. Methane production from lignocellulosic biomass in AD process is however strongly affected by the structure of the lignocellulosic complex where the relatively recalcitrant lignin limits the accessibility to micro-

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Abbreviation

ADF	acid detergent fiber
ADL	acid detergent lignin
BD_{Aero}	bioconversion yield under aerobic condition
BD_{Anae}	bioconversion yield under anaerobic condition
BOD_{28}	biological oxygen demand as mass of oxygen consumed by VS, in 28 days of incubation at 30 °C (g kg^{-1})
BMP_{60}	biochemical methane production by VS, in 60 days of incubation at 35 °C (L kg^{-1})
CELL	cellulose content from Van Soest sequential extraction by VS (g kg^{-1})
Cellulose	cellulose content from NREL extraction procedure by VS (g kg^{-1})
COD_{Tot}	total chemical oxygen demand by TS (g kg^{-1})
COD_{Sol}	chemical oxygen demand by VS in leachate collected from leaching test at a L/S ratio of 10 (g kg^{-1})
ECD	enzymatic cellulose digestibility by VS (g kg^{-1})
EThOH	ethanol extractable fraction from NREL extraction procedure by VS (g kg^{-1})
HEM	hemicellulose content from Van Soest sequential extractions by VS (g kg^{-1})
Hemicellulose	hemicellulose content from NREL extraction procedure by VS (g kg^{-1})
Lignin	lignin content from NREL extraction procedure by VS (g kg^{-1})
NDF	neutral detergent fiber
RES	residual content from Van Soest sequential extractions by VS (g kg^{-1})
SOC	soluble organic carbon by VS (g kg^{-1})
SOL	soluble fraction from Van Soest sequential extractions by VS (g kg^{-1})
TOC	total organic carbon by TS (g kg^{-1})
TS	total solid
VS	volatile solid (g kg^{-1})
WAT	water extractable fraction from NREL extraction procedure by VS (g kg^{-1})

organisms of hemicelluloses and cellulose which are intrinsically more easily biodegradable [16]. Fewer studies have investigated the effects of structural features such as the crystallinity of cellulose [13–15]. All of them have confirmed the negative impact of lignin content on methane production by anaerobic digestion. A recently published study explored the prediction of methane yield in mesophilic solid-state anaerobic digestion of lignocellulosic feedstocks using multiple linear regression and artificial neural network statistical models [15]. The authors underlined the effect of feedstock types on anaerobic digestibility, and divided the substrates into "herbaceous biomass" showing low lignin content and high digestibility and "woody biomass" with high lignin content and low methane yield. A previous study [1] reported similar observations with "non-herbaceous biomass" was characterized by high lignin content and high concentration of crystalline cellulose. However, due to other parameters, lignin content alone was not sufficient to estimate methane potential, in particular for non-herbaceous biomass.

The present study investigated the anaerobic biodegradability of a variety of agriculture and forest by-products and their respective global characteristics (organic content including volatile solid, chemical oxygen demand, soluble organic content), and biochemical characteristics. Two types of lignocellulosic feedstocks were selected, namely crop residues (wheat straws, corn stover and corn stem, sugarcane bagasses), and wood residues (softwood branches, hardwood waste from a composting plant, hazel tree and acacia branches). Several alternative methods were used to quantify organic content, characterize organic fraction, and evaluate biodegradability. Compositional characteristics measured on the substrates studied were gathered and their correlation with biomethane potential investigated using statistical methods.

2. Materials and methods

2.1. Collection and preparation of biomass substrates

Fourteen lignocellulosic biomass substrates were selected to cover a wide range of biochemical profiles. They were collected from agricultural sites, forests and green waste composting plants as indicated in Table 1.

Samples of about 10 kg of each substrate were collected, mixed and transported to the laboratory where they were dried at 60 °C for 3 days, shredded three times with a low-speed shredder Blik® monorotor M420, and sieved to 10 mm to obtain homogenous coarse powders. Each powdered sample was mixed and further grinded using a cutting mill Retsch® SM 200 and sieved to 4 mm. The operation was repeated and the last sieving was done to 1 mm to obtain fine powders which were stored at 2 °C in closed glass flasks until they were analyzed. All analyses were performed in triplicates for each sample.

2.2. Global analytical parameters

Global parameters, including TS, VS, COD, TOC, and SOC, were used to characterize the samples in a general manner with respect to overall groups of components or properties as listed in Table 2.

2.2.1. Organic matter content

Total solid (TS) and volatile solid (VS) were quantified according to standard methods [17,18]. Total carbon content (TC) was determined using OI Analytical® – 1020 A TOC analyzer following the standard procedure ISO 10694 [19] based on catalytic oxidation of the samples with oxygen at 950 °C followed by infrared analysis of the CO_2 produced. Total organic carbon content TOC was measured in the same manner after the sample was acidified with 150 g L^{-1} solution of ortho-phosphoric acid (H_3PO_4) in order to remove inorganic carbon. The chemical oxygen demand (COD) was measured by oxidizing the powdered samples with a solution of potassium dichromate and sulfuric acid for 2 h at a temperature of 135 °C. Dichromate ions were reduced to Cr^{3+} ions which were analyzed by spectrophotometry at 585 nm.

2.2.2. Water soluble organic fraction

To extract water soluble components from the biomass substrates, aqueous suspensions of 10 g of 1 mm powdered samples in 100 mL of deionized water were mixed for 3 h at room temperature in a rotary tumbler set at 0.17 Hz, according to the European standard leaching procedure [20]. For each sample, the extraction step was triplicated. The leachates (aqueous extracts) were filtered through a 0.45 μm pore size membrane and the solutions subsequently analyzed for soluble organic carbon (SOC) and chemical oxygen demand (COD) following standard methods [21,22].