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The effect of process parameters during the thermal-expansionary pretreatment of wheat straw on hydrolysate quality and on biogas yield

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A B S T R A C T

This paper was dedicated to evaluate the impact of thermal-expansionary pretreatment on the quality of hydrolysate and on biogas yield. An aqueous suspension containing 5% wt. of wheat straw was treated under process temperature 170–200 °C with residence time 0–60 min. It has been proven that the organic biomass loss of straw, the rate of disruptions in its microstructure, COD, glucose and acetic acid yields in the liquid phase of hydrolysate increased with an increasing process temperature and residence time, while acidity decreased. This technology has also significantly increased methane yield. A maximum increase of 41% was reached at process temperature 170 °C and residence time 20 min. Nevertheless, based on energy balance of the treatment, it was determined, that heat of regeneration is lower than heat needed to reach process temperature. An addition heat source must be therefore installed in the technology.

1. Introduction

Lignocellulosic biomass, which can be found in such materials such as agricultural and forestry waste, municipal solid waste, waste paper, wood and herbaceous energy crops, represents a potential source for biofuels production and for biogas especially. Its annual production has been estimated at 1×10^{13} tons worldwide [1]. The advantages of exploiting lignocellulosics are that they are available in considerable quantity, at low-cost [2] and also do not compete with plants grown for food, and therefore do not cause upward pressure on food prices [3]. Lignocellulosic biomass is generally composed of cellulose, hemicellulose, lignin and a wide variety of organic and inorganic compounds. Both cellulosic and hemicellulosic fractions are transformed into monosaccharides that can be subsequently fermented into biogas. However, the inherent properties caused by lignocellulosic composite structure make them resistant against enzymatic attack. Untreated lignocellulosic biomass therefore gives very low and commercially unattractive biodegradation yields ranging between 10 and 30 % [4]. Thus, the pretreatment of biomass is an essential step in order to increase cellulose and hemicellulose accessibility and hydrolysis efficacy. Various industrial pretreatment technologies have been developed including dilute acid, ammonia, ethanol solvolysis, ammonia fibre explosion or sulphite pretreatment, etc. [4,5]. The pretreatment of biomass by these technologies is based on a chemical dissolution of the lignocellulosic matrix. However, both inhibitory compounds for a microbial system are formed [6], and hydrolysate must be chemically stabilized owing to anaerobic conditions [7]. Generally concluded, any chemical treatment procedures of lignocellulosics are highly demanding not only in terms of investment costs (high-pressure apparatus, corrosion resistant materials, the need to install additional technologies for the removal of by-products), but also in terms of operating costs [5,8].

The hydrothermal processing of lignocellulosic biomass is an environmentally friendlier technology in comparison with the chemical treatments mentioned above. The boiling of biomass in water maintained by pressure in a liquid state has been used for several decades in the paper industry and in technologies where residues from the food industry, slaughterhouses or biodegradable municipal wastes have been processed. The carbohydrates present are continuously degraded and dissolved during pretreatment and thereby removed from the fibres. It is possible to reach a conversion of organic volatile solids of up to 60% wt. from a lignocellulosic biomass to a liquid [9] and hemicellulose removal of up to 80% wt [1]. Every waste undergoes a hydrolysis reaction in the presence of

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hydronium ions, which are generated by water auto-ionization. The heterocyclic bonds of hemicellulose are the most susceptible ones leading to both the generation of oligosaccharides and the splitting of acetyl groups from the hemicellulosic fraction [10]. The split acetyl groups form acids, which are assumed to catalyse further during the hydrolysis of hemicellulose. However, at a process temperature higher than 220 °C, the products are almost phenolic compounds, having primarily a toxic effect on methanogens [1]. Small amounts of cellulose are also solubilized as oligomers and free glucose, and some are degraded into furfural [11]. Lignin is partially depolymerized and solubilized as well, but complete delignification is not possible using hot water alone, because of the condensation of the soluble components originated from lignin [12]. The major advantages of thermal treatment [5,13,14] are that no chemicals are added, no sludge is generated, no inhibitors are formed and reactor construction is low-cost because of the low-corrosion potential. On the other hand, the major disadvantage is the high heat demanded by the high process temperature. Pérez et al. [15] reported that thermal pretreatment has a great impact on the overall process cost, accounting for up to 33% of total cost.

The effectiveness of thermal pretreatment particularly depends on the composition and concentration of the lignocellulosic biomass in aqueous suspension, on batch acidity, on process temperature and also on residence time. Biomass concentration, referred to as the liquid-to-solid ratio [16], ranges between 2 and 100 ($\mathrm{wt}\cdot\mathrm{wt}^{-1}$). Nevertheless, Jacobsen and Wyman [17] recommend a ratio lower than 10 to avoid the saccharides' degradation into inhibitory compounds. Moreover, Hendriks and Zeeman [4] have reviewed that batch acidity must also be kept within a range of 4–7 to avoid the forming of degradable products. The process temperature typically ranges between 150 °C and 230 °C with a dependence on the biomass composition, its amount in liquid and also on residence time [18]. The residence time varies from several seconds to several hours with the dependence on process temperature, on biomass composition and also on its amount in liquid [16]. Hendriks and Zeeman [4] have mentioned that a short residence time, i.e. the order of seconds, requires a high process temperature, i.e. over 220 °C, and that a long residence time, i.e. the order of minutes, requires a low process temperature, i.e. lower than 180 °C.

A different hydrothermal pretreatment is steam explosion. During this treatment lignocellulosic biomass is put into a reactor, where high temperature steam up to 240 °C and pressure is applied for a few minutes [4]. When residence time is over, the batch is quickly depressurized. Liquid, which is sucked into the biomass pores, changes its phase to vapour and the associated volumetric change causes a high disruption of the lignocellulosic matrix. The effectiveness of a steam explosion particularly depends on particle size, its composition and humidity, on steam temperature and on residence time [1]. Taherzadeh and Karimi [5] have reviewed that steam temperature typically ranges between 160 and 260 °C with residence time from several seconds, i.e. 3–5 s, to several minutes, i.e. 10–20 min. The equivalent hemicellulose removal can be reached both at a high steam temperature with a short residence time (270 °C, 1 min) and at a low temperature with a long residence time (190 °C, 10 min). Nevertheless, Hendriks and Zeeman [4] have concluded that the treatment at a low temperature with a long residence time is more favourable.

Thermal-expansionary pretreatment is a novel global trend in the processing of lignocellulosic biomass in industrial biofuel technologies [19–21]. This two-stage process combines the boiling of an aqueous biomass suspension under high pressure followed by rapid decompression. However, no information about the effectiveness of this pretreatment is available. This paper has been therefore dedicated to investigate the mutual thermal and expansionary effects on the quality of hydrolysate, on the increase in biogas yield and also to simply evaluate electrical and heat balances of the process.

2. Methods

2.1. Raw material

Untreated wheat straw of approximately 200 mm length was used as the model material in experiments. The straw was cut by a combine in the field, collected and stored indoors in containers at an ambient temperature. The total solid content (TS) of wheat straw was determined to be 92% wt. and the volatile solid content (VS) was 86% wt. Total solid content was determined by drying of 5 reference samples in a KBC-25W oven overnight at 105 °C, whereas volatile solid content was investigated by the burning of dried samples in a LE 09/11 furnace at 550 °C until a constant weight was reached. The weight of the material was measured by an SDC31 analytic balance. Using the thermo-gravimetric method [22], cellulose content w_C of 34.1% wt. TS, hemicellulose content w_H of 37.0% wt. TS, lignin content w_L, of 22.8% wt. TS and ash content w_{ANORG} of 6.1% wt. TS were found in the wheat straw. The tested straw was also analysed from the point of view of elementary composition by Elementar Vario EL III. The amounts of carbon c_C being 39.2% wt. TS, of hydrogen c_H being 5.2% wt. TS and oxygen c_O being 41.6% wt. TS were reached.

2.2. Thermal-expansionary pretreatment

The laboratory thermal-expansionary pretreatment technology was used in a batch mode [23], see Fig. 1. The laboratory thermal-expansionary treatment technology is composed of three main parts: the hydrolyser (1), the expansion vessel (2) and the ball valve (*V1*), which is equipped with a pneumatic actuator. The hydrolyser (1) is a batch double-jacketed pressure vessel, which is able to treat a biomass up to 8 L in volume under maximum processing temperature of 200 °C that corresponds with saturated vapour pressure of 1.6 MPa. The substrate is indirectly heated by oil (O) circulating in a double jacket. An electrical spiral with 12 kW of power is used for heating the oil. The time to reach the maximum temperature of 200 °C in the hydrolyser is approximately 40–50 min, depending on composition of the batch. The hydrolyser is not equipped with a mixing system. Batch is therefore mixed only by mass transfer, caused by differences in substrate densities. Because of this fact, there is a non-homogenous temperature distribution, and there is no possibility to directly measure batch temperature. However, using this batch system, it is supposed that the temperature in the hydrolyser corresponds to the temperature of steam at saturation pressure. This means that the temperature of the gaseous phase equals the temperature of the liquid phase. Thus, the pressure in the hydrolyser is directly measured, and the substrate temperature is calculated using the Antoine equation. The expansion vessel (*2*) is an apparatus with an internal atmospheric pressure regulated by its opening to the atmosphere, and it is used for storing the expanded substrate. The dump valve (*V2*) is used to discharge the hydrolysate. This vessel is also equipped with water cooling (*W*) to allow faster vapour condensation after a batch decompression. Thirdly, the ball valve (*V1*), keeps the pressure space in the hydrolyser separate from the atmospheric space in the expansion vessel. Biomass processing by thermal-expansionary technology is based on this principle. At the beginning, the hydrolyser is compacted under atmospheric pressure with a substrate. Then the substrate is indirectly heated. When the predetermined process temperature T_P is reached (in heating time t_H), it is kept constant for a predetermined residence time t_R. As soon as the residence time is