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The effect of thermal-expansory hydrolysis on wheat straw treatment

Introduction

Present-day operating biogas plants are based on the treatment of lignocellulosic biomass which is included in such materials as agriculture and forestry wastes, municipal solid waste, waste paper, wood and herbaceous energy crops. These lignocellulosic substrates are generally composed of cellulose, hemicellulose, lignin and wide variety of organic and inorganic compounds. Both cellulosic and hemicellulosic fractions are converted to monosaccharides that can be subsequently fermented to biogas. However, the inherent properties caused by composite structure make them resistant against enzymatic attack, see Fig. 1. This structure can be easily explained using similarity with reinforced concrete pillar with the cellulose fibers being the metal rods and lignin the matrix cement. The biodegradation of native untreated lignocelluloses is very slow and does not exceed 20% [Pandey, 2009]. Hence, treatment of biomass is an essential step in order to increase cellulose and hemicellulose accessibility and hydrolysis effectivity.

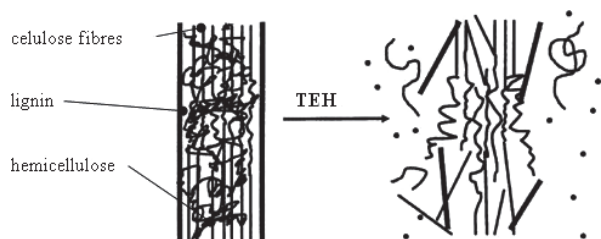


Fig. 1. The effect of thermal-expansory hydrolysis. [Mosier et al., 2005]

Both agriculture and municipal biogas plants especially are currently endeavoured to implement a new physical pre-treatment technology called thermal-expansory hydrolysis (TEH), liquid hot water (LHW) or hot compress water (HCW) hydrolysis as well. During this treatment, lignocellulosic biomass is heated in water maintained by pressure in liquid state. Over the temperature 160°C passive lignocellulosic structure begins to be decomposed which means that nutrients are more accessible for enzymatic attack. The major advantages are no addition of chemicals, no formation of inhibitors and low-cost reactor construction because of low-corrosion potential. On the other hand, the major disadvantage is heat-energy demand caused by high processing temperature [Taherzadeh and Karimi, 2008]. The thermal-expansory hydrolysis has a great impact on overall process cost accounting up to 33% of total cost [Pérez et al., 2007]. Generally, the effectiveness of TEH depends on composition and pH of substrate, processing temperature and residence time [Hendriks and Zeeman, 2009].

Experimental equipment

The lab TEH in batch mode can be used for treatment of various biomass. It is composed of three main parts namely hydrolyser, expansion vessel and ball valve equipped with pneumatic actuator, see Fig. 2. The hydrolyser is double-jacketed pressure vessel which allows treatment of biomass with volume up to 8 litres at maximum processing temperature 200°C and pressure 1.6 MPa. Substrate is indirectly heated by oil circulating in double jacket. Just for information, the electrical spiral with power 12 kW is used for oil heating. The expansion vessel is an apparatus where atmospheric pressure is maintained inside and it is used for storage of expanded substrate. The third main part namely ball valve keeps pressure space in hydrolyser separate from atmospheric space in expansion vessel.

The processing of biomass by batch TEH is based on this principle. The hydrolyser is stuffed with a suspension containing lignocelluloses

and hot water. Substrate is heated and afterwards, when a processing temperature is reached, it is kept constant for a processing time. As follows, the ball valve is rapidly opened and substrate immediately expands to expansion vessel. Two products are formed during expansion namely vapour and hydrolyzate. After vapour condensation, expanded material is removed from the expansion vessel and fermentation tests are carried out.

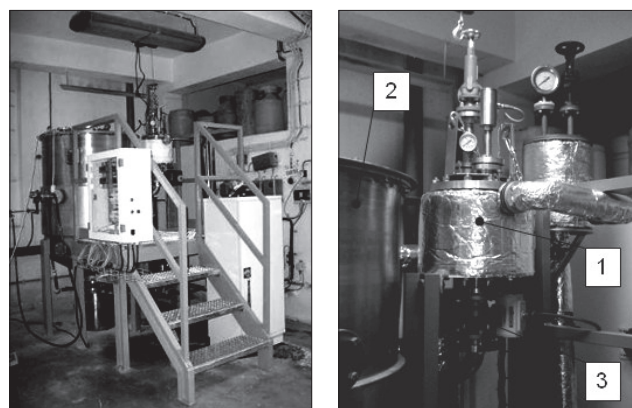


Fig. 2. The apparatus for thermal-expansion hydrolysis. 1 – hydrolyser, 2 – expansion vessel, 3 – ball valve

Experiments

The objectives of this paper were to determine the impact of thermal-expansory pretreatment on wheat straw and to evaluate the effect of expansion on particle size distribution.

General effect of expansion on particle size distribution

Because of resistance to temperature up to 250°C [Kučerová, 2012], purge microcrystalline cellulose was used as a model material in order to determine the impact of expansion on particle size distribution.

The suspension containing 10% of cellulose by weight was treated in hydrolyser at processing temperature 200°C and residence time 5 minutes. The particle size distribution before and after expansion as shown in Fig. 3 was investigated by *FRICTSCH analysette 22 COMPACT*. In detail, the measured values of mode for particle size distribution before and after expansion were 87.433 µm and 25.753 µm. Therefore, the decrease in particle size caused entirely by expansion was 3.5 times. Thus this experiment bears out supposition that not only the effect of temperature causes decrease in particle size. The expansion of material and its implementation in real technologies was found out to be as an intensive step for reduction biomass in size.

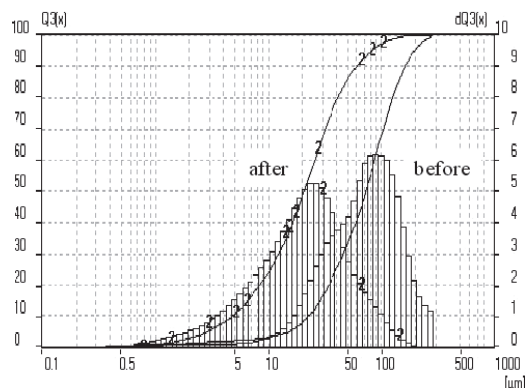


Fig. 3. Cellulose size distribution before and after expansion

Wheat straw treatment

Untreated wheat straw with moisture content 7% was used in experiments. This straw was only cut into 1–6 cm pieces on field and stored in containers at ambient temperature. Just for information about composition, a typical wheat straw contains cellulose in range 33–50% of dry matter *DM*, hemicellulose 24–35.5% *DM* and lignin in range 8.9–17.3% *DM* [Garrote et al., 1999].

As for experimental set up, the suspension containing 5% by weight of straw was used during experiments. At first, the straw was fed into a soaking reactor where it was soaked at elevated temperature 60°C for 60 minutes with the aim to reach good straw maceration. Afterwards this substrate with total volume of 8 litres was filled into hydrolyser. Its initial *pH* value was 7.14±0.05 and the glucose yield 0.14±0.02 g·l⁻¹. The substrate was treated under processing temperature and residence time in ranges 170–200°C and 0–60 minutes. The effectiveness of treatment was evaluated by initial and final changes of *pH* (InoLab *pH*730), glucose yield (EasyGluco IGM-0002A) and structure (visual method).

Fig. 4 and Fig. 5 depict the dependencies of final glucose yield and *pH* on processing temperature and residence time. The final glucose yield grows up with increasing temperature and time, whereas the final *pH* value decreases both with increase in temperature and time. The maximum values of final glucose yield 3.11±0.20 g·l⁻¹ and *pH* 4.10±0.05 were got at processing parameters 200°C and 60 minutes. Both these changes are caused by structural modifications in substrate. Generally known, waste undergoes hydrolysis reaction in presence of hydronium ions which are generated by water auto-ionization. The heterocyclic bonds of hemicellulose are the most susceptible ones leading to both generation of oligosaccharides and splitting of acetyl groups from hemicellulosic fraction [Garrote G., 1999]. Therefore, the changes in final glucose yield are primarily caused by degradation of hemicellulose to oligomers and monomers especially. Whereas decrease of *pH* is primarily caused by reaction of ionize water with split acetyl groups.

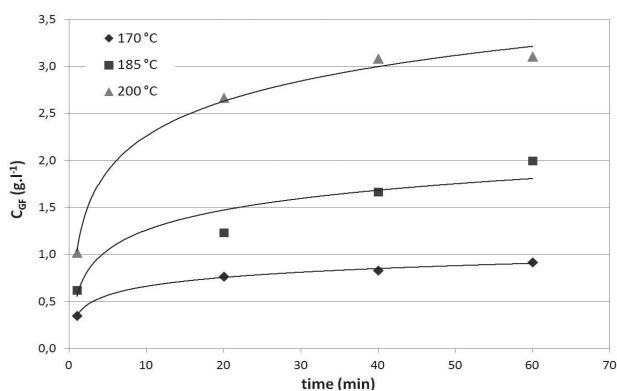


Fig. 4. Dependence of final glucose yield on processing temperature and time

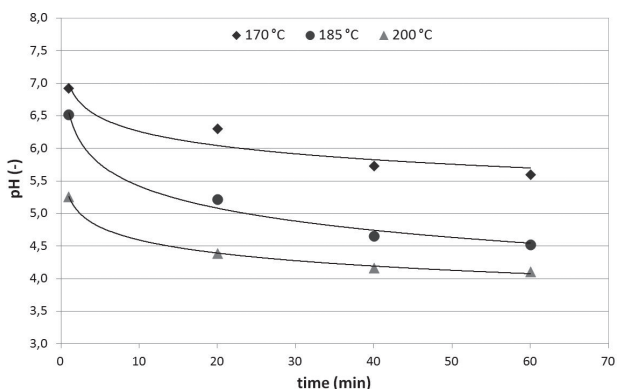


Fig. 5. Dependence of final *pH* on processing temperature and time

The effect of thermal-expansion hydrolysis on structure of wheat straw is shown in Tab.1 and it could be explained as follows. The liquid water under pressure penetrates into pores in biomass. Because of

Tab. 1 Dependence of wheat straw structure on processing temperature and time

| | | processing temperature <i>T</i> [°C] | | |
|-------------------------------|----|--------------------------------------|-----|-----|
| | | 170 | 185 | 200 |
| residence time <i>t</i> [min] | 0 | | | |
| | 20 | | | |
| | 40 | | | |
| | 60 | | | |

rapid expansion liquid water changes phase to vapour and associated volumetric change causes disruption of substrate and cell walls especially. As shown in Tab.1, the structure of wheat straw is being mushy with increasing processing temperature and residence time. The pulpy suspension with minimum amount of fibres was obtained at temperature 200°C and residence time higher than 20 minutes.

Conclusions

The thermal-expansive pre-treatment is environment – friendly technology which can be used not only for various species of lignocellulosic biomass. Generally, this pre-treatment significantly improves biodegradation of raw material.

- Its effectiveness grows up with increasing processing temperature and time.
- Expansion process inflicts an intensive destruction of material.
- The maximum biodegradability of non-treated wheat straw was found to be at temperature 200°C and residence time higher than 40 minutes.
- Treated substrate under these conditions is well-pulpy and well-homogenized as well.

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