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Characterization of wheat straw pretreatment by thermo-gravimetric method

Introduction

Lignocellulosic materials which can be found in such materials as agriculture and forestry wastes, municipal solid waste, waste paper, wood and herbaceous energy crops represent a potential source of biomass for biogas production in biogas plants. In general, lignocellulosic biomass is composed of cellulose, hemicellulose, lignin, organic, and inorganic compounds and exhibits composite structure. However, the composite structure makes the biomass resistant to microbial attack. Therefore a pre-treatment of lignocellulosic biomass is an essential step in order to increase cellulose and hemicellulose accessibility and hydrolysis efficiency.

In our research group the effect of thermal-expansion hydrolysis (TEH) on biogas production has been intensively studied. This method has been based on liquid hot water process that is followed by substrate suspension expansion through a ball valve into atmospheric expansion vessel. By this way the effect of LHW process has been combined with cell disruption caused by shear forces acting during expansion.

The problem is how to characterize simply, effectively and cheaply content and conversion of individual fractions after pretreatment. The lignocellulosic structure of biomass can be qualitatively identified by thermogravimetric analysis (TGA).

The main goal of this work is to assess the effect of process-pretreatment temperature onto wheat straw pretreatment by the sequential static thermogravimetry.

Experimental

Materials

Untreated wheat straw and solid residue after TEH were analysed in experiments. The untreated wheat straw was cut only into 1÷6 cm pieces on field and stored in containers at ambient temperature. The raw wheat straw composition was found: moisture 7% wt., total solids TS = 93% wt. and volatile solids VS = 89.5% wt.

The raw wheat straw was pretreated by thermal-expansionary hydrolysis in our laboratory equipment of volume 8 litres [*Krátký et al., 2011*]. The aqueous wheat straw suspension was placed into the hydrolyser. The substrate was heated up to process temperature T_{TEH} and afterwards this temperature was kept constant for a residence time 40 minutes. Then the ball valve was rapidly opened and the substrate immediately expanded to the expansion vessel. After vapour condensation, expanded material was removed out of the expansion vessel. The expanded material, i.e. solid residue after TEH, was mechanically dewatered before the analysis. Each material was sampled and analysed 3 times.

Apparatus and experimental conditions

The material analysed was placed into a ceramic cup and the wet material mass was measured by analytic balance (PCB350-3, *Kern & Sohn Ltd*. Germany). The moisture was removed by drying in an oven (KBC-25W, WAMED Poland) at temperature 105 °C until the constant weight was reached. The thermal degradation was studied by static thermogravimetry at various temperatures. The total removal of volatile solids was assumed until temperature of 550°C. The material was heated in the furnace (LE 09/11, *LAC Ltd*. Czech Republic) in stagnant air atmosphere up to temperature T. This temperature was kept constant until the constant weight was reached. After cooling in a dessicator the sample mass m_T was measured. This procedure was repeated until the temperature of 550°C was gradually reached.

Data treatment

Assuming that the initial total solid mass m_0 corresponds to mass at 105°C m_{105} [g] and the residual mass after thermal decomposition m_∞ corresponds to mass at 550°C m_{550} [g], then the dimensionless mass m^* describing mass loss during thermal decomposition is defined as follows:

$$m^* = \frac{m_T - m_\infty}{m_0 - m_\infty} = \frac{m_T - m_{550}}{m_{105} - m_{550}} \quad (1)$$

and conversion rate α is defined as follows:

$$\alpha = \frac{m_0 - m_T}{m_0 - m_\infty} = \frac{m_{105} - m_T}{m_{105} - m_{550}} \quad (2)$$

where: m_T [g] is the actual sample mass at temperature T. The conversion rate represents the sample amount that was decomposed. The dimensionless mass m* and conversion rate α are related as follows:

$$m^* + \alpha = 1 \quad (3)$$

The temperature dependence of conversion rate α was described by S-curve as follows:

$$\alpha(T) = \frac{1}{1 + \exp(a_0 + a_1 T)} = \frac{1}{1 + \exp\left(1 + \ln(1/9^2)\frac{T - T_{0.5}}{T_{0.9} - T_{0.1}}\right)} \quad (4)$$

where: a_0 [-], a_1 [°C^{-1}] are parameters, T [°C] is a temperature, $T_{0.5}$ [°C] is a temperature when the conversion rate reaches 50%, $(T_{0.9} - T_{0.1})$ [°C] is temperature difference from 10% to 90% of conversion that characterizes the conversion steepness. The parameters statistically treated for analysed materials are presented in Table 1. The comparison of experimental data and S-curve correlation for all materials is depicted in Fig. 1. The agreement of model curve and experimental data is very well for all materials. The effect of process temperature T_{TEH} onto conversion rate is depicted in Fig. 2.

Tab. 1. S-curve parameters

Sample	a_0 [-]	a_1 [°C^{-1}]	$T_{0.5}$ [°C]	$(T_{0.9} - T_{0.1})$ [°C]	I_{yx} *1 [-]
untreated wheat raw	11.2838	-0.04049	278.8	108.5	0.9973
solid residue T_{TEH} = 170°C	9.7788	-0.03758	260.2	116.9	0.9924
solid residue T_{TEH} = 185°C	10.4953	-0.04127	254.3	106.5	0.9977
solid residue T_{TEH} = 200°C	9.9777	-0.03721	268.1	118.1	0.9633

Notice: *1 correlation index.

Based on conversion curve the material composition was estimated. *Pasangulapati* [*2012*] found by TGA in air atmosphere at heating rate 50 °C/min that the cellulose and xylan were decomposed in the ranges 235÷355 °C and 180÷285 °C respectively. *Belderok* [*2007*] studied xylan decomposition by TGA in nitrogen atmosphere at various heating rates from 1°C/min to 100°C/min. For heating rates 1°C/min and 50°C/min the xylan was decomposed in the temperature ranges 180÷310°C and 200÷350°C respectively with maximum peak 250°C and 300°C respectively. *Gu et. al.* [*1992*] present the effect of heating rate on the maximum temperature peak during pyrolysis of milkweed (55% of cellulose, 24% of hemicellulose, 18% of lignin) in air. For the heating rate 50°C/min the maximum temperature peak was about 50°C higher comparing with the peak at heating rate 1°C/min. Based on these published data the temperature ranges 265÷300°C and 180÷265°C were estimated

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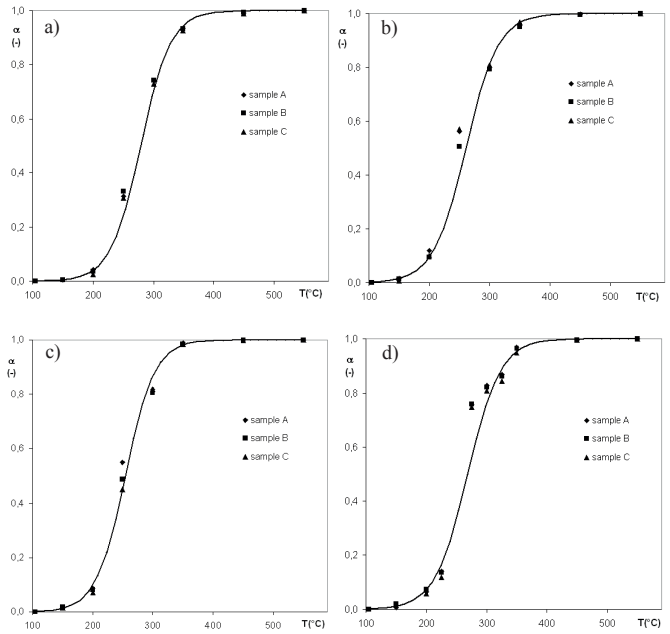

Fig. 1. S-curve correlation: wheat straw untreated (a), solid residue T_{TEH} = 170 °C (b), solid residue T_{TEH} = 185°C (c), solid residue T_{TEH} = 200°C (d)

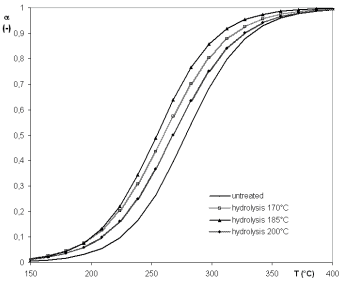

Fig. 2. S-curve correlation – effect of process temperature, residence time = 40 min

for thermal decomposition of cellulose and hemicellulose respectively at static thermogravimetry.

Assuming that the hemicellulose and cellulose are decomposed in the temperature ranges 180÷265°C and 265÷300°C respectively, and the lignin mass corresponds to mass loss between 300°C and 550°C, the weight ratios of hemicellolose, cellulose and lignin (on dry basis) can be calculated as follows:

$$w_H = \frac{m_H}{m_{TS}} = \frac{m_{180} - m_{265}}{m_{105}} = (\alpha_{265} - \alpha_{180})(1 - m_{550}/m_{105}) \quad (5)$$

$$w_C = \frac{m_C}{m_{TS}} = \frac{m_{265} - m_{300}}{m_{105}} = (\alpha_{300} - \alpha_{265})(1 - m_{550}/m_{105}) \quad (6)$$

$$w_L = \frac{m_L}{m_{TS}} = \frac{m_{300} - m_{550}}{m_{105}} = (1 - \alpha_{300})(1 - m_{550}/m_{105}) \quad (7)$$

where conversion rates α_T at temperature T are calculated by Eq. (4). The material composition estimated is presented in Table 2.

Tab. 2. Material composition estimated

Sample	w_H [-]	w_C [-]	w_L [-]	m_{550}/m_{105} [-]
untreated wheat raw	0.334	0.326	0.286	0.0375
solid residue T_{TEH} = 170°C	0.490	0.267	0.180	0.0164
solid residue T_{TEH} = 185°C	0.553	0.255	0.129	0.0192
solid residue T_{TEH} = 200°C	0.425	0.289	0.229	0.0218

Results and discussion

The thermal degradation of untreated wheat straw started practically (α = 0.05) at 206°C and finished practically (α = 0.95) at 351°C. The 50% conversion was reached at temperature 279°C. Based on conversion rate curve the following weight composition was found: 33.4% wt. of hemicellulose, 32.6% wt. of cellulose and 28.6% wt. of lignin. The composition calculated accorded with published data [*Frassoldati et al., 2006*] (27÷30% wt. of hemicellulose, 29÷32% wt. of cellulose, 25÷18% wt. of lignin, 1÷5% wt. of inorganics).

The thermal degradation of solid residue after hydrolysis at temperatures 170°C, 185°C and 200°C occurred practically in the temperature ranges 182÷339°C, 183÷326°C and 189÷347°C respectively. The 50% conversion was reached at the temperatures 260°C, 254°C and 268°C respectively. The thermal-expansionary hydrolysis affects significantly wheat straw structure. The liquid water under pressure penetrates into pores in the biomass. Because of rapid expansion liquid water changes phase to vapour and associated volumetric change causes disruption of substrate and cell walls especially. The remaining fibres are still visible very well at hydrolysis temperature 170°C. At the temperature 185°C the fibre amount is much lower. The pulpy suspension with minimum amount of fibres was obtained at temperature 200°C.

Conclusions

The sequential static thermogravimetry was tested for assessment of the effect of hydrolysis temperature onto wheat straw pretreatment. The mass loss was characterized by conversion rate. Based on conversion curve the material composition was estimated. The dependence of conversion rate on temperature was described by S-curve. The agreement between S-curve and experimental data was very well. The effect of pre-treatment condition can be simply characterized by temperature of 50% conversion $T_{0.5}$ and the conversion steepness ($T_{0.9} - T_{0.1}$). It was found that the temperature of 50% conversion $T_{0.5}$ is lower for all studied solid residues after hydrolysis comparing with untreated straw regardless of hydrolysis temperature. Lower value of $T_{0.5}$ indicates that the straw structure was destructed by hydrolysis into more volatile products. The weight fractions of light fraction like hemicellulose and middle fraction like cellulose are higher comparing with untreated straw for all three hydrolysis temperatures. The minimum temperature $T_{0.5}$ and corresponding highest fraction of light fraction was observed at hydrolysis temperature 185°C. The question, whether the minimum $T_{0.5}$ value represents optimal conditions for maximum biogas yield, will be answered by future experiments.

LITERATURE

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