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DIELECTRIC MONITORING OF BIOMASS HYDROLYSIS PROCESSES

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Abstract
Development of biomass utilization technologies is one of the main area of researches in nowadays. Many biomass utilization process use enzymatic hydrolysis step. Monitoring of the efficiency of hydrolysis plays crucial role in the determination of optimum process time and contributes to achieve lower energy demand and better economy of technologies. Therefore, development of fast, but reliable and non-destructive measurement methods has high relevance not just for the science, but also for the practice. Dielectric measurements have great potential for these purposes, but there are very few experiences related their applicability for detection of conversion efficiency of enzymatic hydrolysis and fermentation processes. Therefore, our research has focused on the investigation of the applicability of dielectric measurements at the frequency range of 200-2400 MHz for the detection of the efficiency of sludge treatment processes, and monitoring the enzymatic hydrolysis of lignocellulosic biomass. Our results have shown that the cellulose degradation during the enzymatic hydrolysis of corn cob residue, and, as well as, the increment of organic matter solubility after different sludge disintegration methods can be monitored by the measurement of dielectric constant at the frequency range of 200-1000 MHz. The correlation between the indicators of biomass hydrolysis processes and dielectric parameters enables to develop on-line and real-time monitoring methods.

Key words: dielectric constant, biomass, sludge, hydrolysis

Introduction

Dielectric properties can widely use to quantify and characterize the electric polarization when the sample is exposed to electromagnetic field. The polarization ability of the system can be measured by the complex permittivity. The real part of the complex permittivity (i.e. the dielectric constant, ε') corresponds to the ability of the medium for energy storage exposed to electromagnetic radiation; the imaginary part (dielectric loss factor, ε") relates to the energy dissipation of the medium [1].

The dielectric parameters can be determined by resonant cavity methods, using of parallel plate capacitors, free space methods, transmission line methods and coaxial techniques, respectively. Novel developed open-ended coaxial cable probes provide a low-cost and easy implementable method for the fast determination of dielectric parameters in a wide frequency range, based on the measurement of reflection coefficient by impedance analyser or vector network analyser (VNA) [2]. VNA can be used mainly for high frequency measurements (kHz-GHz ranges). In measurements with open-ended coaxial probes need a direct contact with sample surface. Errors and uncertainties of dielectric measurement process with an open-ended coaxial probe can be arisen mainly from the inhomogeneity of samples, probe-sample contact, and/or probe-sample pressure.

The dielectric parameters of the medium influence the reflection coefficient (given as Γ or S11 parameter) of an open-ended probe that is attached to sample surface. Therefore, for example, air-gap between the surface of material under test (MUT) with high roughness and the dielectric probe decreases the reliability of the measurements. Dielectric parameters can use for modelling and optimization of microwave heat treatments, determine the moisture content of biomaterials, detect the presence of specific compounds in different multicomponent system, or monitoring of chemical and biochemical reactions, as well [3, 4].

The frequency of dielectric measurements depends on the system/material. Degradation of high voltage transformer oils can be monitored with complex dielectric permittivity measurements in frequencies between 100 MHz and 3 GHz [5]. For determination of the dielectric behaviour of biological tissues a lower frequency range (17 MHz to 2 GHz) can be applied [6]. Measurements of dielectric properties and behaviour with open-ended coaxial probes have lower accuracy if the measuring frequency is below 200 MHz and the dielectric constant and loss factor of MUT has low in magnitude. High temperature in high water contented system (suspension, solution) can led to forming of vapour bubbles on the surface of the probe that disturb the reflection of electromagnetic waves [7].

Dielectric measurements have several advantages over the conventional analytical and material testing methods, such as its non-destructive, non-invasive characteristics, no need for chemicals, and easy sample preparation [8]. Furthermore, by using reflection-based methods in vivo and in vitro measurements can be carried out in biological systems and samples, respectively. Accurate knowledge of dielectric parameters of biological tissues has great importance in medical diagnostic and electromagnetic medical (therapeutic) technologies for dosimetry calculations, as well [9].

Dielectric constant at 2450 MHz is suitable to predict the molecular weight of macromolecules produced in caprolactone polymerisation, furthermore, the dielectric parameters measured on-line show good correlation with the progress of the ring opening of caprolactone monomer [10]. At higher frequencies, the inflection point of dielectric constant and the peak value of dielectric loss correlates well with the change of dipolar relaxation time. Asymptotic value of dielectric constant indicates the end of cross-linking process [11].

In solids, water content and water activity determines mainly the dielectric behaviour. Dielectric constant increases with the increasing of water content and water activity at the microwave frequency of 915 MHz and 2450 MHz. This general tendency enables to use dielectric measurement for estimation the change of moisture content of food, for example [12].

The dielectric measurement have great potential for monitoring of chemical and biological processes, but there is a gap in the knowledge related its practical applicability. Therefore, our main aim was to investigate the applicability of dielectric constant for monitoring of the progress and efficiency of enzymatic hydrolysis of lignocellulosic biomass and preliminary hydrolysis of food industry wastewater sludge, respectively.

Experimental

For the lignocellulosic enzymatic hydrolysis tests 5 m/m% suspension (based on dry matter content) made from the grit fraction of corn cob residues (COBEX GM20) was used. This fraction has an average particle size of 780 ± 90 μm, and the cellulose/hemicellulose/lignin percentage ratio of 47.1/37.3/6.8%.

Cellic CTEC2 (Novozymes) enzyme blend was used in a dosage of 120 FPU/g_{DM} for the enzymatic hydrolysis tests carried out at the temperature of 50°C and pH of 5.2. Reducing sugars were measured by DNSA spectrophotometric method.

To increase the organic matters solubility of meat industry wastewater sludge alkaline (pH=12) and microwave pre-treatment and their combination were used. The specific energy intensity of microwave treatment (J/g) was calculated from the power of magnetron (operating at frequency of 2450 MHz), the exposure time, and the weight of the irradiated sample.

The solubility of organic matters was characterized by the ratio of soluble to total chemical oxygen demand (SCOD/TCOD). The chemical oxygen demand was measured by colorimetric

method (Hanna, COD cuvet test, after 2 hours thermodigestion at 180 °C), for separation of soluble fraction of organic matters filtration with 0.45 μm pore sized syringe filter was used after centrifugation (10 min, RCF=5500).
Dielectric constant (ε') was measured with an open-ended coaxial-line probe (SPEAG DAK 3.5), connected to a vector network analyser (ZVL-3 VNA, Rhode&Schwarz) at the frequency range of 200-2400 MHz. Immersion depth of dielectric probe was 10 mm; the temperature of the samples was controlled at 25°C during the dielectric measurements by thermostatic water bath.

Results and discussion
At the first stage of our experiments, the dielectric behaviour of meat processing sludge exposed to different pre-treatments was determined. The organic matter solubility (given as SCOD/TCOD) of the raw sludge was 0.23±0.05 and due to the microwave, alkaline and combined microwave-alkaline pre-treatment it increased to 0.34±0.08, 0.39±0.11 and 0.48±0.12, respectively. It is verified, that microwave and alkaline pre-treatments are capable to increase the organic matter solubility of sludge [13]. The dielectric behaviour of sludge has been changed after pre-treatments. Compared to the raw sludge (Control) the dielectric constant of treated sludge decreased in the frequency range of 200-1000 MHz (Figure 1).

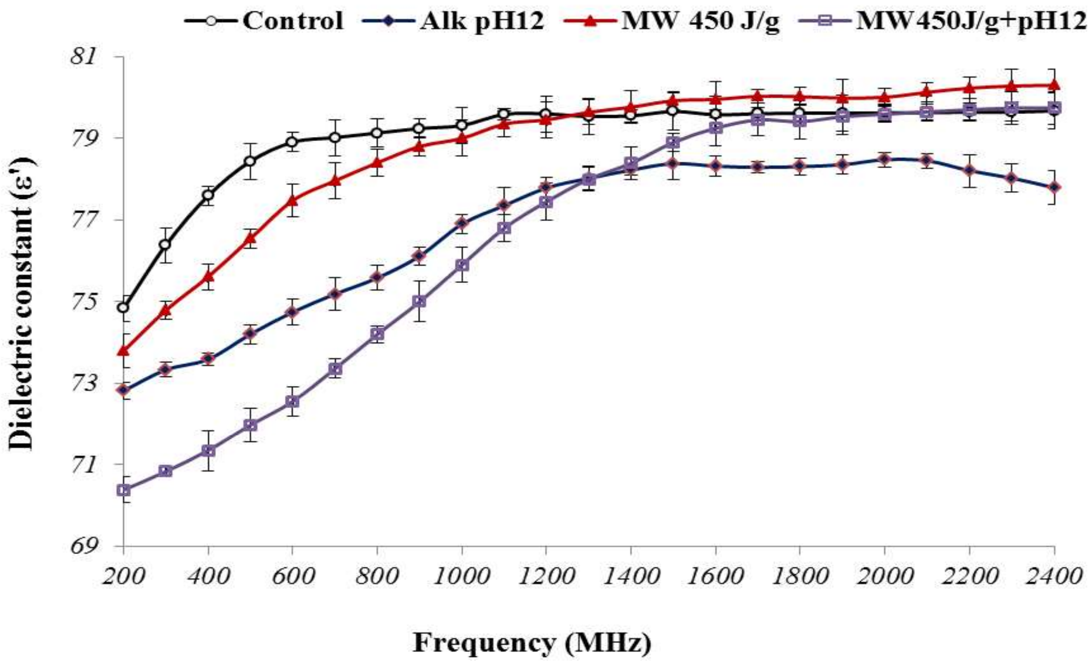

Figure 1. Dielectric constant meat industry wastewater sludge treated by alkaline (alk), microwave (MW) and with coupled method (MW+pH12) (t=25°C)

Alkaline and microwave treatment, and their combination disintegrate the sludge particles; increase the solubility of organic matter and the higher molecular weight compounds degraded partially to smaller molecules. These physicochemical changes can alter the polarisation ability of the medium which is indicated by the change of dielectric constant. At higher frequencies, there can not be found unambiguous correlation between the type and efficiency of different treatment methods and the change of dielectric constant.
During the enzymatic hydrolysis of corn-cob residue (COBEX GM) the reducing sugar yield increased to 15±1.3 mg_{RS}/g_{DM},(1.day), 53±3.6 mg_{RS}/g_{DM} (3.day), 114±7.8 mg_{RS}/g_{DM} (5.day),

and 133±6.9 mg_{RS}/g_{DM} (7.day), respectively. The frequency depending dielectric constant was also investigated for the enzymatically hydrolysed lignocellulosic biomass samples at the different hydrolysis stages. The results show that the dielectric constant decreased with the cellulose degradation in the enzymatic hydrolysis process (Figure 2).

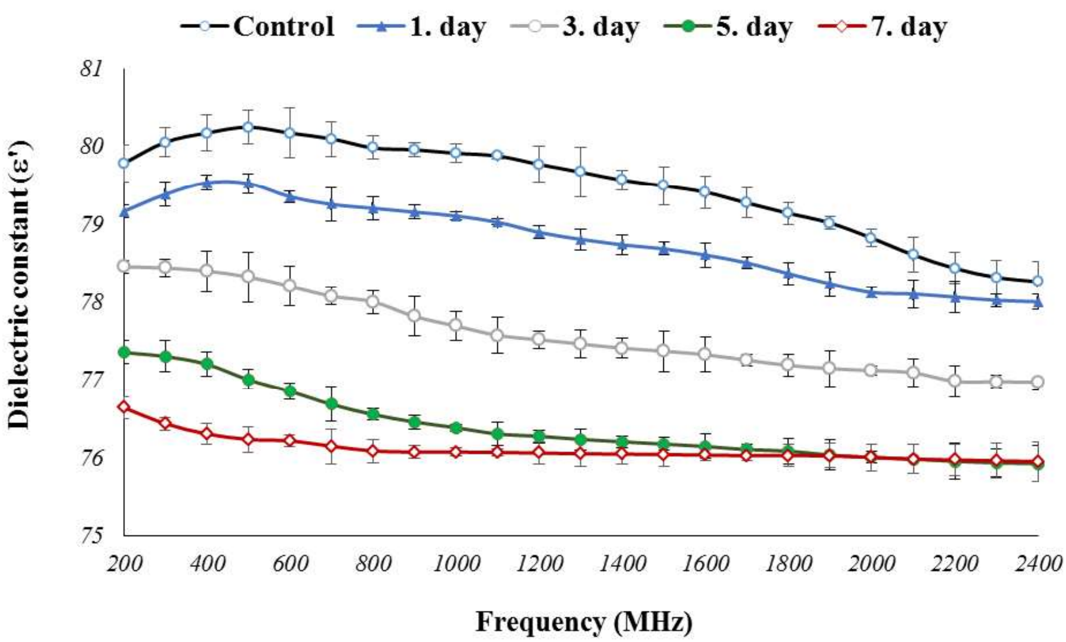

Figure 2. Dielectric constant of enzymatically hydrolysed lignocellulosic biomass (COBEX) measured at different hydrolysis time (t=25°C)

The higher difference in dielectric constant measured at different time of enzymatic hydrolysis process was found at lower frequencies (200-1000 MHz). Higher the frequency of dielectric constant lower the sensitivity of measurement for detection of cellulose degradation. At higher frequencies (1900-2400 MHz) there was any significant difference in dielectric constant of samples enzymatically hydrolysed for 5 days and 7 days (despite of the different reducing sugar yields), for example. These results verified, that the lower molecular weight compounds, produced in enzymatic cellulose degradation process, can be polarized easier in the electric field [14], therefore the dielectric constant has decreasing tendency during the hydrolysis.

Conclusion

The main aim of our research was to examine the applicability of dielectric measurements for monitoring of lignocellulosic biomass hydrolysis, and detection of the efficiency of sludge disintegration methods. For the investigation of the change of dielectric behaviour of corn cob residue contented suspension during enzymatic hydrolysis, and sludge exposed to microwave and alkaline treatments, an open-ended coaxial probe was used. Our results verified, that with the measurement of dielectric constant at frequencies of 200-1000 MHz the cellulose degradation degree and sludge disintegration efficiency can be monitored, as well. The change of dielectric behaviour has a good correlation with the standardized analytical parameters, used for the estimation of the efficiency of biomass hydrolysis.

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