SUMMARY OF RESEARCH FINDINGS
Project number: K105021

1 Introduction to the advancement of research

The following research was conducted in accordance with the work plan, as defined in section reporting period:

1.a. Membrane fouling mitigation by sonication

Based on the available scientific literature examination of the membrane separation and sonification fit equipment was designed and built for investigation of ultrasound coupled membrane processes. The equipment is able to run simultaneous as an ultrafilter or microfilter with sonication. It can work for the two different frequencies and the power is continuously variable; in addition the ultrasonic treatment could be performed at one time. Experiments were performed to determine whether the ultrasound damaging the membrane, and what kind of effect could be shown on the flux and the retention of organic material during milking model waste water filtration whit combined effect. We found that the structure of the membrane was not damaged by applying ultrasonic treatment, the flux increased significantly during ultrafiltration, and the polarization layer resistance reduces significantly meanwhile there was only a slightly reducing in the retention of organic material. In addition, the model has been set up to characterize the filtering mechanism.

The ultrasound coupled membrane processes was used for meat industrial, model dairy waste water, and enzyme recovery of fermentation of cellulose containing substrates. It was found the ultrasound has smaller effect on flux in case of whey separation than it was measurable in the case of waste water models. The result that the enzymes recovered by sonification preserved activity is a very considerable success. These results show that the method is applicable for systems containing bioactive components. The material of the membrane had not showed any different effect on the separation.

The effects of vibration on nano- and ultrafiltration modules also were investigated. In further investigations the effect of mechanical vibrations and the effect of ultrasound on membrane filtration parameters will be compared, to achieve more information about the effect of different frequencies of vibration on membrane filtration parameters as flux, retention and filtration resistances.

Whey and cellulose solution broken down by enzyme also were used as feed solution. The results show that the ultrasonication effectively decreased the polarization layer resistance at whey solution. The flux was increased by US when this coupled techniques were applied for enzyme recovey from model or real fermented liquid due to the reducing of the resistances. There has been measured the effect of different US parameter (distance between transducer and membrane surface, intensity of US) on flux as well. The best results were obtained at distance as far as 3 cm, and 50% intensity, since higher intensity than 50 % caused harmfully high temperature increasing (up to 80°C).

The enzyme activity test verified that the US did not modify the enzyme configuration, i.e. did not change the enzyme activity, even more there is slightly increasing at US treated samples.

1.b. Examination of mitigation by TiO_2 nanoparticles

The effect of TiO_2 nanoparticles coated regenerated cellulose ultrafiltration membrane was examined on dairy effluent filtration parameters. Our results show that the TiO_2 coats on the surface decrease the flux and increase the membrane resistance.

To test the stability of coating nanoparticles on different membrane materials (polytethrafluoethylene (PTFE), thin-film and polyamide composite, polyethersulfone) several types of membrane were coated by TiO_2 nanoparticles. It was found that the hydrophobic-hydrophilic character of the membrane basically determine the stability of the membrane coating. The best results were obtained by coating polyethersulphone (PES) membranes, thus the further examinations were performed with this membrane. Polyethersulfone membranes with different pore sizes (0.05 and 0.2 μm) were coated with commercial TiO_2 (Aeroxide P25) and synthesized TiO_2 nanoparticles (NP) by filtering the TiO2 suspension through the membrane. Coated membranes had significantly lower water fluxes compared to the neat membranes. Contact angle measurements showed that TiO2 P25 formed a very hydrophilic coat on the membranes on the contrary TiO2 NP increased the hydrophobicity of the surface. UV irradiation had an effect on both the neat and coated membranes flux values, it slightly increased the flux values. In order to test the photocatalytic activity of the TiO2 coated membranes, Acid Red 1 dye solution was irradiated in the presence of the coated membranes for 1 hour and then filtered with them. It was proven that the TiO2 coatings have photocatalytic activity; dye decolonization was measured with spectrophotometry.

The polarization layer resistance erected during model dairy wastewater ultrafiltration can be reduced effectively by illuminating the TiO_2 modified membrane with UV light. The active radicals borne photocatalytic activity of TiO_2 effectively clean the surface of the membrane, thereby reducing clogging of the membrane.

Other high-performance processes such as ozone or Fenton reaction during combined ultrafiltration were examined in the dairy wastewater filtration model parameters to achieve a better understanding of processes to clarify the mechanism. The results of these studies show that high efficiency in the oxidation pre-treatment processes can effectively reduce the polarization layer resistance and improve the efficiency of filtration.

Filtration combined with Fenton reaction can be an appropriate method for treating dairy wastewaters, but the efficiency depends on the characteristic of the wastewater. In case of milk powder containing model wastewater decreasing the pH resulted in flocculation; these flocs were less degradable, so more time was necessary for the Fenton treatment to eliminate these molecules. It resulted in lower flux and higher COD retention during filtration and little higher membrane resistances in long term treatment. While treating whey powder solution, its higher lactose content resulted in good Fenton elimination efficiency, as it is an easily degradable component.

Other high-performance processes such as ozone during combined microfiltration were examined in the model waste thermal waters. Wastewater filtration models were evaluated to achieve a better understanding of processes to clarify the mechanism. The results of these

studies show that high efficiency in the oxidation pre-treatment processes can effectively reduce the fouling and polarization layer resistance and improve the efficiency of filtration.

2.a) Microwave post-treatment

The main aim of research task was to verify that microwave treatment has advantageous effect on biodegradation of sludge produced in phase separation processes. Experiences related to the effect on organic matter solubility and the efficiency of anaerobic digestion is controversial in scientific works, and there is not known information about the efficiency of microwave treatment of food industry wastewater sludge and effluents. To test our hypothesis need to investigate and analyze the change of organic matter solubility and aerobic and anaerobic biodegradability with using novel indicators which appropriate to test the efficiency of microwave process.

During the first phase of experimental work the initial organic matter solubility, aerobic and anaerobic biodegradability of different liquid waste and by-products were determined, such as meat processing wastewater, dairy wastewater and whey. Because of the varying solubility and biodegradability of different originated raw materials, new indicators were needs to measure their change during the pre-treatments.

Based on the standardized analytical methods (such as chemical oxygen demand, biochemical oxygen demand, total organic carbon measurement) and with the modification of analytical methods according to the specific characteristics of different sludge samples with high organic matter concentration and containing organic compounds in particulate and dissolved forms, biodegradation index (BDI) and solubilization index (SLI) was defined, as novel control parameters. To evaluate the change of organic matter solubility after MW treatment applying *t* time of irradiation and to eliminate differences originating from different initial solubility of raw sludge - $(SCOD/TCOD)_i$ - the dimensionless solubilization index (SLI) was calculated as follows

$$SLI = \frac{(SCOD/TCOD)_t - (SCOD/TCOD)_i}{(SCOD/TCOD)_{max}} [-]$$

The change in the ability of organic matter for biological degradation resulted by MW treatment was characterized by the dimensionless biodegradation index (BDI) with the following equation:

$$BDI = \frac{(CBOD_5 / SCOD)_t - (CBOD_5 / SCOD)_i}{CBOD_{5max} / SCOD_{max}} \quad [-]$$

where subscript 5 means the degradation time during the tests.

According to the results of preliminary experiments, the effect of microwave specific process parameters, i.e. the irradiated microwave energy (IMWE) and the specific microwave power level (MWPL) was examined in the range of 90-1050 kJ and 0.5-5 Wg^{-1}, respectively.

By applying SLI and BDI as control parameters to characterize the change in physicochemical structure of sludge due to microwave pre-treatment was verified the hypothesis that beside the irradiated microwave energy (IMWE) the specific microwave power level (MWPL) has also significant effect on the change of organic matter solubility related to disintegration of sludge structure and the aerobic and anaerobic biodegradability of food industry wastewater sludge.

Based on the results obtained from response surface analysis it was concluded that increasing of IMWE and MWPL has a positive effect on solubilization, but over a certain value of them the value of BDI was worsened. Maximal SLI was obtained for meat processing wastewater sludge if the IMWE reach the value of 650 kJ and MW intensity was over MWPL of 2 Wg^{-1}, higher value of irradiated energy or higher intensity of MW treatment caused any further increment in the SLI (Fig.1.)

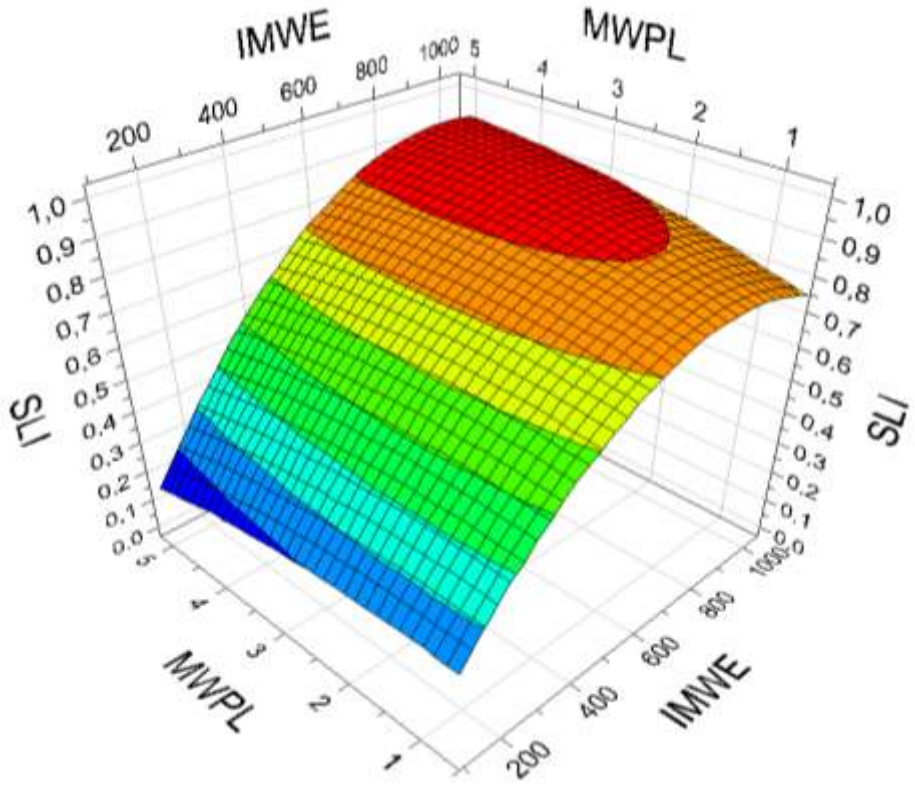

Fig. 1. Response surface for SLI.

$$SLI = 0.8085 + 0.301x_1 + 0.014x_2 + 0.0706x_1x_2 - 0.237x_1^2 + 0.036x_2^2 \quad [-]$$

IMWE is encoded as x_1 and MWPL is encoded as x_2

To achieve the maximum biodegradability IMWE of 550-700 kJ, and MWPL of 1.75-3.5 Wg^{-1} can be considered as optimum region. Applying IMWE and MWPL at optimum level, the

initial BDI of raw sludge (0.21) increased to above 0.8 due to the microwave treatment. On the contrary to the results related to SLI, if the MW pre-treatment was carried out with higher intensity than the optimum region, or the irradiated energy was higher than that of it, a decreasing of BDI occurred (Fig.2).

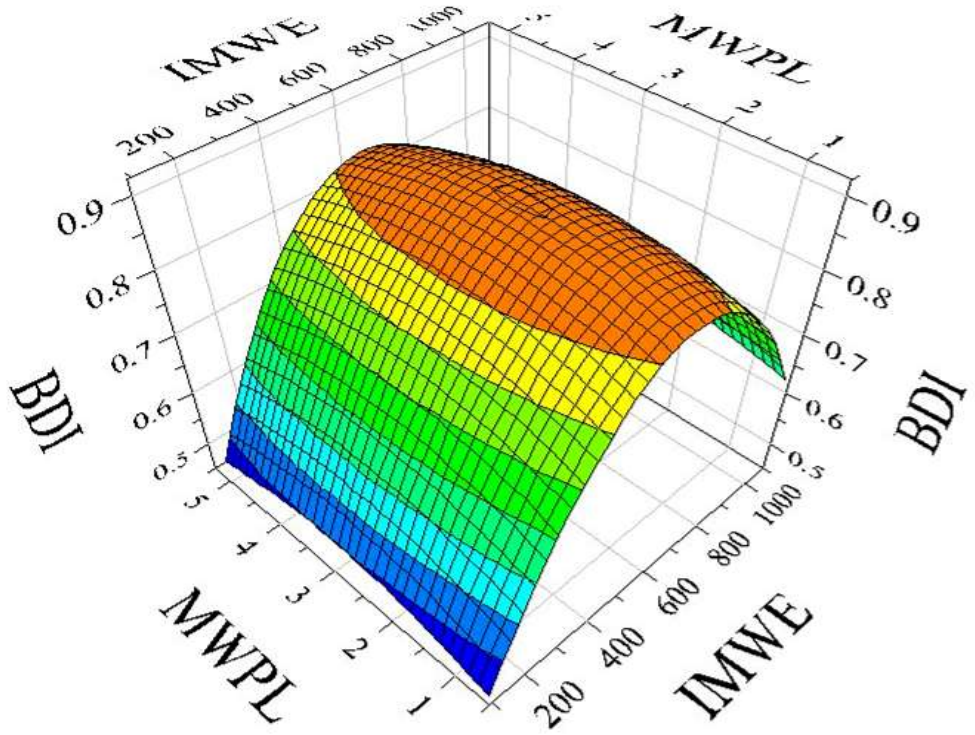

Fig.2. Response surface for BDI. $\boldsymbol{BDI = 0.8921 + 0.071x_1 - 0.002x_2 - 0.298x_1^2 + 0.043x_2^2}$ [–]

IMWE is encoded as x_1 and MWPL is encoded as x_2

Results of batch mesophilic anaerobic digestion (AD) tests confirmed that microwave pre-treatments are suitable to shorten the initial lag phase of anaerobic decomposition, and to accelerate of biogas production with higher biogas yield. In order to examine the energy efficiency of MW process the net energy products (ΔE) of pre-treated sludge were also calculated from the power of magnetron, time of irradiation and the volume of produced methane.

Results of our calculations show, that despite of higher biogas yield the MW pre-treatment at higher MWPL and using increased IMWE were not favorable from energetic aspects.

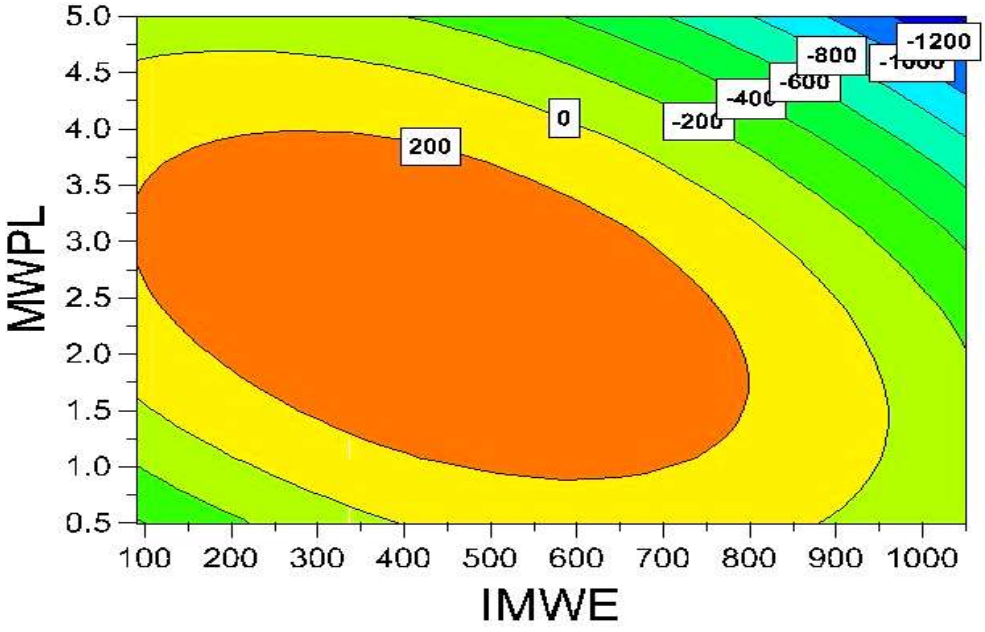

Fig.3. Contour plot for ΔE.

$\Delta E = 326.12 - 27.29X_1 - 237.74X_2 - 4.017X_1^2 - 470.79X_2^2 - 385.9X_1X_2$ $[J]$. *IMWE is encoded as x_1 and MWPL is encoded as x_2*

The optimum range of IMWE and MWPL for enhanced biogas production from food industry originated wastewater sludge was concluded as 600-650 kJ and 2.5-3.0 Wg^{-1}, respectively (Fig.3.).

2.b) Microwave related properties and continuous microwave system

Development of continuously flow microwave treatment unit is needed to investigate the efficiency of microwave sludge conditioning process. Efficiency of microwave process can be evaluated by applying microwave irradiation as pre-treatment before anaerobic digestion examining the effect on anaerobic decomposition kinetic. On the other hand, the energetic efficiency of microwave heating is determined by the dielectric properties of materials. Therefore suitable apparatus and algorithms are needed to measure the microwave specific dielectric parameters, such as dielectric loss factor and dielectric constant and their possible relationships with the structural change of sludge.

To investigate the applicability of microwave sludge conditioning method and to make possible to determine the main determinative factors for scale-up the process a continuously flow, semi pilot microwave equipment was designed and constructed. To allow the possibility for the examination of the effect of different power intensity of microwave pre-treatment, the equipment contains a variable power water-cooled magnetron with an operating frequency of 2450 MHz.

To ensure the ability of microwave conditioning in continuously flow operation mode a toroidal cavity resonator was applied and peristaltic pump for pumping of sludge. Furthermore, the microwave sludge conditioning unit contains real time temperature measurement and data acquisition system.

The operation of continuously flow microwave was tested by meat processing wastewater and dairy effluents, such as dairy wastewater and whey originated from membrane concentration process. To investigate the efficiency of continuously flow microwave sludge pre-treatments the biochemical oxygen demand, chemical oxygen demand, total organic carbon concentration was measured from the total sample matrix and from water soluble fraction, additionally the biogas production was determined by lab-scale continuously stirred mesophilic anaerobic digestion system.

Our results show that the membrane concentrated fraction of whey has approximately 40% lower biodegradability than that of obtained from whole whey. The biological degradation ability of permeate fraction is higher than that of the whole whey or concentrate due to the relatively higher concentration of lower molecule size and hereby easier decomposable components. These differences in biogas yield can be decreased by the application of microwave pre-treatments. Applied pre-treatments could enhance the efficiency of bio-transformation of organic matter into biogas during the different stage of anaerobic digestion process. In the case of whey concentrate the advantageous effect of microwave pre-treatments could be manifested in higher increasing of biogas production, furthermore the ratio of methane component enhanced in the produced biogas.

The anaerobic digestion tests have confirmed that during whey processing the specific power intensity and as well as the residence time, depending from the actual flow rate, affect the efficiency of the biogas fermentation significantly when the whey was co-fermented with sewage sludge. Experiments conducted in continuously flow microwave equipment resulted that the final temperature achieved during pre-treatment is not much affected the biogas yield and the rate of anaerobic digestion as the duration of pre-treatment. By higher volumetric flow rate the effect of increased microwave power intensity has stronger effect on the biogas production and the rate of anaerobic digestion that of obtained by pre-treatment with lower flow rate and longer residence time. In industrial scale application of microwave pre-treatment make possible to decrease the hydraulic retention time and increase the loading rate of operating mesophilic anaerobic digesters, or decrease the bioreactor size of AD plant.

One of our hypothesis was that exist connection between the change of physicochemical structure of sludge and microwave related properties. For determination of dielectric parameters, i.e. dielectric loss factor (ε") and dielectric constant (ε') a tailor made dielectrometer has been designed and built. ε' and ε" was calculated from the reflection coefficient (Γ), phase shift (ϕ), and standing wave ratio (VSWR). The scheme of measuring and calculation is given in Fig 4.

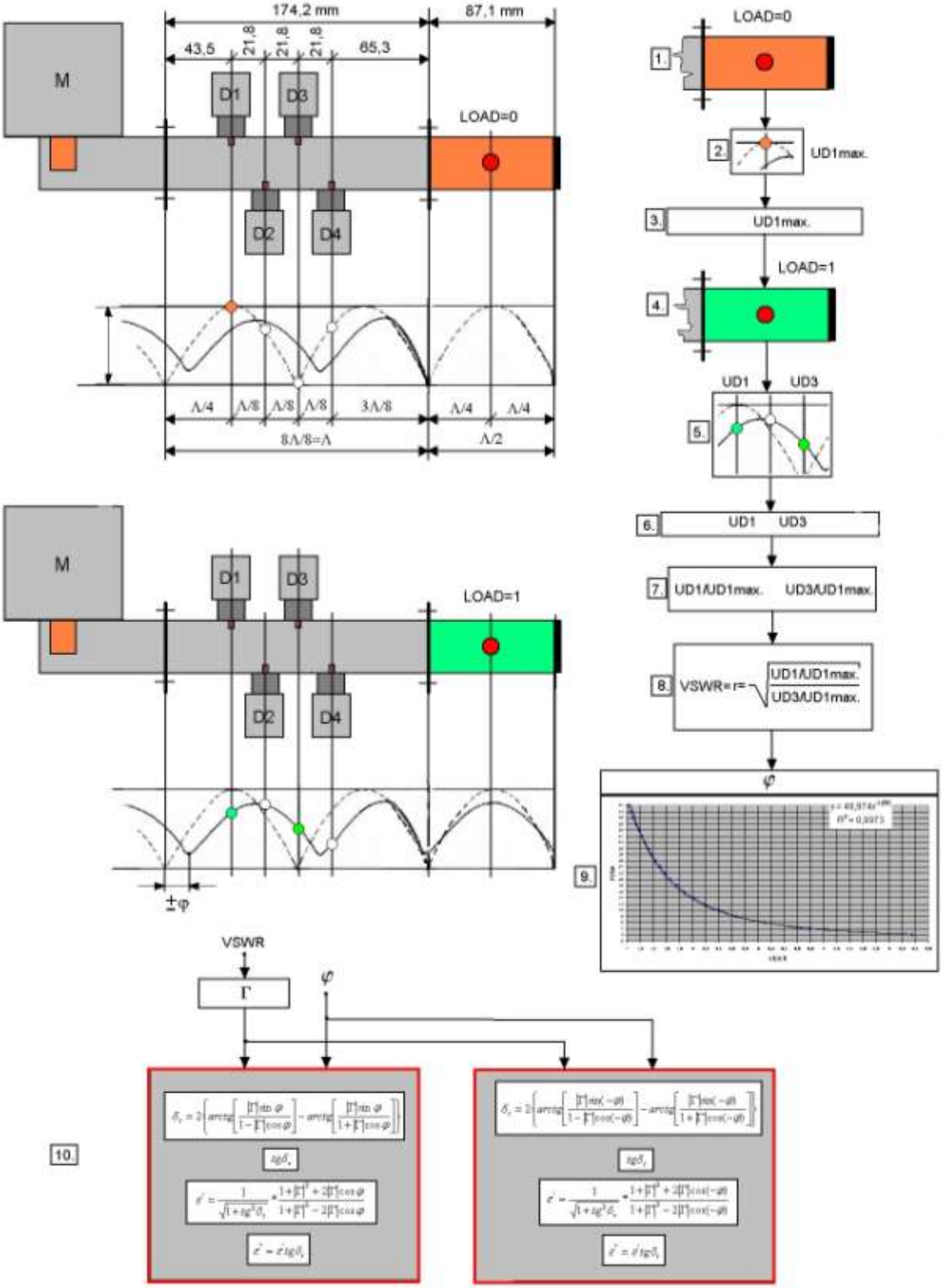

Fig.4. Scheme of measurement and calculation of dielectric properties

The dielectrometer is suitable to determine the dielectric loss and dielectric constant in static and in continuously flow mode. Therefore the dielectrometer can be connected into the sludge pumping line of the developed continuously flow microwave sludge conditioning system. The microwave related parameters are not known for food industry sludge, and with the developed equipment these dielectric parameters can be determined.

Our experimental results show, that despite of the high moisture content of sludge, temperature depending behavior of ε' was different that of can be known for water. Dielectric constant of sludge had a decreasing tendency in the temperature range of 20-60˚C, but over a critical value of the temperature an increment was induced in the value of ε'. Change of dielectric loss factor, as the function of temperature, has a similar tendency to ε'. The breaking point for ε" was depended on origin, dry matter content and organic matter content of sludge (Fig. 5.).

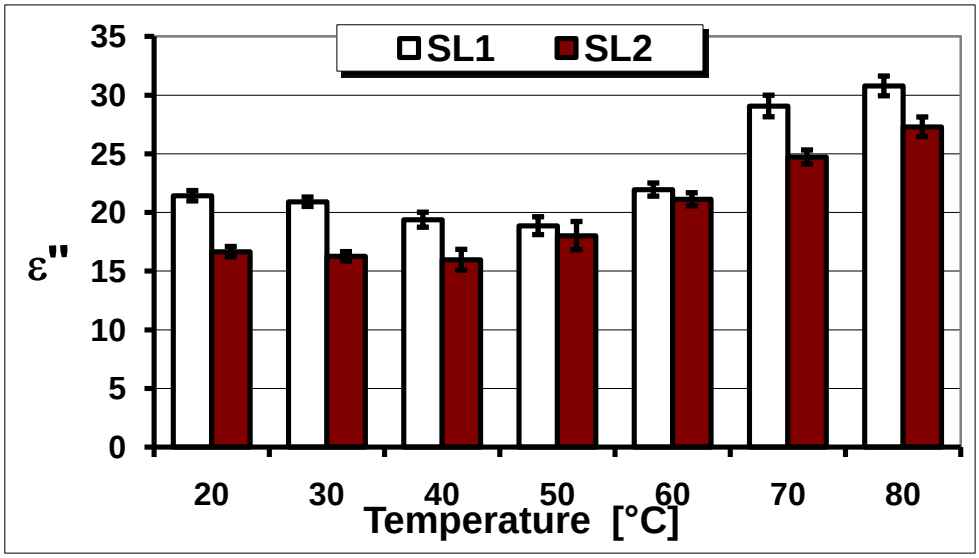

Fig.5.. Change of dielectric loss factor as a function of temperature. *(Meat processing sludge, dry matter content: SL1=9,7 w%; and SL2=14,8 w%)*

Analysis of the change of organic matter content (solubility ratio and ratio of biochemical oxygen demand to the chemical oxygen demand) during microwave irradiation resulted that microwave treatment efficiently disintegrate the original sludge structure. Therefore the migration ability of ions increased due to disruption of sludge flocks and decreased viscosity of sludge liquor. Furthermore, the ratio of free water content to the bounded water increased, as well.

On the other hand, the thermally degraded cell walls led to the liberation of intracellular substances and the hydrolysis of macromolecules resulted in a higher concentration of polar compounds. Above a certain temperature, when sludge disintegration reach a critical value, the change of dielectric parameters are more influenced by the ionic migration than the dipole rotation.

These physicochemical changes resulted in increased dielectric loss factor. Results of our analysis show that the change of disintegration degree (given by the soluble to total COD) and biodegradability indicators has a good correlation with the change of dielectric loss factor (Fig. 6).

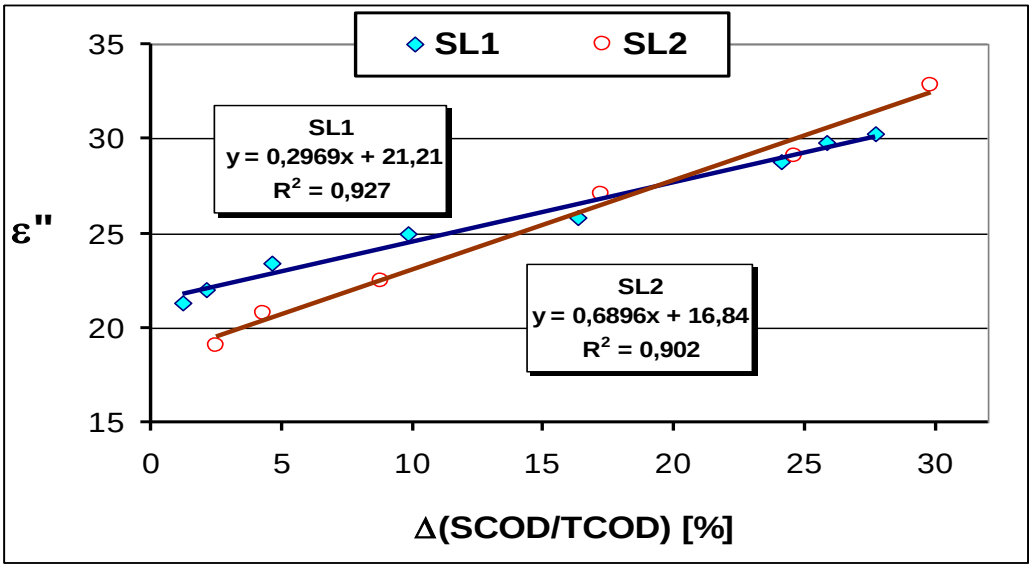

Fig.6. Correlation of dielectric loss with the change of organic matter solubility

(Meat processing sludge, dry matter content: SL1=9,7 w%; and SL2=14,8 w%)

Correlation between the electrical parameters and biodegradability indicators makes suitable to develop in-line and real-time measuring and control system for the continuously flow microwave sludge conditioning technology. Research work was extended to test the applicability of the measurement of dielectric parameters for other liquid materials. Results show that microwave assisted trans-esterification method is suitable to produce biodiesel from vegetable oils in continuously flow microwave reactor with short process time demand. Results show that dielectric parameters are appropriate to investigate and increase the energy efficiency of the process.

The results of the project were summarized in several publications, 20 scientific article (8,769 impact factor) 29 conference papers were published until the end of the project and further results (detailed in the final report) are under publication.