

DETERMINATION OF TWO-LIQUID MIXTURE COMPOSITION  
BY ASSESSING ITS DIELECTRIC PARAMETERS  
2. MODIFIED MEASURING SYSTEM FOR MONITORING THE  
DEHYDRATION PROCESS OF BIOETHANOL PRODUCTION

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In Part 2 of the work we describe a modified measuring system for precise monitoring of the dehydration process of bioethanol production. This is based on the earlier proposed system for measuring the concentration of solutions and two-liquid mixtures using devices with capacitive sensors (1-300pF), which provides a stable measuring resolution of  $\pm 0.005$  pF at measuring the capacitance of a sensor. In this part of our work we determine additional requirements that are to be imposed on the measuring system at monitoring the ethanol dehydration process and control of bioethanol production. The most important parameters of the developed measuring system are identified. An exemplary calculation is given for the thermo-compensated calibration of measuring devices. The results of tests have shown a good performance of the developed measuring system.

**Keywords:** *capacitive sensor, bioethanol, concentration.*

## 1. INTRODUCTION

In Part 1 [1] of the work we described in detail a precise and effective system for measuring concentration in mixed liquids by estimation of their dielectric parameters. We also pointed out there wide possibilities for application of the measuring system and provided a guidance for estimation of the key parameters and operating modes of the system with a capacitive sensor. To maximally use the advantages of the developed measuring system, it is necessary first to define its parameters, such as the temperature range of the liquid sample, the type of the capacitive sensor, its operating frequency, supply voltage, and the expected equivalent capacity range determined by the properties of liquid. Apart from that, it is necessary to estimate the resolution of the measuring device, the least amount of the sample liquid to be measured (in some cases even pico-litres [2]) as well as the influence of the active component of its equivalent conductance on the device precision [1,3]. A number of factors that together define the measuring system's quality are mutually contradictory; therefore, compromise solutions are required.

## 2. USE OF THE DEVELOPED MEASURING SYSTEM IN BIOETHANOL PRODUCTION

The measuring system [1] was adapted to the determination and monitoring of the composition of ethanol-water mixture in the ethanol production process at different locations of condensate that flows through a dehydration column.

The bioethanol is ethanol (ethyl alcohol) obtained from biomass. To minimize gas emissions caused by the use of agricultural land for cultivation of plants from which biofuel is produced the EU legislature recently required of member states urgent transition to new forms of biofuel production from such biomass kinds as straw, seaweed and the biodegradable fraction of waste.

Bioethanol as a component of fuel for vehicles, unlike ethanol used in the food industry, is not fully purified from different admixtures – esters, methanol, aldehydes, etc.

In the technological procedure of ethanol dehydration a high concentration of the final product 99.5% - 99.7% alc/vol (alcohol by volume) is achieved.

Raw alcohol is used as source material for the industrial production of bioethanol. The production process consists of hydrolysis from starch, sucrose or wood-based natural plant products containing carbohydrates, with deriving glucose to be used for fermentation where yeasts serve for excretion of zymase (the enzyme complex); this last acts as a catalyst in the fermentation process to produce ethanol (with carbon dioxide as a by-product). The yeasts die at the ethanol concentration exceeding 11%-18% alc/vol., which limits the achievable ethanol purity. To obtain the  $96 \pm 0.2\%$  ethanol, this is separated from the ethanol-water mixture by fractional distillation.

The unique characteristic of ethanol is its ability to form a homogeneous binary mixture of ethanol-water azeotropes, so by fractional distillation it is impossible to remove the last 4% of water. This is explained by the fact that there is a common boiling point of the binary mixture – though differing for each component.

Currently, in the dominating ethanol dehydration technology, 60-70% of the total necessary energy is consumed for bioethanol production. A new bioethanol dehydration method has been developed at the Latvia University of Agriculture (LUA) [4] based on the bioethanol semi-dry congruent dehydration principle (EU patent application [5]). According to this method, water is separated from the liquid mixture by moving granules absorbing water. In the dehydration process the water-saturating pellets are regenerated at elevated temperatures and return to the dehydration container. This innovative technology gives up to 70% of energy saving and ensures the continuity of the production process. Therefore, the device for determination of the ethanol composition in the dehydration process was designed taking into account the technology of bioethanol production [4, 5].

To adapt our system [1] for use in the specific process of alcohol dehydration the measuring device was equipped with a cylindrical capacitive sensor of stainless steel (capacity 10 pF in the air). A platinum thermal sensor (resolution  $0.001^{\circ}\text{C}$ , precision  $\geq 0.02^{\circ}\text{C}$ , operating temperature  $15^{\circ}\text{C}$ - $30^{\circ}\text{C}$ ) is built in the electrode (inner diameter 3mm) of capacitive sensor. The maximum voltage initiating the sinusoidal alternating current of the sensor is 400 mV.

The measurement range of ethanol-water mixture in the bioethanol samples is 80%-100% alc.vol. If necessary, the measurement ranges of temperature and sample concentration can be widened in the process of calibration of the measuring device. The minimum volume of liquid required for the measurements was set at 10 ml.

The sensor and the measurement data processing devices (microcontroller included) are integrated in a common 120 mm long sensor unit with a diameter of 14 mm (Fig. 1a).

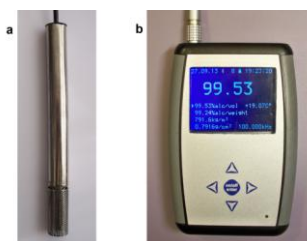


Fig. 1. View of the measuring device: a – sensor unit; b – recording and control unit.

The recording section of the measuring device, together with the second microcontroller, control unit and colour LCD display, is shown in Fig. 1b.

For using the measuring system in the ethanol dehydration process, particular attention was given to the calibration of the device for measuring the sample concentration, to reading the actual temperature, and to adjusting the results to the standard temperature (20°C).

To carry out calibration, two types of the thermostat with electronic control were designed: a two-contour flow-type thermostat and a 14 l stationary thermostat.

The thermostats maintain the temperature of a measured sample from +10 °C to 80°C, with the temperature setting accuracy of  $\pm 0.1^\circ\text{C}$  and the temperature maintaining accuracy of  $\pm 0.02^\circ\text{C}$ . For the temperature measurements a mercury thermometer (resolution  $\pm 0.01^\circ\text{C}$ ) and a platinum thermal sensor (resolution  $\pm 0.02^\circ\text{C}$ ) were also used.

The mathematical computation of the temperature-compensated ( $c_{\%TC}$ ) concentration (% alc/vol.) of a given liquid sample is based upon a polynomial calibration equation (obtained as shown below). In order to illustrate the proposed computations, an example for thermo-compensated measuring device will be provided.

It is recommended that the procedure for calculation of the thermo-compensated volume concentration of a binary liquid sample is carried out step-wise as follows.

Step 1. Dividing the measurement range of sample concentration (defined above) into smaller segments and setting the upper concentration limit ( $c_{\%U}$ ) for each segment. In our case the range from 80% to 100% was divided into five segments (see Table 1).

Step 2. Preparing the reference sample mixture with the ethanol concentration ( $c_{\%R}$ ) of 81, 85, 90, 95, 99.98 % alc/vol. The number of data points should be as great as possible.

Table 1

**Concentration and its upper limits by segments of a binary liquid sample**

Concentration segment	Concentration, $c_{\% \text{ vol}}$	Concentration upper limit, $c_{\% \text{ U}}$
A, or $A_{80} - A_{85}$	80 – 85%	85.0%
B, or $B_{80} - B_{85}$	85 – 90%	90.0%
C, or $C_{80} - C_{85}$	90 – 95%	95.0%
D, or $D_{80} - D_{85}$	95 – 97.5%	97.5%
E, or $E_{80} - E_{85t}$	97.5 – 99.8%	100%

Step 3. Preparing and sorting the measured data  $n_s$  for Table 2 by ascending percentages of concentration. Reading and recording the measured concentration of the reference sample  $c_{\% \text{ R}}$  value  $n_s$  set to the measured sample temperatures  $t_f$  20°C and 25°C.

Table 2

**Measured  $n_s$  values sorted by ascending percentages of the reference sample concentration  $c_{\% \text{ R}}$  and by measured sample temperatures  $t_f$** 

Concentration segment	Concentration, $c_{\% \text{ R}}$	Temperature, $t_f$	Measured $n_s$
$A_{80}$	81.0 %	20.01°C	$n_1 = 13185$
$A_{80}$	81.0 %	25.01°C	$n_2 = 12849$
$A_{85}; B_{85}$	85.2 %	20.00°C	$n_3 = 12435$
$A_{85}; B_{85}$	85.2%	25.00°C	$n_4 = 12112$
$B_{90}; C_{90}$	90.0 %	20.02°C	$n_5 = 11519$
$B_{90}; C_{90}$	90.0 %	25.02°C	$n_6 = 11212$
$C_{95}; D_{95}$	95.1 %	20.00°C	$n_7 = 10645$
$C_{95}; D_{95}$	95.1 %	25.00°C	$n_8 = 10366$
$D_{97.5} E_{97.5}$	97.5 %	20.01°C	$n_9 = 10115$
$D_{97.5} E_{97.5}$	97.5 %	25.01°C	$n_{10} = 9848$
$E_{99.8}$	99.8 %	20.00°C	$n_{11} = 9556$
$E_{99.8}$	99.8 %	25.00°C	$n_{12} = 9359$

Step 4. Using the measured and recorded  $n_s$  values (Table 2):  $n_1, n_3, n_5, n_7, n_9, n_{11}$  obtained at the sample temperature of 20°C, to perform a regression analysis. The result is the volume percent ethanol concentration ( $c_{\%}$ ) depending on the  $n$  values according to the calibration equation:

$$c_{\%20} = 1.47607 \cdot 10^{-10} \cdot n^3 - 5.19895 \cdot 10^{-6} \cdot n^2 + 0.05532 \cdot n - 82.84077 \quad (1)$$

Similarly, using the appropriate  $n$  values measured at the sample temperature of 25°C the following calibration equation is obtained:

$$c_{\%25} = 1.30738 \cdot 10^{-10} \cdot n^3 - 4.46297 \cdot 10^{-6} \cdot n^2 + 0.04498 \cdot n - 36.40556 \quad (2)$$

The squared correlation coefficient of both curves in Fig. 2 corresponding to Eqs. (1), (2) is  $R^2 = 0.99999$ .

Step 5. Doing exemplary calculation of the thermo-compensated volume concentration  $c_{\% \text{ TC}}$  of a given ethanol-water mixture sample:

a) For the actual sample temperature  $t_m$  and concentration  $n$  (expressed in notional units  $n$ ) measured and fixed using the developed measuring device.

For the chosen sample the values  $t_m = 23^\circ\text{C}$  and  $n_m = 11360$  are measured and recorded.

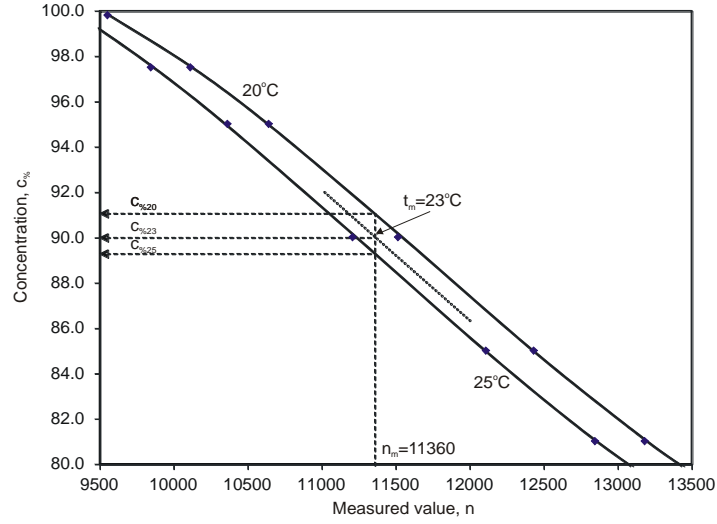


Fig. 2. The calculated thermo-compensated volume concentration  $c\%$  for a given ethanol-water mixture sample at the actual measured sample temperature  $t_m$ .

b) Using Eqs. (1) and (2) and assuming  $n_m = 11360$ , the following volume percentages are obtained:

$$c_{\%20} = 91.064\% , \text{ and } c_{\%25} = 89.285\% .$$

c) Substituting the above  $c\%$  values, for  $t_m = 23^\circ\text{C}$  the thermo-compensated liquid measured concentration is calculated by the equation:

$$c_{\%TC} = c_{\%20} + [(c_{\%20} - c_{\%25}) (20 - t_m)] / \Delta_t \quad (3)$$

In our case  $\Delta_t = 25 - 20 = 5$ .

As a result, we will have:

$$c_{\%TC} = 91.064 + [(91.064 - 89.285) (20 - 23)] / 5 = 89.997 = 90\% .$$

The microcontroller of the sensor unit performs the calibration and recording of measured data as well as processes the data of the previous example, and records the final results.

### 3. DISCUSSION

The existing measuring system [1] has been successfully developed to enable measurements of ethanol concentration in a binary aqueous solution. To widen its application scope and increase convenience at use of the developed measuring device it was equipped with a number of auxiliary accessories and supplements. The measured ethanol concentration of the ethanol-water mixture is calculated and recorded in different mutually convertible units: percentage by

volume (% alc/vol), weight (% alc/wt), and weight of ethanol per volume ( $\text{kg/m}^3$ ) or ( $\text{g/cm}^3$ ). Furthermore, the measuring device also provides the option to see the actual measured temperature of the mixture, the measurement time (hour, minute, second) and the date (day, month, year). The data received from the sensor unit together with the results obtained from the recording and control section are optionally shown on a liquid-crystal display located in the recording section of the measuring device. The measuring unit and display are controlled by the microcontroller using five buttons located under the display. The data can also be displayed on the computer screen using a wireless *bluetooth* (*Smart Bluetooth Module*) link (Fig.3). The operating distance of the wireless link is up to 10 m.

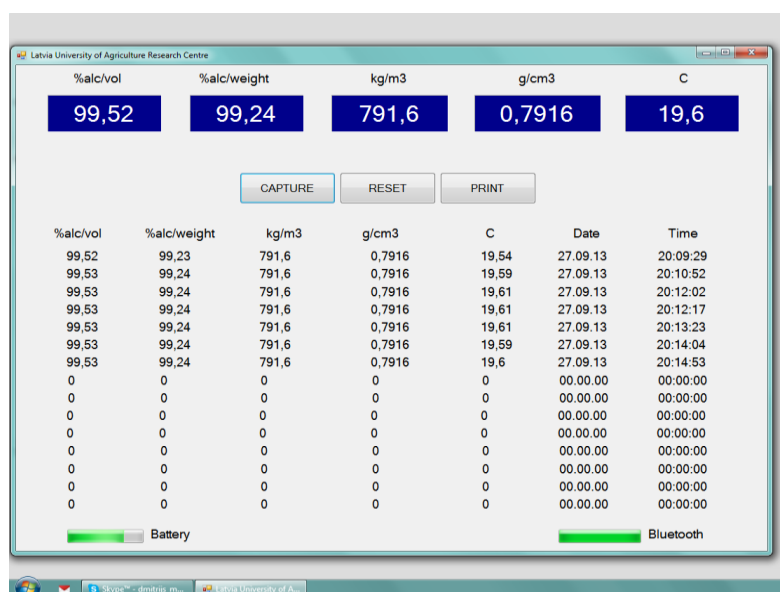


Fig. 3. The computer screen showing the measurement data and the results obtained from the recording and control section of the measuring device.

To calibrate the measuring device, the certified ethanol and double-distilled deionized water mixture samples were used. The test results have shown that the sensor capacitance values can be determined with a stable resolution of  $\pm 0.005$  pF. These values, which characterize the ethanol concentration in the solution, enable the measurements with resolution  $\pm 0.01\%$  and accuracy  $\pm 0.1\%$  throughout the measurement range. In work [1], we have shown that the measurement accuracy decreases when the measured conductivity of the sample solution increases. Also, the water content and ionic contamination is found to affect the electrolytic conductivity of the sample solution. The conductivity of pure synthetic ethanol is  $\sim 5 \mu\text{S/m}$  [6], while for bioethanol this can reach the value up to  $0.5 \text{ mS/m}$  and greater.

The measurements on solution samples from different places in the dehydration column taken during the bioethanol dehydration process have shown a significant spread in their electrical resistance. In turn, the impedance measurements made with a high-precision commercial LCR-821 meter using the

developed capacitive sensor at a frequency of 100.000 kHz and a sample temperature of 20°C evidence that this resistance ( $\sim 40 \text{ k}\Omega$  for high-quality water and ethanol mixtures) can be up to 20 times lower. Applying (in the case of neutral pH of the sample) a higher frequency of the sensor's excitation current (500.000 kHz) has allowed keeping high resolution and accuracy at the concentration measurements.

#### 4. CONCLUSIONS

In order to extend the range of application for our measuring system so that it also enables monitoring and control of bioethanol dehydration process during bioethanol production, the operation mode of capacitive sensor was optimized and the system was equipped with appropriate supplements and auxiliary accessories. To this end, the frequency of the capacitive sensor's excitation current was raised up to 500.000 kHz, the measured data were recorded in five different mutually convertible measuring units, and the possibility of data transfer to a computer screen via wireless *bluetooth* link was realized.

Results of the measurements and tests confirm that the developed measuring system maintains its high quality indicators also in such application as monitoring and control of the bioethanol dehydration process.

#### ACKNOWLEDGEMENT

*This work has been supported by European Regional Development Fund project (agreement No. 2010/0281/2DP/2.1.1.1.0/10/APIA/VIAA/003).*

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DIVU ŠĶIDRUMU MAISĪJUMA SASTĀVA NOTEIKŠANA,  
IZVĒRTĒJOT TO DIELEKTRISKOS PARAMETRUS  
2. MODIFICĒTA MĒRĪŠANAS SISTĒMA BIOETANOLA  
DEHIDRATĀCIJAS PROCESA MONITORĒŠANAI

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K o p s a v i l k u m s

Rakstā esam apskatījuši mūsu izstrādātās divu šķidrumu maisījumu sastāva precīzas noteikšanas mērīšanas sistēmas izmantošanas iespējas dehidratācijas tehniskā procesa monitorēšanai un kontrolei. Mērīšanas sistēmas darbība balstīta uz kapacitīva sensora (no 1 pF līdz 300 pF) izmantošanu, un tās pielietošanas iespējas tika pārbaudītas, nosakot bioetanolā ražošanas galaprodukta kvalitāti atbilstoši sertifikātā paredzētajiem parametriem. Šajā mērīšanas ierīces konfigurācijā pie sensora ierosināšanas strāvas frekvences 100.000 kHz eksperimentālie pārbaudījumu rezultāti parādīja stabila sensora kapacitātes mērīšanas izšķirtspēju  $\pm 0,005$  pF, procentuālo bioetanolā tilpuma koncentrācijas mērīšanas izšķirtspēju ne zemāku par  $\pm 0,01\%$  un koncentrācijas mērīšanas precizitāti ne sliktāku par  $\pm 0,1\%$  visā mērīšanas diapazonā.

Lai panāktu līdzvērtīgus mērīšanas kvalitatīvos rādītājus, mērot bioetanolā un ūdens maisījuma paraugus, kas dehidratācijas tehnoloģiskā procesa gaitā ņemti no dehidratācijas kolonnas dažādām vietām, tika palielināta kapacitīvā sensora ierosināšanas strāvas frekvence (500.000 kHz). Frekvences palielināšanas nepieciešamība ir saistīta ar to, ka, salīdzinājumā ar sertificētu bioetanolu, šo šķidruma paraugu elektrolītiskā vadāmība var būt pat līdz 20 reizu lielāka, kas palielina parauga bioetanolā koncentrācijas mērīšanas kļūdu. Sensora palielinātā ierosināšanas strāvas frekvence (pie neitrālas parauga pH vērtības) ļauj pilnvērtīgi izmantot izstrādātās mērīšanas sistēmas priekšrocības arī bioetanolā ražošanas dehidratācijas procesa monitorēšanai un kontrolei. Papildus tam ar šim nolūkam modificēto mērīšanas ierīci izmērītie dati tika reģistrēti piecās dažādās savstarpēji konvertējamās mērvienībās, kā arī tika realizēta datu pārraide uz datora ekrāna ar bezvadu *bluetooth* saites starpniecību, kas paplašina mērīšanas ierīces ekspluatācijas iespējas. Rakstā skaitliska piemēra veidā parādīta arī mērāmā parauga etanola termokompensētas koncentrācijas vērtības noteikšanas metodika un izteikti apsvērumi mērīšanas ierīces precīzai kalibrēšanai.

27.12.2013.