Ultrasonic Based Sensor Array for the Simultaneous Analysis of Sugar and Ethanol for the Bioethanol Production

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Introduction

Principles of ultrasound, problem, solution, method

Experimental setup

Measurement method, time of flight -measurement, impedance measurement, assemblies

Results

Measurement in liquid mixtures without carbon dioxide (p=0), binary mixtures, ternary mixtures, calibration model for the ultrasound velocity, determination of concentration in ternary and standardised mixtures, determination of concentration in beer probes, influence of dissolved carbon dioxide (p≠0)

Summary

Outlook
Principles of Ultrasound

Ultrasound → mechanical, elastic waves; frequency: $20 \text{ kHz} < f < 10 \text{ GHz}$

Relevant for the research project:
Longitudinal waves:
(in gas, fluids, solids)

Interactions with acoustical media:

1. Reflection

\[
A_r = A_i \frac{Z_1 - Z_2}{Z_1 + Z_2}
\]

2. Transmission

\[
A_t = A_i \frac{2Z_2}{Z_1 + Z_2}
\]

3. Absorption

\[
A_{out} = A_i e^{-\alpha d}
\]

Material Parameters:
\( \kappa \) - isothermal compressibility
\( \rho \) - density
\( Z = \rho \times \text{USV} \) – acoustic impedance
\( \alpha \) – absorption coefficient
Problem

Sugar fermenting industry

Process in the fermentation tank

Various sugars (Mono-, Di-, Polysaccharides)

\[ \text{fermentation} \]

Ethanol + carbon dioxide

\[ \text{reaction progress} \]

Concentration increasing $\uparrow$

Concentration $\phi_S$

Concentration decreasing $\downarrow$

Concentration $\phi_E$

Concentration $\phi_{CO_2}$

Important for the production process:
Determination of the concentration values of sugar ($\Phi_S$) and ethanol ($\Phi_E$) as indicators for the fermentation reaction.

Disadvantage of existing measuring methods (e.g. SCABA analyser, oscillating U-tube):
Probe preparation necessary, complex measurement assembly, high cost, high service effort, online process surveillance not possible

Advantages of an ultrasound measurement method:
High accuracy, low measurement effort, low cost, online measurements during the production process possible
Solution Method

Fermentation tank, contains fermentation fluid (water, various sugars, ethanol, minority components) + carbon dioxide

Direct measurable physical parameters:
USV - ultrasound velocity
Z – acoustic impedance
T – temperature
p - pressure

Determination of concentrations
Φ_S (Sugar)
Φ_E (Ethanol)

Goal of the research project:
Well-defined connection of the concentration values Φ_S, Φ_E with the physical parameters USV, Z, T, p:

\[
\phi_S = \phi_S(USV, Z, T, p) \\
\phi_E = \phi_E(USV, Z, T, p)
\]
Method

Liquid mixtures water-sugar-ethanol with various concentrations of sugar ($\Phi_S$), ethanol ($\Phi_E$)

Carbon dioxide equilibrium pressure $p = \text{const.}$

Temperature $(T)$ variation

Measurement of the characteristic curves

Sound velocity

$$USV = USV(\phi_S, \phi_E, T, p)$$

Impedance

$$Z = Z(\phi_S, \phi_E, T, p)$$

Establishing of a calibrating model:

Derivation of the relations

$$\phi_S = \phi_S(USV, Z, T, p)$$
$$\phi_E = \phi_E(USV, Z, T, p)$$

by numerical analysis of the measurement data field (by linear regression or similar methods)
Measurement Method

Simultaneous measurement

1. Ultrasound Velocity (via time of flight of the ultrasonic pulse)
   Blue Arrows
   Blue Signal Part

2. Acoustic Impedance (via amplitude height of reflected pulse)
   Green Arrows
   Green Signal Part

Electronic Setup for Transducer Excitation and Signal Analysis

Piezoelectric Transducer

Wall 1

Probe Fluid

Wall 2

Temperature T = variable
Pressure p = variable

Impedance Measurement
Sound velocity (= Time of Flight) - Measurement

Amplitude

Time
Determination of Ultrasound Velocity

\[ USV = \frac{2 \times L}{TOF} \]

(L – length of acoustical path, TOF – time of flight of ultrasonic pulse)

Methods of Time of Flight Measurement

- zero crossing
- first maximum
- global maximum
- pattern recognition
1. Signal Height $A_n$
Amplitude of the n-th echo depends on reflection coefficient $R_2$:

$$A_n = (1 - R_1) \ast (R_1 \ast R_2)^n \ast A_i \ast e^{-2n \alpha d}$$

Impedance of the probe fluid

\[ Z_{\text{probe}} = Z_{\text{wall}} \left( \frac{1 - R_2}{1 + R_2} \right) \]

2. Signal Integration
Integration of the commutated pulse sequence
Assemblies

Equipment for measurement with dissolved carbon dioxide at a constant container pressure ($p \neq 0$)

Submersible probe

... in a tempering container
Measurements at Liquid Mixtures without Carbon Dioxide (p=0)

1. Binary Mixtures
(water-saccharose, water-ethanol):
2%-16% sugar, 1%-6% ethanol

2. Ternary Mixtures
(water-saccharose-ethanol)
Relation of components accordant the stoichiometric relation at the yeast fermentation
Sugar start concentrations: 8%, 10%, 12%, 14%

3. Ternary Mixtures
Low-, high-concentration range
→ enhancement of calibration model
Binary Mixtures (Water-Saccharose, Water-Ethanol)

Characteristic temperature-USV-curves

Polynomial of 3rd order in temperature:

\[
USV(\phi_{\text{Sugar/Ethanol}}, T) = A_0 + A_1 T + A_2 T^2 + A_3 T^3
\]

from literature

\[
USV(\phi_{\text{Sugar/Ethanol}}, T) = USV_{\text{Water}}(T) + \underbrace{\Delta USV_{\text{Sugar/Ethanol}}(\phi_{\text{Sugar/Ethanol}}, T)}_{\text{sugar/ethanol component}}
\]

additive component at overall sound velocity
Binary Mixtures (II)

Component $\Delta USV_{\text{Sugar} / \text{Ethanol}}$ (interpolated plains)

$\Delta USV_{\text{Sugar} / \text{Ethanol}}$ at a constant temperature (example $T = 2^\circ C$)

Polynomial of 2nd order in concentration:

$\Delta USV_{\text{Sugar}} = A_0(T) + A_1(T) * \phi_S + A_2(T) * \phi_S^2$

$\Delta USV_{\text{Ethanol}} = B_0(T) + B_1(T) * \phi_E + B_2(T) * \phi_E^2$
Ternary Mixtures (Water-Saccharose-Ethanol)

Sugar/ethanol additive component at overall sound velocity

\[ USV_{\text{Water-Sugar-Ethanol}}(\phi_{\text{Sugar}}, \phi_{\text{Ethanol}}, T) = USV_{\text{Water}}(T) + \Delta USV_{\text{Sugar-Ethanol}}(\phi_{\text{Sugar}}, \phi_{\text{Ethanol}}, T) \]

Sugar/ethanol component

\[ \Delta USV_{\text{Sugar-Ethanol}} = \Delta USV'_{\text{Sugar}} + \Delta USV'_{\text{Ethanol}} \]

Ternary Mixtures

Binary Mixtures

\[ \Delta USV'_{\text{Sugar}} \neq \Delta USV_{\text{Sugar}} \]

\[ \Delta USV'_{\text{Ethanol}} \neq \Delta USV_{\text{Ethanol}} \]

Sugar/ethanol components in ternary mixtures are not the same as in binary mixtures!
Empirical approach for the calibration - (interpolation-) function:
- Up to 3rd order in temperature (T)
- Up to 2nd order in concentration \((\Phi_S, \Phi_E)\)

\[
\Delta USV_{Sugar-Ethanol} = \Delta USV_{Sugar-Ethanol}(\Phi_S, \Phi_E, T, T^2, T^3)
\]

Coefficients of \(\Delta USV_{Sugar-Ethanol}\) determined by linear regression

Calibration function \(\Delta USV_{Sugar-Ethanol}\):

Planes \(\Delta USV_{Sugar-Ethanol}(\Phi_{Sugar}, \Phi_{Ethanol}, T=\text{const.})\)

Continuous, monotone

\[\Phi_S, \Phi_E \uparrow \quad \Delta USV_{S-E} \uparrow\]
\[T \uparrow \quad \Delta USV_{S-E} \downarrow\]

Each set of value \((\Phi_S, \Phi_E, T)\) related definitely to one Value \(\Delta USV_{Sugar-Ethanol}\)
Concentration Determination in Ternary Mixtures (Carbon Dioxide Pressure p=0)

2 measurements with the same probe fluid:
- **Measurement 1:**
  - $T(1) = 2^\circ C$
  - $\Delta USV_{\text{Sugar-Ethanol}}(1) = 50\text{ m/s}$
- **Measurement 2:**
  - $T(2) = 30^\circ C$
  - $\Delta USV_{\text{Sugar-Ethanol}}(2) = 35\text{ m/s}$

Manifolds (lines) of pairs $(\Phi_S, \Phi_E)$ of the same sound velocity in the planes
- $\Delta USV_{\text{Sugar-Ethanol}}(\Phi_S, \Phi_E, 2^\circ C)$
- $\Delta USV_{\text{Sugar-Ethanol}}(\Phi_S, \Phi_E, 30^\circ C)$

Unambiguous intersection of the projection of the lines
- $\Phi_E(\Phi_S, \Delta USV_{S-E} = 50\text{ m/s}, T=2^\circ C)$
- $\Phi_E(\Phi_S, \Delta USV_{S-E} = 35\text{ m/s}, T=30^\circ C)$

in the plane of concentrations $\Phi_S, \Phi_E$

Determination of concentration

Example: $\Phi_S = 9.25\text{ g/100g}, \Phi_E = 1.8\text{ g/100g}$
Determination of Concentration in Ternary Mixtures (II)

Necessary for determination of concentration:

Reverse calibration function $\Phi_E(\Phi_S, \Delta USV_{\text{Sugar-Ethanol}}=\text{const.}, T=\text{const.})$

(equivalent $\Phi_S(\Phi_E, \Delta USV_{\text{Sugar-Ethanol}}=\text{const.}, T=\text{const.})$

Optimized approach for $\Phi_E(\Phi_S, \Delta USV_{S-E}, T)$
(found by minimization of the difference $\Phi_E$ (experiment)-$\Phi_E$ (approximation function))

$$
\phi_E = R_0 + R_1 \phi_S + R_2 \phi_S^2 + R_3 \Delta USV_{S-E} + R_4 T + R_5 T^2
$$
$$
+ R_6 \phi_S \Delta USV_{S-E} + R_7 \phi_S^2 \Delta USV_{S-E} + R_8 \phi_S \Delta USV_{S-E}^2
$$
$$
+ R_9 \phi_S T + R_{10} \phi_S^2 T + R_{11} \phi_S T^2 + R_{12} \phi_S^2 T^2
$$
$$
+ R_{13} T \Delta USV_{S-E} + R_{14} T^2 \Delta USV_{S-E} + R_{15} T \Delta USV_{S-E}^2
$$
$$
+ R_{16} T^2 \Delta USV_{S-E}^2
$$

Determination of the constant coefficients $R_0 \ldots R_{16}$:

Insertion of measurement value sets $(\Phi_E(i), \Phi_S(i), \Delta USV_{\text{Sugar-Ethanol}}(i), T(i))$

linear regression
Determination of Concentration in Ternary Mixtures (III)

Calibration function \( \Phi_E(\Phi_S, \Delta USV_{S-E}, T) \) for \( T = 2^\circ C \)

Relative frequency of deviation \( \Phi_E \) (experiment) - \( \Phi_E \) (approx. function)
(standard deviation: 0.039 g/100g)

\[
\Phi_E(g/100g)
\]

\[
\Phi_S(g/100g)
\]

\[
\Delta USV_{S-E}(m/s)
\]

<table>
<thead>
<tr>
<th>Coefficient</th>
<th>Value</th>
<th>Standard Deviation</th>
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<tbody>
<tr>
<td>( P_0 )</td>
<td>0.27852196</td>
<td>0.001504104</td>
</tr>
<tr>
<td>( P_1 )</td>
<td>-0.33970086</td>
<td>0.000646999</td>
</tr>
<tr>
<td>( P_2 )</td>
<td>-0.00401999</td>
<td>6.63044E-05</td>
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<tr>
<td>( P_3 )</td>
<td>0.08303479</td>
<td>2.90109E-05</td>
</tr>
<tr>
<td>( P_4 )</td>
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<td>0.00017407</td>
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<tr>
<td>( P_5 )</td>
<td>0.00042111</td>
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<td>( P_6 )</td>
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<td>1.66362E-05</td>
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<tr>
<td>( P_7 )</td>
<td>-2.2948E-06</td>
<td>1.1727E-06</td>
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<tr>
<td>( P_8 )</td>
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<td>( P_9 )</td>
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<td>( P_{10} )</td>
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<td>( P_{11} )</td>
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<td>1.1624E-06</td>
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<td>( P_{12} )</td>
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<td>( P_{13} )</td>
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<td>( P_{14} )</td>
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<td>( P_{15} )</td>
<td>-1.8341E-05</td>
<td>1.06677E-07</td>
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<tr>
<td>( P_{16} )</td>
<td>4.405E-07</td>
<td>4.36042E-09</td>
</tr>
</tbody>
</table>
Determination of Concentration in Ternary Mixtures (IV)

1. Measurement of the characteristic curves $USV(T)$ of the probe fluid

$$USV(T_2)$$

$$USV(T_1)$$

Temperature ($^\circ$C)

2. Determining the sound velocity at 2 Temperatures $T_1$, $T_2$

3. Separating the Sugar-Ethanol Component $\Delta USC_{\text{Sugar-Ethanol}}$ by subtracting $USV_{\text{Water}}(T)$

4. Plotting the curves $\Phi_E(\Phi_S, \Delta USV_{S-E}(T_1), T_1)$, $\Phi_E(\Phi_S, \Delta USV_{S-E}(T_2), T_2)$

Intersection point yields Concentration Values

$T = 2^\circ$C
$\Delta USV_{S-E} = 58.46$ m/s

$T = 30^\circ$C
$\Delta USV_{S-E} = 38.98$ m/s
Determination of Concentration in standardised Mixtures (Water-Saccharose-Ethanol)

Example

Mixture,  3.7g/100g sugar
        4g/100g ethanol

Result of determination of concentration
(dashed red Lines):

3.8g/100g sugar    (+0.1g/100g)
3.95g/100g ethanol  (-0.05g/100g)

<table>
<thead>
<tr>
<th>Concentration Determination Ultrasound</th>
<th>Reference</th>
<th>Deviation</th>
</tr>
</thead>
<tbody>
<tr>
<td>g/100g Sugar</td>
<td>g/100g Sugar</td>
<td>g/100g Sugar</td>
</tr>
<tr>
<td>2.12</td>
<td>5.86</td>
<td>1.8</td>
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<tr>
<td>5.13</td>
<td>4.2</td>
<td>5.7</td>
</tr>
<tr>
<td>3.8</td>
<td>4.93</td>
<td>3.7</td>
</tr>
<tr>
<td>4.3</td>
<td>2.87</td>
<td>3.8</td>
</tr>
<tr>
<td>8.1</td>
<td>2.9</td>
<td>7.8</td>
</tr>
</tbody>
</table>
Determination of Concentration in Beer Probes

Commercial beer probes, completely degased (= no carbon dioxide fraction)

Determination of concentration via measuring $\Delta USV_{\text{Sugar-Ethanol}}$ at the temperatures $T_1 = 2^\circ C$ and $T_2 = 30^\circ C$

Comparison with an Anton-Paar-analyser (oscillating U-tube)

<table>
<thead>
<tr>
<th>Beer Grade</th>
<th>Concentration Determination</th>
<th>Concentration Determination</th>
<th>Deviation</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Ultrasound</td>
<td>Anton-Paar Anal.</td>
<td></td>
</tr>
<tr>
<td></td>
<td>g/100g Sugar</td>
<td>g/100g Sugar</td>
<td>g/100g Ethanol</td>
</tr>
<tr>
<td>Ratskrone Export</td>
<td>4.63</td>
<td>4.62</td>
<td>4.0</td>
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<tr>
<td>Dinkelacker Privat</td>
<td>3.89</td>
<td>4.01</td>
<td>3.9</td>
</tr>
<tr>
<td>Krombacher Pils</td>
<td>3.8</td>
<td>3.63</td>
<td>3.89</td>
</tr>
<tr>
<td>Stuttgarter Hofbräu Volksfestbier</td>
<td>4.42</td>
<td>4.4</td>
<td>4.4</td>
</tr>
<tr>
<td>Kloster Pilsner</td>
<td>3.77</td>
<td>3.78</td>
<td>3.86</td>
</tr>
<tr>
<td>Paulaner Volksfestbier</td>
<td>4.89</td>
<td>4.97</td>
<td>4.44</td>
</tr>
<tr>
<td>Schöfferhofer Weizen</td>
<td>3.91</td>
<td>3.85</td>
<td>3.86</td>
</tr>
</tbody>
</table>
Reasons for deviations of concentration values between ultrasound – Anton Paar method

- Fermentation fluid from real production not standardised, contains various sugar types (e.g. saccharose, glucose, maltose, fructose) with different components $\Delta USV_{Sugar}$

New calibration model considering the influence of various sugar types with their typical concentrations

- Influence of minor components (e.g. varying protein content)
Influence of Carbon Dioxide in Solution ($p \neq 0$)

Example: mixture
9.9g/100g sugar
1.0g/100g ethanol
+ liquid-solicited carbon dioxide

Positive
temperature dependant,
pressure dependant
shift of $\Delta USV_{Sugar-Ethanol}$
(e.g. $4.0\text{m/s at } p = 1 \text{ bar, } T= 2\text{°C}$
$6.9\text{m/s at } p = 2 \text{ bar, } T= 2\text{°C}$)

Extended calibration model:

$$USV(\phi_S, \phi_E, p, T) = USV_{Water}(T) + \Delta USV_{Sugar-Ethanol}(\phi_S, \phi_E, T) + \Delta USV_{Carbon Dioxide}(\phi_S, \phi_E, p, T)$$

Sugar+Ethanol Comp. Carbon Dioxide Comp.

Inclusion of the acoustic impedance:

$$Z(\phi_S, \phi_E, p, T) = ...$$
The ultrasound measurement principle presented in this (lecture) talk is a low cost method with high accuracy and very little effort on measurement technique and probe preparation. Online measurements monitoring the production process are possible.

The pulse echo-measurement method allows simultaneous measurement of ultrasound velocity and acoustic impedance.

Sugar and ethanol fractions in aqueous solutions deliver additive components to the overall sound velocity.

The sound velocity in ternary mixtures can be described by a numerical model. The appropriate calibration is continuous, monotone, and assigns to each set of values \((\Phi_S, \Phi_E, T)\) unambiguously one value of sound velocity.

Due to this unambiguousness, it is possible to determine the concentrations of sugar and ethanol in degased probes only by measuring the sound velocity at two temperatures.

For online measurements during the production process (fluids with carbon dioxide fraction) it is necessary to extend the calibration model and to include the acoustic impedance as a further measured value.
Enhancement of the calibration models to increase the accuracy of the determination of the concentration

Further development of the acoustic impedance measurement methods

Extension of the calibration models including the carbon dioxide influence and the acoustic impedance as a new parameter

Measurements at various probes from commerce and industrial bioethanol production

Constructing of a process connection and evaluating of the method in a real production chain

Thank you for your attention!