

Measurement of Methane Content in Upgraded Biogas Using Pulse-Echo Ultrasound

Johan E. Carlson^{1,*}, Jesper Martinsson¹, and Magnus Lundberg Nordenvaad²

¹EISLAB, Dept. of Computer Science and Electrical Engineering,

Luleå University of Technology, SE-971 87 Luleå, Sweden, Johan.Carlson@ltu.se

²Div. of Systems and Interaction, Dept. of Computer Science and Electrical Engineering,

Luleå University of Technology, SE-971 87 Luleå, Sweden

Abstract: In this paper we present an ultrasonic pulse-echo technique for estimating the methane (CH₄) content in binary mixtures of CH₄ and carbon dioxide (CO₂). The method is based on parametric estimation of phase velocity and frequency dependent attenuation in combination with Partial Least-Squares Regression (PLSR). The technique is verified using experiments on mixtures with a volume fraction of CO₂ in the range of 0 % –10 %. The experiments show that the CH₄ content can be accurately estimated with high repeatability.

Keywords: Gas analysis, multivariate calibration, PLS regression

A. Introduction

Biogas manufactured from urban waste has been identified as a potential replacement of fossil fuels in the transport sector. The biogas is upgraded to a high methane content and then inserted into a natural gas grid. In order for this to work, the quality of the upgraded gas must be guaranteed, which means it should essentially contain only methane (CH₄) with a small fraction of carbon dioxide (CO₂), i.e. < 10 % by volume.

For natural gas, which is by far the most commonly available energy gas, several measurement techniques are available, see for example [1], [2]. For other gas mixtures, like biogas or synthesis gas (CO, H₂ and CO₂), there is a lack of non-invasive on-line techniques. The long term goal of this project is to develop a method based on ultrasound for combined volume flow measurement and gas composition analysis. The method should be applicable to a wide variety of gas mixtures.

Previous work shows that the composition of a gas mixture significantly affects the acoustic wave propagation through the gas [3], [4]. Some work has also suggested how to extract these effects from experimental data using multivariate statistical tools, see [5], [6] and references therein.

In [7], it was identified that Partial Least-Squares Regression (PLSR) can be used to connect measured ultrasonic pulse spectra to the composition of mixtures of ethane and oxygen. The paper used a non-parametric method to estimate pulse spectra, which showed some limitations, mainly due to the high uncertainty of the spectral estimation, and the inherent sensitivity to experimental

noise in this procedure.

This paper extends the results of [7] by estimating the frequency dependent attenuation and phase velocity of the gas mixtures using a parametric technique [8], and then using PLSR to estimate the gas composition.

B. Theory

When sound propagates through gases, two properties can be directly observed: speed of sound and attenuation. Both of these are frequency dependent. They depend on the details of underlying physics [3], [4], [9], [10]. Good physical models are crucial for the understanding of the problem, so that proper instrumentation can be designed. However, even if a good model of the underlying physics is available, the parameters of such a model are not necessarily identifiable from bandlimited ultrasound data. Furthermore, the end goal is not to describe the model, but to measure some implicit property (e.g. energy content or volume fractions). The choice of model should therefore depend on the objective of the study.

Using the pulse-echo setup described in Section C. we obtain two echoes that have traveled different distances through the gas mixture. Given these two echoes, we then estimate the frequency dependent attenuation and the phase velocity. These two quantities serve as input to a multivariate statistical calibration technique called Partial Least Squares Regression (PLSR) used to estimate the composition of the gas mixture.

B.1. Attenuation and phase velocity

Assuming linear acoustics, estimating the frequency dependent attenuation and phase velocity from ultrasound pulses essentially concerns estimation of the spectrum of a linear system $H(\omega)$, representing the gas mixture. Given the transfer function $H(\omega)$, we can calculate the attenuation $\alpha(\omega)$ and the phase velocity $c_p(\omega)$, where ω is the frequency (in rad/s). In the ultrasonic pulse-echo setup, the input and output signals $p_1(t)$ and $p_2(t)$ needed to identify $H(\omega)$ are defined as in Fig. 1.

The estimation procedure for determining $H(\omega)$ is described in detail in [8]. In addition to the estimate of $H(\omega)$, the identification procedure also yields an estimate of the covariance of the parameters of $H(\omega)$. This enables us to do the uncertainty analysis described in Sec. B.3..

From the estimate of $H(\omega)$ we calculate attenuation and phase velocity. Let each row, \mathbf{x}_n^T , of the matrix \mathbf{X} be the attenuation and phase velocity corresponding to a given volume fraction of CO_2 , sampled at the frequencies $\omega = \omega_k$, where $\omega_k = 2\pi F_s k/K$, $k = 0 \dots K-1$, K is the number of samples, and F_s is the sampling frequency. The volume fraction of CO_2 is then the corresponding row, y_n , of the response matrix \mathbf{Y} . That is

$$\mathbf{X} = \begin{bmatrix} \alpha_1^T & \mathbf{c}_1^T \\ \alpha_2^T & \mathbf{c}_2^T \\ \vdots & \vdots \\ \alpha_N^T & \mathbf{c}_N^T \end{bmatrix}, \quad \mathbf{Y} = \begin{bmatrix} y_1 \\ y_2 \\ \vdots \\ y_N \end{bmatrix} \quad (1)$$

where $\alpha_n = [\alpha(\omega_0) \quad \alpha(\omega_1) \quad \dots \quad \alpha(\omega_{K-1})]^T$, $\mathbf{c}_n = [c_p(\omega_0) \quad c_p(\omega_1) \quad \dots \quad c_p(\omega_{K-1})]^T$. Here, the subscript n denotes the n :th row of \mathbf{X} and \mathbf{Y} , corresponding to experiments with different volume fractions of CH_4 .

B.2. PLS Regression

The PLS method was developed by Herman Wold [11], and has been applied to many areas in experimental sciences. The details of the PLS calculations can be found in [7] and [12]. Here, only a brief summary is given.

The central idea of PLS, as opposed to principal component regression (PCR) and ordinary least-squares (OLS) estimation [13], is that PLS determines a set of basis functions (PLS components) for both the \mathbf{X} block and the \mathbf{Y} block, in such a way that they best describe the cross-covariance between the blocks. In other words, instead of looking at variations in phase velocity and attenuation alone (the \mathbf{X} block), we look at variation in \mathbf{X} that correlates with variation in \mathbf{Y} .

B.2.1. Predicting \mathbf{Y} from \mathbf{X}

Using Eqs. (3)–(11) in [7], the \mathbf{X} block and \mathbf{Y} block are first transformed into their PLS component representation,

$$\mathbf{X} = \mathbf{TP}^T + \mathbf{E}, \quad (2)$$

$$\mathbf{Y} = \mathbf{TQ}^T + \mathbf{F}, \quad (3)$$

where \mathbf{E} and \mathbf{F} are residual matrices of the \mathbf{X} and \mathbf{Y} blocks, respectively. Given an existing set of PLS components, the estimate of \mathbf{Y} is given by

$$\hat{\mathbf{Y}} = \mathbf{X}\tilde{\mathbf{W}}\mathbf{Q}^T, \quad (4)$$

where $\tilde{\mathbf{W}}$ and \mathbf{Q} are given by Eqs. (15) and (11) in [7], respectively. Here, the matrix $\tilde{\mathbf{W}}\mathbf{Q}^T$ is determined from a calibration experiment, and later used to estimate $\hat{\mathbf{Y}}$.

B.2.2. Determining PLS model order

As in all modeling, finding an appropriate model order is an important, and difficult, problem. There are numerous criteria available for model order selection, some which tend to overestimate the model-order, while others are overly conservative [14]. For PLS modeling problems, cross-validation is the most commonly used method [15].

In this paper we have one training data set to estimate a PLS model and one validation set. We evaluate the model

by looking at the Q^2 statistic [16] as a function of the number of components in the PLS model. For our experiments, we found that two PLS components is the best model order, which yields a Q^2 value of 0.9998.

B.3. Uncertainty analysis

The phase velocity and attenuation for each gas composition are estimated using the parametric model in [8]. Along with these estimates we also obtain a covariance matrix for the parameters of $H(\omega)$. This enables us to generate a randomized distribution of the attenuation and phase velocity curves, and eventually also a randomized distribution of the estimated gas compositions.

Given the covariance matrix for the model parameters, the following procedure is applied in order to obtain a randomized distribution of the estimated gas compositions:

1. Randomize a large number of model parameter vectors, given the covariance matrix, \mathbf{C}_θ , where θ is a vector with the parameters of the model $H(\omega)$ (i.e. the prior distribution).
2. Calculate the attenuation and phase velocity corresponding to each of the models.
3. For each randomized model, run the PLSR as described above, to obtain an empirical (posterior) distribution of the estimated gas compositions.
4. Estimate the uncertainty from the empirical distributions obtained in step 4.

Note that this procedure incorporates both uncertainty due to the noise in the ultrasonic measurements, as well as estimation errors from the PLSR step.

C. Experiments

C.1. Experimental design

In order to evaluate the performance of the proposed method, a series of experiments was designed. For all measurements, we used calibration gas mixtures from Air Liquide Gas AB (Kungsängen, Sweden) with an analysis uncertainty of 1 % (relative to the CO_2 content).

Experiments were made at a static pressure of 8 bar at room temperature (see details in the next section), for volume fractions of CO_2 of 0 %, 2 %, 4 %, 6 %, 8 %, and 10 %, respectively. The order of the experiments was randomized in order to avoid misinterpretations due to systematic variations in any ambient variables beyond our control.

C.2. Setup

For all the experiments in this paper, the ultrasound echoes were measured in a pulse-echo configuration (see Fig. 1). A 300 kHz air transducer (D-Flow Technology AB, Luleå, Sweden) was mounted in a measurement cell, transmitting pulses through the gas towards a spherical stainless steel reflector. As input to the phase velocity and attenuation estimation algorithm, the second and fourth echo, as indicated in Fig. 1, were used. The reason for not using the first echo was that it contained some traces from the excitation. The fourth echo was exploited instead

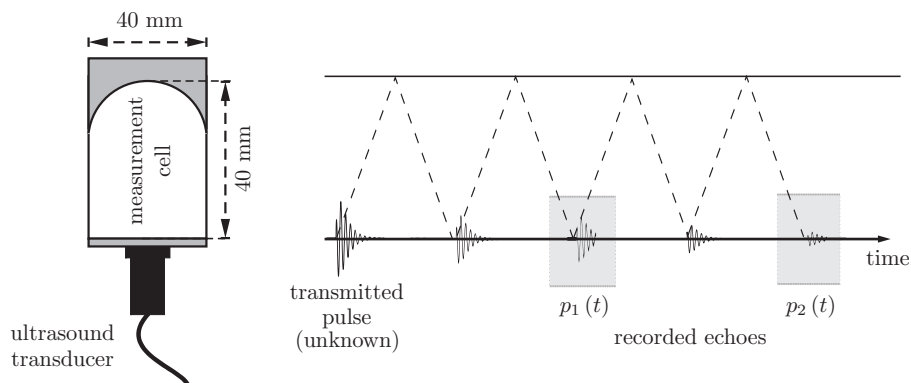


Fig. 1. The measurement cell and the pulse-echo principle. The transducer emits an unknown sound wave. The reflections from the bottom of the measurement cell is then recorded. Consecutive echoes can be recorded, as indicated in the figure. In this paper, the second and the fourth echo are used, denoted $p_1(t)$ and $p_2(t)$, respectively.

of the third in order to maximize the propagation path and thus amplify the effects of dispersion and attenuation in the gas mixture.

A custom-built pressure chamber was used to achieve the desired static pressures. For the experiments presented here, the static pressure was set to 8.0 bar ± 0.01 bar. The pressure in the chamber was measured with an *ANDERSON TPP Pressure Transmitter*.

To excite and receive ultrasound pulses, a *Panametrics Pulser/Receiver Model 5052* was used. In transmitting mode, the pulser/receiver was set to deliver maximum energy to the transducer, which corresponds to a short voltage peak with 380 V amplitude with an energy of 104 μJ . In the measurements presented here, the gain of the pulser's receiver input was set to 40 dB.

All pulses were sampled at 100 MHz using a 14-bit *CompuScope 14100* oscilloscope card (Gage Applied Technologies Inc., Lachine, QC Canada). The pulses were later down-sampled 12 times off-line to reduce the amount of data to process.

For each measurement, the temperature was recorded using an encapsulated PT100 probe mounted through the wall of the pressure chamber. The average temperature of the gas mixtures throughout the measurements was 20.4 $^{\circ}\text{C} \pm 0.2$ $^{\circ}\text{C}$ ($\pm \sigma$), where σ is the standard deviation of all measured temperatures.

D. Results

Figures 2 and 3 show the results of from the parametric estimation of attenuation and phase velocity, respectively. Fig. 2 shows the result for pure CH_4 and for a mixture containing 10 % CO_2 and 90 % CH_4 . Fig. 2 also presents the corresponding $\pm 2\sigma$ intervals, estimated using the procedure described in Sec. B.3.. For the phase velocity, Fig. 3 illustrates all estimates. From the figure we see that there is a significant change in phase velocity as the composition of the gas mixture changes. In Fig. 3 no uncertainty intervals are shown, for the simple reason that they are much too narrow to be visible in the plot.

The attenuation and phase velocity estimates then served as input to the PLSR step. The PLS model was built from one experiment series, and the estimates in Fig. 4 were ob-

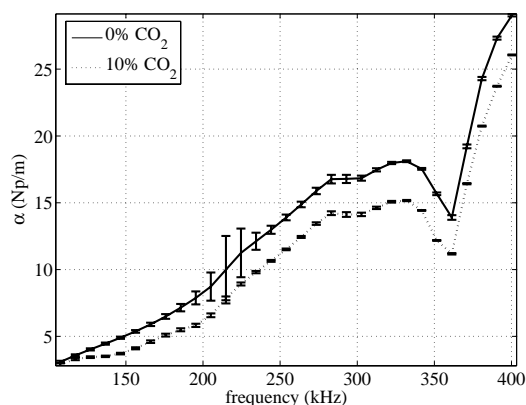


Fig. 2. Estimated attenuation coefficients α (in Np/m) as a function of the frequencies present in the pulse, for 0 % and 10 % CO_2 . The error bars indicate the $\pm 2\sigma$ uncertainties. The corresponding curves for volume fractions of 2 %, 4 %, 6 %, and 8 % lie in between these curves and have been left out for the sake of clarity.

tained using a repeated experiment. Fig. 4 shows that accurate estimates of the CO_2 volume fractions were obtained. Studying the uncertainty intervals ($\pm 2\sigma$) we also note that the resolution is excellent, enabling the measurement of small changes in CO_2 content.

E. Discussion

The use of a spherical reflector in the measurement cell (see Fig. 1) could cause bias errors in the estimates of phase velocity and attenuation, since the distance from the transducer surface to the reflector is not unambiguously known in the current setup. For this reason, we can not claim that the measurements of phase velocity and attenuations are correct, to an absolute value. However, since the PLS regression step explores *variations* in these properties and not absolute values, the nature of the setup should not affect the final estimate of the CO_2 and CH_4 content.

As in all ultrasound measurement systems, environmental factors such as pressure and temperature fluctuations, will affect the measured ultrasound pulses. Pressure and temperature can be measured and incorporated into the

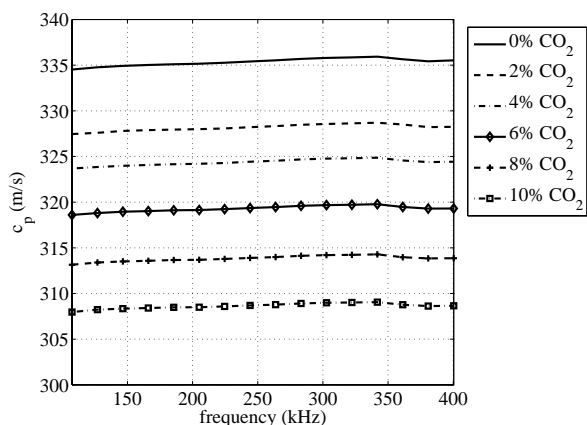


Fig. 3. Estimated phase velocities c_p (in m/s). The figure shows the average value over 10 000 estimates. The uncertainties are too small to be shown in the plot.

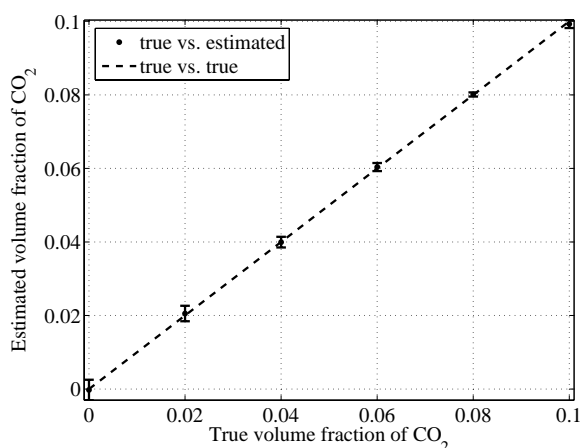


Fig. 4. True vs. estimated volume fractions of CO_2 . The error bars indicate the $\pm 2\sigma$ interval for each estimated volume fraction.

PLS regression model, or if their effects are known, into the estimates of the attenuation and phase velocity. Even if changes in pressure and temperature are monitored, they are likely to decrease the performance of the estimator unless they are properly taken care of. This will be addressed in future research. However, for the small changes observed in the experiments presented in this paper, no significant effect on the estimated volume fractions should be expected.

F. Conclusions

In this paper we have demonstrated how the principle of PLS regression (PLSR) can be combined with parametric estimation of frequency dependent attenuation and phase velocity to obtain accurate estimates of the quality of upgraded biogas. We show that under constant pressure and temperature conditions, the volume fraction of CO_2 can be accurately estimated with high repeatability, using a technique based solely on ultrasonic pulse-echo measurements. Since the gas is a binary mixture of CO_2 and CH_4 , this also gives an estimate of the CH_4 content, which is the dominant factor when assessing the quality of upgraded biogas.

G. Acknowledgements

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H. Literature

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