

Nationellt Samverkansprojekt Biogas i Fordon



Mätning av energi och sammansättning av gasblandningar med ultraljud

610402

ISSN 1651-5501

Projektet delfinansieras av Energimyndigheten

Mätning av energi och sammansättning av gasblandningar med ultraljud

Slutrapport 2004

Johan E. Carlson och Jerker Delsing

EISLAB
Inst. för Systemteknik
Luleå tekniska universitet
971 87 Luleå

Epost: Johan.Carlson@ltu.se

Sammanfattning

Denna rapport är en sammanställning av det arbete som utförts vid EISLAB, Luleå tekniska universitet inom ramen för samverkansprojektet *Biogas i fordon*. Projektet syftar till att utveckla en mätmetod baserad på ultraljud som (on-line) kan mäta energivärde och sammansättning av bio- och naturgas.

Under 2004 har grundläggande teoretisk forskning sammanställts i form av en doktorsavhandling. Resultaten visar hur utbredningen av ultraljud i gaser påverkas av gasernas molekylära sammansättning. Med hjälp av multivariata statistiska metoder har det även påvisats att värdefull information kan extraheras från uppmätta ultraljudspulser. Preliminära experimentella resultat visar att denna information korrelerar väl med gasernas sammansättning.

Under 2004 har projektet resulterat i följande akademiska publikationer:

- En doktorsavhandling (försvarad offentligt 20 september 2004).
- Ett arbete publicerat i samband med en internationell konferens.
- Två artiklar inskickade till vetenskapliga tidskrifter.

Summary

This report summarizes the results of the work performed at EISLAB, Luleå University of Technology, within the framework of the program "Biogas as a Vehicle Fuel". The goal of the project is to develop a measurement methodology based on ultrasound for on-line measurement of energy content and composition of biogas and natural gas.

During 2004, results of fundamental theoretical research have been summarized in a doctoral thesis. The results show that propagation of ultrasound is affected by the molecular properties of the constituent gases. With the help of multivariate statistical methods it has also been shown that valuable information can be extracted from measured ultrasound pulses. Preliminary experimental results show that this information correlates well with the composition of the gas mixtures.

During 2004, the project resulted in the following scientific publications

- One doctoral thesis (PhD), defended on September 20, 2004.
- One paper presented at an international conference.
- Two articles submitted reviewed scientific journals.

Bakgrund

Biogas har pekats ut som ett alternativ till diesel och bensin och det finns en starkt uttalad vilja att öka andelen biogas som drivmedel inom transportsektorn. Det är därför av intresse för både leverantörer och producenter att kunna mäta energiinnehåll och sammansättning hos biogas. Detta för att få tillförlitlighet i slutprodukten.

Man beräknar också att användandet syntetgas (kolmonoxid och vätgas) kommer att öka. I syntesprocessens olika steg förekommer olika gasblandningar, och för att optimera processen och säkra kvaliteten i slutprodukten finns ett behov av att kunna mäta sammansättningen av dessa gasblandningar. Liknande problem finns även inom petrokemisk industri, vid framställandet av olika industrigaser. Olika gaser skickas mellan olika processer och idag saknas billiga och tillförlitliga metoder för kvalitetsmätning on-line av dessa.

Naturgas som importeras till Sverige kommer från flertalet olika källor i Europa, vilket medför att gasblandningens sammansättning kan variera över tiden. Detta påverkar gasens energivärde, och därmed också elproduktionen. En korrekt mätning av energivärdet därför viktig, för korrekt debitering av levererad energi. För att undvika haverier i gasturbinerna är det önskvärt med en snabb och robust reglering av kraftproduktionsprocessen.

I dagsläget saknas on-line-metoder som är snabba, pålitliga, enkla och billiga.

En generell ultraljudmetod skulle kunna användas för bio-, natur- och syntetgas, och skulle därför vara intressant både inom petro- och processindustrin och för producenter och leverantörer av gas för drivmedels- och elproduktion.

Ultraljud har även visats vara användbart för mätning av gas- och vätskeflöden. På lite längre sikt är det därför troligt att en ultraljudsmetod kan användas både för gasanalys och för gasflödesmätning.

Tidigare arbete¹ visar att ultraljud är en potentiell metod för att mäta energiinnehåll i bio- och naturgas. Metoden baseras på mätning av olinjära effekter i gasens ljudhastighet. Dessa effekter beror av trycket, temperaturen och ljudets frekvens. Arbetet visar att om dessa storheter kan mätas separat, erhåller vi de ekvationer som kan användas till att analysera blandingsförhållandet för upp till sex ingående gaskomponenter.

En doktorand har under de senaste fyra åren jobbat med att teoretiskt modellera hur olika gasers molekylära sammansättning påverkar dess akustiska egenskaper². Detta för att kunna förutsäga och modellera de storheter som sedan mäts med ultraljud.

Andra resultat³ visar hur man kan kombinera ultraljudmätningar med metoder för multivariat dataanalys, för att på så sätt komma åt gasblandningens komposition (molsamband mellan de ingående komponenterna).

Syfte

På lång sikt är målet med projektet att ta fram en ultraljudsmetod som, on-line, kan:

- Mäta energivärde för en gasblandning och energiflöde för gasflöden.

- Detektera förekomsten av föroreningar i gasen.
- Bestämma koncentrationen av de olika komponenterna i gasblandningen.

I det delprojekt som denna rapport avser har målet varit att sammanställa teoretiska modeller som ska ligga till grund för fortsatt forskning, samt att genomföra inledande praktiska mätningar.

Genomförande

Genomförda delmål

Förutom att sammanställa de teoretiska resultaten i en doktorsavhandling har inledande experiment genomförts enligt projektplanen i ansökan. Utöver detta har en vidareutveckling av den laborativa miljön inletts. Nya mätinstrument har införskaffats och förbättrad programvara är under utveckling.

Resultat

I projektbeskrivningen som låg till grund för den beviljade finansieringen för 2004, angavs följande mål för 2004: *Praktiska mätningar för verifiering och sammanställning av teoretiska modeller.*

De teoretiska modellerna har sammanställts, huvudsakligen i form av en doktorsavhandling av Pär-Erik Martinsson. Praktiska mätningar och resultat av dessa presenteras i de artiklar som antingen publicerats eller skickats in för publicering. Förutom doktoranden Pär-Erik Martinsson som disputerat den 20 september, har en efterföljare, Jesper Martinsson, anställts i projektet.

Under 2004 har projektet resulterat följande vetenskapliga publikationer:

- P.-E. Martinsson, "Characterization of energy gases by ultrasound - Theory and experiments", Ph.D. Thesis, Sept 2004.
- J. E. Carlson and P.-E. Martinsson, "Ultrasonic Measurement of Molar Fractions in Gas Mixtures by Orthogonal Signal Correction", in Proc. of IEEE Int. Ultrason. Symp. (Montreal, Canada), August 24-27, 2004.
- J. E. Carlson and P.-E. Martinsson, "Ultrasonic Volume Fraction Measurement in Two-Component Gas Mixtures Using Orthogonal Signal Correction and Principal Component Analysis", Inskickad för publicering i *J. Acoust. Soc. Am.* Under revision för publicering.

Artikeln behandlar en statistisk metod för att isolera akustiska effekter som uppstår när man blandar gaser. Dessa effekter kan inte beskrivas utifrån observationer av de olika gaskomponenterna var och en för sig, men uppvisar ett tydligt samband med sammansättningen av gasblandningen.

- J. E. Carlson and R. Carlson, "Prediction of Molar Fractions in Two-Component Gas Mixtures Using Pulse-Echo Ultrasound and PLS Regression", Inskickad för publicering i *IEEE Trans. on Ultrason., Ferroelec., and Freq. Contr.* Under granskning.

Artikeln visar hur PLS Regression (Partial Least Squares) kan användas för att

uppskatta halten etan i en blandning av etan och syrgas. Artikeln beskriver teorin bakom PLS och redovisar experimentella resultat där sammansättning, tryck och temperatur varierats.

Doktorsavhandlingen och konferensbidraget bifogas denna rapport. Övriga artiklar genomgår granskning och kommer att översändas när de accepterats för publicering.

Framtida arbete

Det teoretiska arbetet visar att utbredningshastighet och dämpning av ultraljud ändras på olika sätt beroende på vilka gaser som ingår i blandningen. Dessa egenskaper är frekvensberoende och utgör i sig ett erkänt besvärligt mättekniskt problem. Arbetet har påbörjats för att ta fram en robust modellbaserad metod för bestämning av dessa egenskaper.

Den laborativa miljön är under utveckling och mätningar på bio- och naturgasblandningar kommer att genomföras.

Hittills uppnådda resultat har visat att multivariata statistiska metoder kan användas för att isolera systematisk variation i ultraljudssignalerna som härstammar från sammansättningen av gasblandningarna. En koppling av dessa observerade data och fysikaliska modeller för vågutbredning måste utvecklas för att åstadkomma en robust mätmetod.

Projektet kommer under 2005 att drivas med stöd från SGC ramprogram.

Slutsatser

Resultaten av årets arbete visar att metoden har mycket goda möjligheter att uppnå de långsiktiga målen. Det teoretiska arbetet visar hur olika gaser påverkar utbredning av ultraljud och de experimentella resultaten visar att det går att extrahera värdefull information ur uppmätta pulser. Denna information kan sedan kopplas till de fysikaliska modellerna med hjälp av multivariata statistiska metoder. Experimentet har genomförts för varierande gastryck och temperatur och resultaten visar att det bör vara möjligt att utveckla en metod som hanterar denna typ av variationer i omgivningen.

Referenser

1. J. Delsing and I. Blom, "On-Line Measurements of Energy Content of Bio Gas and Natural Gas Mixtures," Tech. Rep. ISSN: 0282-3772, Lund Institute of Technology, 1995.
2. P.-E. Martinsson and J. Delsing, "Ultrasonic Measurements of Molecular Relaxation in Ethane and Carbon Monoxide," in Proc. IEEE Int. Ultrason. Symp., (Munich, Germany), pp. 494–499, IEEE, October 8–11 2002.
3. P.-E. Martinsson and J. E. Carlson, "Investigating the Feasibility of Using Principal Component Analysis for Ultrasonic Classification of Gas Mixtures," in Proc. IEEE Int. Ultrason. Symp., (Honolulu, Hawaii, USA), pp. P1K–6, IEEE, Oct. 5–8 2003.

Ultrasonic Measurement of Molar Fractions in Gas Mixtures by Orthogonal Signal Correction

J. E. Carlson*, P.-E. Martinsson

EISLAB, Dept. of Computer Science and Electrical Engineering, Luleå University of Technology, SE-971 87 Luleå, Sweden.

*Email: Johan.Carlson@csee.ltu.se

Abstract—Within Sweden and the EU, an increased use of biogas and natural gas is encouraged. To support more effective manufacturing, distribution, and consumption of energy gases, new methods for the measurement of the calorimetric value or the gas composition are needed.

In this paper we present a method to quantify variation in ultrasound pulse shape, caused by interaction effects between the constituents of a two-component gas mixture.

The method is based on a combination of *Principal Component Analysis* [1] and *Orthogonal Signal Correction* [2]

Experiments on mixtures of oxygen and ethane show that the extracted information correlates well with the molar fraction of ethane in the mixture.

I. INTRODUCTION

Natural gas contains a mixture of several gases, like methane, ethane, hydrogen, etc. Sometimes also small, but highly undesired fractions of oxygen. With the use of different sources of gas (i.e. different gas fields) the energy content of the gas delivered to customers may vary considerably. Variations up to 20% are common [3]. It is of interest to both provider and customer to know the composition of such gas mixtures, since this determines the energy content (calorimetric value) and thus, the combustion properties and the monetary value of the gas.

Today, the energy content of gases is measured using either gas chromatography or calorimetry. Both methods are accurate, but require samples of the gas to be removed and analyzed separately, which makes them relatively slow. They are also relatively expensive. Because of this, the existing techniques are not suitable for on-line measurement at the customer side of the distribution line.

Typically, both the speed of sound and the attenuation of sound within a gas vary with temperature, frequency, pressure, etc. Hence, both these parameters can help to monitor changes in experimental conditions. This has recently been studied in both theory and experiments by Dain and Lueptow [4], [5], Martinsson [6], and Townsend and Meador [7].

The frequency dependence of the attenuation is fairly easy to measure, but the speed of sound is much more difficult [8]. Both of these affect the shape of the received pulse. In this paper we develop a method to empirically quantify changes in pulse shape, and evaluate this for mixtures of oxygen and ethane.

Fig. 1 shows three pulses obtained using the experimental setup described in Sec. III-A. The first pulse was measured in pure oxygen, the second in pure ethane, and the third in a mixture of the two, containing molar fraction of 40% of

ethane. As the figure shows, there is a small change in pulse shape between pure oxygen and ethane. It is, however, more difficult to notice how this changes when mixing the gases.

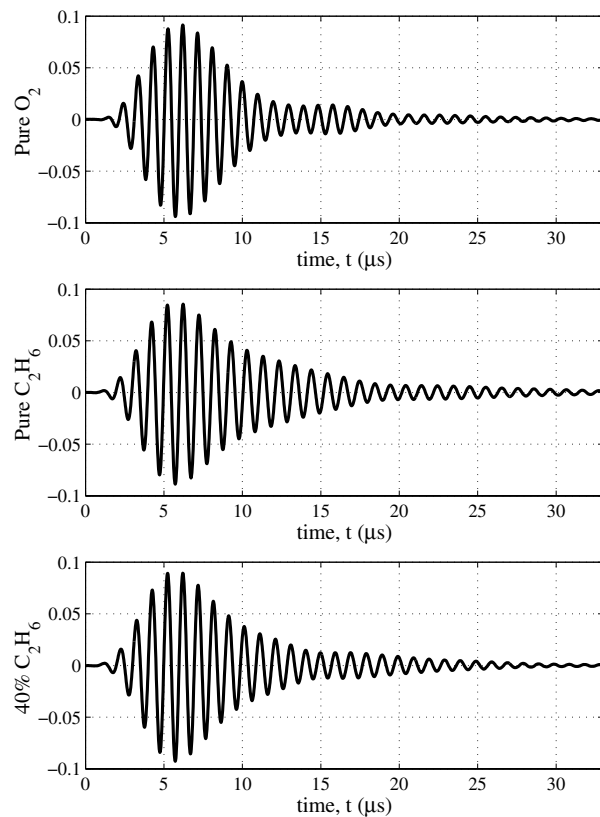


Fig. 1. Example of pulses measured in pure oxygen, pure ethane, and a mixture with a molar fraction of 40% ethane, all measured at a static pressure of 5.0 bar. The temperature was 20 °C.

In this paper, we develop a subspace-based filter, that can be used to suppress variations in pulse shape originating from the pure gases. The filter is based on a principle known as *Orthogonal Signal Correction* (OSC) [2]. Pulses measured in a mixture will be affected by the pure gases, and by the inter-gas interaction effects. These interaction effects are much smaller than the effects of the pure gases, but highly interesting when the goal is to study the composition a mixture. The OSC filter is implemented as a projection matrix that projects the measured pulses onto the orthogonal complement of a basis spanning the experimental variation caused by the pure gases. The remaining experimental variation is then analyzed using PCA [1].

The technique is evaluated with experiments on pure oxygen (O_2), pure ethane (C_2H_6), and mixtures of the two, for molar fractions of ethane in the range of 20%–80%. The results show that the remaining variation can be explained by one principal component, which correlates well with the molar fraction of ethane.

II. THEORY

Principal Component Analysis (PCA) [1] is a powerful tool for analyzing multivariate data. The central idea is to reduce the dimensionality of a data set consisting of a large number of interrelated variables, but at the same time preserving as much as possible of the systematic experimental variation in the data.

In the experiments (see Sec. III-B), we have two data sets. The first containing pulse-echo measurements of pure oxygen and pure ethane, and the second containing measurements on mixtures of the two. If the effects of oxygen and ethane were to add linearly when mixing the two, the dimensionality of the data set would not increase. That is, the same principal components could be used to describe the experimental variation in both data sets. If, however, there are any interaction effects between the gases in the mixture, we would need some additional principal components to describe these (i.e. the dimensionality of the data set is increased). Now, if the interaction effects are small, which they will certainly be when the molar fraction of one of the gases is small, they will be practically drowned by the effects of the pure gases.

If the goal is to quantify the effect of mixing gases we need some method to remove the effects originating from the pure gases. The way we approach this problem is by *Orthogonal Signal Correction* (OSC) [2]. This process can be seen as a filter, suppressing the effects of the pure gases by projecting the whole data set onto a subspace *orthogonal* to the subspace spanned by the pure gases. In order to do this, we first need to find a basis for the variation caused by the pure gases. This is obtained by performing a PCA on the first data set (containing only measurements of pure gases). For this to work, the data set has to be pre-processed to remove the effect of propagation delay and scalar attenuation. This information is, of course, still accessible, but by removing these effects, we do not *a priori* assess any greater significance to any of the measured pulses, even if they are more attenuated. The aim here is to study changes in pulse shape.

The next subsection will describe the pre-processing of the ultrasound pulses, and Sec. II-B then describes the OSC and the PCA.

A. Pre-Processing

The pre-processing consists of two steps:

- 1) Normalizing the pulses to unit energy, thus removing the effect of a scalar attenuation due to the propagation distance.
- 2) Aligning the pulses in time and thereby removing the effect of changes in propagation delay through the medium, and the effect of any sampling jitter caused by the digitizing hardware.

The time-delay estimation is done by combining a standard cross-correlation estimator (to obtain an estimate in whole samples), and then refining the estimate using the sub-sample estimator by Grennberg and Sandell [9].

B. Orthogonal Signal Correction

After the pre-processing, we are left with a set of measurements that essentially vary only in pulse shape. In this section, we describe the remaining steps of the analysis, that is:

- 1) Find a basis for the experimental variation caused by the pure gases (PCA), for oxygen and ethane, for different static pressures.
- 2) Project the measurements of mixtures onto the orthogonal complement of the basis determined in step 1 (OSC).
- 3) Find a new basis for the remaining experimental variation (PCA).

Let \mathbf{X}_0 be a matrix where the columns are pulses measured in pure oxygen (O_2) and pure ethane (C_2H_6), for different pressures. Let \mathbf{X}_1 be the matrix with columns corresponding to mixtures of the gases, each representing different molar fractions of ethane.

Finding a basis of for the experimental variation spanned by the columns of \mathbf{X}_0 means determining the principal components (PC:s) of \mathbf{X}_0 . In this paper, the PCA is implemented using *Singular Value Decomposition* (SVD) [10]. With the SVD, any rank r matrix \mathbf{X}_0 can be factored as:

$$\mathbf{X}_0 = \mathbf{U}_0 \mathbf{S}_0 \mathbf{V}_0^T, \quad (1)$$

where the columns of \mathbf{U}_0 and \mathbf{V}_0 are the unit-norm eigenvectors of $\mathbf{X}_0 \mathbf{X}_0^T$ and $\mathbf{X}_0^T \mathbf{X}_0$, respectively. The non-zero diagonal elements, σ_i of \mathbf{S}_0 are the square-roots of the eigenvalues of $\mathbf{X}_0 \mathbf{X}_0^T$ and $\mathbf{X}_0^T \mathbf{X}_0$, sorted so that $\sigma_1 \geq \sigma_2 \geq \dots \geq \sigma_r$. This can be seen as a change of basis, where the new basis for the columns of \mathbf{X}_0 is given by the columns of \mathbf{U}_0 (also called *principal components* or *loading vectors*), and the weights for the new basis (*scores*) are given by the columns of $\mathbf{S}_0 \mathbf{V}_0^T$.

The change of basis means that all pulses (columns of \mathbf{X}_0) can now be represented as a linear combination of the columns in \mathbf{U}_0 , using the weights in $\mathbf{S}_0 \mathbf{V}_0^T$.

To examine how much of the total experimental variation (in %) each column in \mathbf{U}_0 explains, we study the scaled singular values. Let $\bar{\sigma}_i$ be scaled versions of the r non-zero singular values σ_i , as

$$\bar{\sigma}_i^2 = 100 \frac{\sigma_i^2}{\sum_{k=1}^r \sigma_k^2}. \quad (2)$$

Now, if the effects of the constituent gases would add linearly, then the same set of basis vectors (columns of \mathbf{U}_0) would also span the variations in pulse shape caused by the gas mixtures. That is, the columns of \mathbf{X}_1 could all be written as linear combinations of the columns of \mathbf{U}_0 . If this is not the case, a basis for the additional variation, i.e. inter-gas interaction effects, will be given by $\tilde{\mathbf{U}}_1$, where

$$\tilde{\mathbf{X}}_1 = \tilde{\mathbf{U}}_1 \tilde{\mathbf{S}}_1 \tilde{\mathbf{V}}_1^T, \quad (3)$$

where

$$\tilde{\mathbf{X}}_1 = \mathbf{\Pi}_{\mathbf{X}_0}^\perp \mathbf{X}_1, \quad (4)$$

i.e. the SVD of the matrix \mathbf{X}_1 , after projecting onto the orthogonal complement of \mathbf{X}_0 . The projection matrix $\mathbf{\Pi}_{\mathbf{X}_0}^\perp$ is given by [10]:

$$\mathbf{\Pi}_{\mathbf{X}_0}^\perp = \mathbf{I} - \hat{\mathbf{U}}_0 \left(\hat{\mathbf{U}}_0^T \hat{\mathbf{U}}_0 \right)^{-1} \hat{\mathbf{U}}_0^T, \quad (5)$$

where $\hat{\mathbf{U}}_0$ is the matrix consisting of the n ($n < r$) most significant components of \mathbf{U}_0 . This is determined by looking at the cumulative sum of the scaled singular values from Eq. (2).

Since the columns of $\hat{\mathbf{U}}_0$ are by construction orthonormal [10], Eq. (5) simplifies to

$$\mathbf{\Pi}_{\mathbf{X}_0}^\perp = \mathbf{I} - \hat{\mathbf{U}}_0 \hat{\mathbf{U}}_0^T, \quad (6)$$

In other words, we can say that the columns of $\tilde{\mathbf{U}}_1$ form a basis for the experimental variation that remains after removing the contribution of the pure gases. The matrix $\mathbf{\Pi}_{\mathbf{X}_0}^\perp$ in Eq. (6) projects the data in \mathbf{X}_1 onto a smaller subspace, orthogonal to the subspace spanned by $\hat{\mathbf{U}}_0$. This is why this process is called *Orthogonal Signal Correction*.

C. Summary of the Algorithm

The analysis principle described in the previous sections can be summarized as:

- 1) Normalize and align the pulses as described in Sec. II-A.
- 2) Calculate principal components (\mathbf{U}_0) of the pure gases using Eq. (1).
- 3) Remove the effect of the pure gases from the gas mixture, using Eq. (4).
- 4) Determine the principal components, $\tilde{\mathbf{U}}_1$, of the remaining variation ($\tilde{\mathbf{X}}_1$), using Eq. (3).

III. EXPERIMENTS

A. Experimental Setup

A pulse echo measurement scheme was used to measure the attenuation and speed of sound for oxygen and ethane. The acoustic properties of interest vary with frequency, f , and pressure, P . The temperature and frequency dependence on sound velocity and acoustic attenuation, has previously been investigated by, for example, Martinsson [6], Lueptow [4], [5], and Bhatia [11]. Changes in frequency and pressure are normally studied as the ratio f/P [4]. In this paper, a 1 MHz air transducer was used while the static pressure was varied.

A custom-built pressure chamber (see Fig. 2) was used to achieve different static pressures. The pressure was varied between 1.54 to 7.4 bar in 12 steps for each gas. Since the attenuation in ethane is extremely high at low pressures and high frequencies, we were limited to make measurements at higher pressure for that particular gas (above 1.86 bar).

The pressure in the chamber was measured with an *ANDERSON TPP Pressure Transmitter*. The transmitter has an accuracy of approximately 30 mbar. This includes the combined effects of linearity, hysteresis and repeatability.

The transducer was mounted on a stainless steel measurement cell, as seen in the lower left corner of Fig. 2. The measurement cell was then immersed into the pressure chamber. The whole setup was then placed in a temperature controlled

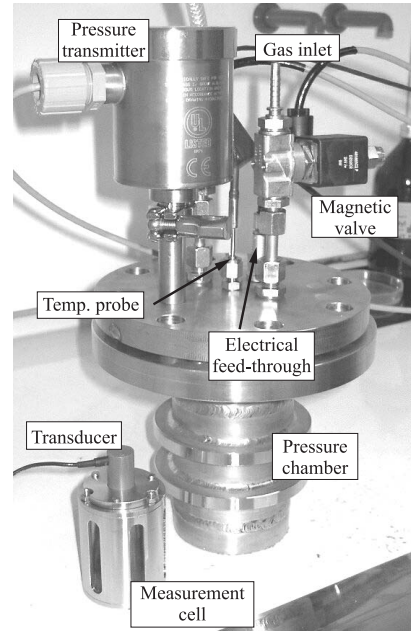


Fig. 2. The measurement equipment. All measurements were performed in a pressure chamber. The pressure was varied between 1.54 bar and 7.4 bar. The air transducer has a center frequency of 1 MHz.

chamber (*Heraeus Vötsch HT4010*), where the temperature could be kept at a constant.

To excite and receive acoustic pulses from the transducer, a *Panametrics Pulser/Receiver Model 5072* was used.

All pulses were sampled with a *Tektronix TDS 724*, 1 GHz oscilloscope. For each experimental setting, 50 pulses were recorded and transferred to a PC for further processing.

For each measurement, the temperature was recorded using an encapsulated PT100 sensor mounted through the wall of the pressure chamber.

B. Experiments

The first set of experiments was with pure ethane and pure oxygen, at 20 °C, for pressures of 1.54–7.4 bar. This resulted in 12 measurements of ethane and 12 of oxygen. After aligning and normalizing, as described in Sec. II-A, all 24 were stored as columns of the matrix \mathbf{X}_0 . The second set of experiments was with mixtures of ethane and oxygen, for molar fractions of 20%, 40%, 60%, and 80%, for the same pressure range, also at 20 °C. These pulses were then stored as columns of the matrix \mathbf{X}_1 .

C. Results

Following the steps of described in Sec. II-C, we first obtain a basis for the experimental variation in the pure gases. The basis vectors (Principal Components) are the columns of \mathbf{U}_0

Looking at the cumulative sum of the scaled eigenvalues (Eq. (2)), $\bar{\sigma}_i^2$, we saw that the first three components are enough to describe approximately 99% of the total experimental variation (c.f. Fig. 3). The matrix $\tilde{\mathbf{U}}_0$ is thus given by the first three columns of \mathbf{U}_0 .

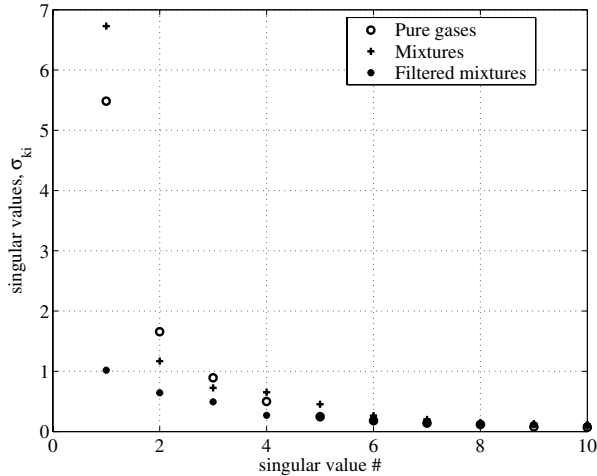


Fig. 3. Singular values of the pure gases (\mathbf{X}_0), the mixtures \mathbf{X}_1 and the mixtures after projection $\tilde{\mathbf{X}}_1$. It is clear that the pure gases contributes to most of the variation. The filtering reveals the relatively small interaction effects.

The OSC processing removes all experimental variation already explained by the linear effects of the pure gases. The remaining variation is significantly smaller and lies close to the noise level (c.f. Fig. 3). The interaction effects can essentially be described using only one of the principal components of $\tilde{\mathbf{X}}_1$.

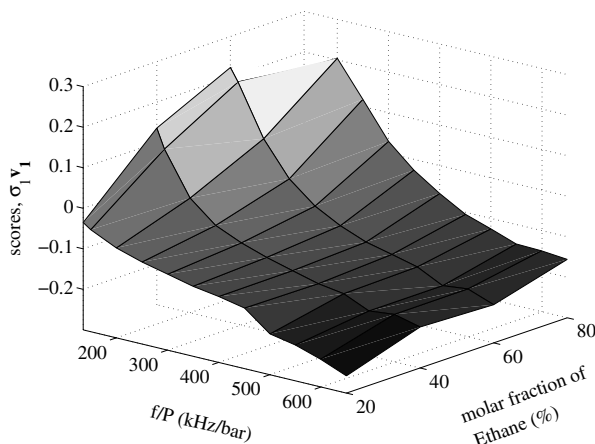


Fig. 4. Scores of the first principal component, $\tilde{\sigma}_1 \tilde{\mathbf{v}}_1$, of $\tilde{\mathbf{X}}_1$, as function of frequency to pressure ratio and molar fraction of ethane.

Fig. 4 shows the *scores* of the first component, as function of frequency to pressure ratio (f/P) and molar fraction of ethane. For high f/P values, the acoustic attenuation is very high, and the signal-to-noise-ratio (SNR) drops. For these f/P values, the inter-gas interaction effects are almost drowned by the experimental noise, and thus become difficult to extract. This can be seen in Fig. 4 as the surface reaches an almost constant level. For higher SNR, there is a strong correlation between molar fraction of ethane and the scores of the first principal component. This suggests that the inter-gas interaction effects can be quantified with this technique.

IV. DISCUSSION

The results presented in this paper show that it is possible to quantify effects on the shape of an ultrasound pulse, stemming from interaction effects between the constituent gases in a mixture. A question that we have not considered in this paper is *what underlying physical properties cause these interaction effects?*. Current research focuses on studying these phenomena, but to date, it is not possible to draw any conclusions regarding this.

In Fig. 4 there is a ridge for high pressures and approximately 50% of ethane. At first this might seem odd, but looking more closely at the algorithm it makes perfect sense. The OSC procedure removes variations in pulse shape, already described by the pure gases. When one of the gases are dominant in the mixture, the interaction effects should also be much smaller. The corresponding scores in Fig. 4 should therefore be almost zero under these conditions. For high pressures (low f/P values), i.e. when the SNR is high, the OSC process also succeeds in removing most of the variation. For low SNR values, this is not the case, which also shows in the lower right corner of Fig. 4.

In this paper we have only considered a two-component gas mixture. The long-term goal is to develop method for on-line measurement of the energy content of energy gases. In practice, these are always mixtures of more than two gases. Although molar fractions would enable us to calculate the energy content, it might be easier to quantify the energy content directly, using the same methodology as described in this paper.

In Sec. II-A, we mention the importance of aligning the pulses in time before processing. If this is not done, the time-delays will cause the dimensionality to increase (i.e. more principal components are needed). Compensating for the time-delays is more difficult than one might think. The change in pulse shape that we are interested in quantifying, is also a source of error when we try to estimate the time-delays. The reason for this is that the time-delay between pulses with different shape is not well-defined. Future research will have to incorporate a more accurate alignment algorithm.

V. CONCLUSIONS

In this paper we presented a technique for quantifying inter-gas interaction effects in a two-component gas mixture. The principles of *Principal Component Analysis* and *Orthogonal Signal Correction* were used to extract variations in the ultrasound pulse shape, not explained by looking at the constituent gases by themselves.

The experimental results show that, for a mixture of oxygen an ethane, the interaction effects can be described with only one principal component, and that the weights (coefficients) of this component correlate well with the molar fraction of ethane in the mixture.

VI. ACKNOWLEDGMENTS

The authors wish to express their sincerest gratitude toward Prof. Jerker Delsing, for supporting this work. Generous grants from the *Swedish Energy Agency* are also gratefully acknowledged.

REFERENCES

- [1] I. T. Jolliffe, *Principal Component Analysis*. New York: Springer Verlag, 2nd ed., 2002.
- [2] S. Wold, H. Antti, F. Lindgren, and J. Öman, "Orthogonal Signal Correction of Near-Infrared Spectra," *Chemometrics and Intelligent Laboratory Systems*, vol. 444, pp. 175–185, 1998.
- [3] J. Delsing and I. Blom, "On-Line Measurements of Energy Content of Bio Gas and Natural Gas Mixtures," Tech. Rep. ISSN: 0282-3772, Lund Institute of Technology, 1995.
- [4] Y. Dain and R. M. Lueptow, "Acoustic Attenuation in Three-Component Gas Mixtures - Theory," *J. Acoust. Soc. Am.*, vol. 109, pp. 1955–1964, 2001.
- [5] Y. Dain and R. M. Lueptow, "Acoustic Attenuation in Three-Component Gas Mixtures - Results," *J. Acoust. Soc. Am.*, vol. 109, pp. 1974–1979, 2001.
- [6] P.-E. Martinsson and J. Delsing, "Ultrasonic Measurements of Molecular Relaxation in Ethane and Carbon Monoxide," in *Proc. IEEE Int. Ultrason. Symp.*, (Munich, Germany), pp. 494–499, IEEE, October 8–11 2002.
- [7] L. W. Townsend and W. E. Meador, "Vibrational Relaxation and Sound Absorption and Dispersion in Binary Mixtures of Gases," *J. Acoust. Soc. Am.*, vol. 99, pp. 920–925, 1995.
- [8] J. E. Carlson, F. Sjöberg, and P.-E. Martinsson, "A Noise-Tolerant Group Delay Estimator Applied to Dispersion Measurement in Gases," in *Proc. IEEE Int. Ultrason. Symp.*, (Honolulu, Hawaii, USA), pp. 254–257, IEEE, Oct. 5–8 2003.
- [9] A. Grennberg and M. Sandell, "Estimation of Subsample Time Delay Differences in Narrowband Ultrasonic Echoes Using the Hilbert Transform Correlation," *IEEE Trans. Ultrason., Ferroelec., and Freq. Contr.*, vol. 41, no. 5, pp. 588–595, 1994.
- [10] G. Strang, *Linear Algebra and its Applications*. San Diego: Harcourt Brace Jovanovich, 3rd ed., 1986.
- [11] A. B. Bhatia, *Ultrasonic Absorption - An Introduction to the Theory of Sound Absorption and Dispersion in Gases, Liquids and Solids*. New York: Dover Publications, 1985.