HEATING VALUE SENSOR FOR PRODUCER GAS

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ABSTRACT

Today, producer gas is being utilized as a fuel gas in boilers, internal combustion engines and turbines for heat and power generation. The composition of producer gas varies depending upon the gasification parameters. For improved process control and optimum utilization of these heat and power generating systems, it is desirable to monitor the producer gas composition in real-time. A new method and apparatus has been developed and lab-tested for quantitative characterization of producer gas. Spectroscopic and non-spectroscopic measurements are performed in order to detect both – spectrally active and inactive gases. Both methods are cross-sensitive to more than one gas. The measurements are then processed using multivariate statistical methods – principal components regression and partial least squares to fit a regression model which correlates the experimental measurements to the composition and heating value of producer gas. The fitted regression model is used to estimate the properties of unknown mixtures. The measurements and data processing are done in real time using a high speed hardware control and data acquisition system. A commercialized version of this sensor is expected to cost less than half the price of gas chromatographs, which are widely used in the gas industry today.

NOMENCLATURE

\( \lambda \) wavelength

\( I_0(\lambda) \) reference intensity at a wavelength \( \lambda \)

\( I(\lambda) \) sample intensity at a wavelength \( \lambda \)

\( A(\lambda) \) absorbance at a wavelength \( \lambda \)

\( X \) data matrix which contains spectral and non-
spectral measurements performed on calibration mixtures

\( Y \) matrix of compositions and heating values of calibration mixtures

\( y_{\text{actual}} \) known concentration or heating value of a mixture

\( y_{\text{predicted}} \) predicted concentration or heating value of a mixture

\( \text{RMSEP} \) root-mean-squared-error of prediction

\( N \) number of mixtures used for validating the calibration model

INTRODUCTION

Producer gas from gasifiers is being utilized as fuel in boilers for heat generation, internal combustion engines for electricity generation or in combined heat and power generation. Gasification mechanisms involve partial combustion of carbonaceous materials by limited supply of air or oxygen/nitrogen mixtures. The quantity and composition of the gas depends on reactor type, temperature, pressure, fluidization velocity, height of reactor bed, equivalence ratio, air to steam ratio, characteristics of biomass resources and the extent to which different reactions occur in the process.

The producer gas is composed of carbon monoxide, carbon dioxide, hydrogen and hydrocarbons. The composition of producer gas varies by a large amount for each gasifier. In order to prevent damage to heat and power generating equipment, it is necessary to monitor the composition and heating value of producer gas in real-time. Conventional methods used for fuel characterization are chromatography and calorimetry. The gas chromatography (GC) has slow response...
(~ 5 to 20 minutes), requires skilled operators and is expensive. Therefore, it does not provide real time information of the gas. Calorimeters, on the other hand, have relatively fast response (from several tens of seconds to a few minutes), however, they cannot be used to measure mixture composition.

In the last few decades, near infra red (NIR) absorption spectroscopy has become a popular method for multicomponent analyses. The method has been implemented for non-intrusive, real-time analysis of natural gas [1–3] and landfill gas [4]. Gas Technology Institute and North Carolina State University have completed laboratory development and preliminary testing of a real time gas quality sensor (GQS) system that is expected to cost 50% less than gas chromatographs. The sensor system utilizes NIR light absorption properties of hydrocarbon gases, carbon monoxide, carbon dioxide and an analog signal from a MOSFET technology based hydrogen sensor to measure the composition and heating value of producer gas.

EXPERIMENTAL SETUP

Figure 1 and Figure 2 show the overall layout and photograph of the GQS, respectively. The experimental setup includes a flow control system, an NIR optical system, hardware control and high speed data acquisition system.

The flow control system includes four MKS mass flow controllers for four gases – methane, carbon dioxide, hydrogen and nitrogen. These are used to prepare mixtures of predetermined compositions.

The optical system includes a NIR spectrometer, NIR light source, an optical cell and fiber optic cable. The fiber optic cable connects light source to the cell and cell to the spectrometer. It is secured to spectrometer and light source using SMA905 connectors. The light source is a tungsten-halogen lamp (LS-1-LL, Ocean Optics Inc.) having spectral output in the range 700 to 2100 nm. Light from this source passes through the fiber optic cable to the cell. The cell is fitted with quartz windows at both ends. At one end of the cell, light is collimated into a parallel beam and is focused onto the slit of a spectrometer at the other end. The spectrometer is a Hamamatsu TG series C9406GC model having spectral response in the range 900 to 1700 nm and spectral resolution halfwidth of 7 nm.

The optical system, at this stage of development, is capable of measuring hydrocarbons and carbon dioxide. However, the spectral range can be extended to the mid infrared region to measure carbon monoxide. The fuel cell is made of stainless steel, approximately 500 mm long and is designed to work at elevated pressures. The length of the cell allows sufficient light absorption to improve signal-to-noise ratio. A pressure transducer and a thermocouple fitted to the fuel cell measure the pressure and temperature of the gas.

A solenoid valve is used to switch the flow between purging gas and fuel gas. The reference light intensity spectrum may change depending on the temperature of light source. Thus, it is necessary to acquire the reference intensity periodically. It also helps in minimizing the effects of variation in the background noise.

For measuring the concentration of hydrogen gas, a commercially available hydrogen sensor (HPS100C, Applied Sensor, Inc.) is connected before the GQS. The hydrogen sensor is a metal oxide semiconductor field effect transistor (MOSFET). Depending on the amount of hydrogen present in a gas mixture, resistance of the MOSFET changes. The change in resistance is converted to an appropriate voltage output. The response time of the sensor is approximately 30 seconds. It can measure hydrogen concentration in the range 0 to 100% and is cross-sensitive to methane.

The hardware control and data acquisition system includes a National Instruments cDAQ9172 chassis with analog/digital input/output modules, a thermocouple module and a program developed in LabVIEW. The data from spectrometer, pressure transducer and thermocouple is collected and processed in real time. The software updates the measurements ten times every second, even when a large number (up to 50) of spectra are averaged during each measurement cycle for better accuracy.

The experimental procedure involves measurement of absorption spectra and hydrogen sensor output for each mixture. In order to measure an absorption spectrum, the fuel cell is periodically purged with nitrogen and reference intensity $I_0(\lambda)$ is measured. The transmitted intensity $I(\lambda)$ is measured for each mixture. The absorption spectrum is then computed using Eq. (1). All the spectra are measured at atmospheric pressure and temperature conditions.

$$A(\lambda) = -\log_{10} \left[ \frac{I(\lambda)}{I_0(\lambda)} \right]$$

Figure 1. Schematic of experimental setup.

EXPERIMENTAL PROCEDURE

The experimental procedure involves measurement of absorption spectra and hydrogen sensor output for each mixture. In order to measure an absorption spectrum, the fuel cell is periodically purged with nitrogen and reference intensity $I_0(\lambda)$ is measured. The transmitted intensity $I(\lambda)$ is measured for each mixture. The absorption spectrum is then computed using Eq. (1). All the spectra are measured at atmospheric pressure and temperature conditions.
Figure 2. Photograph of experimental setup.

DATA ANALYSIS

Producer gas is primarily composed of carbon monoxide, carbon dioxide, methane, hydrogen and nitrogen. Of these five gases, methane and carbon dioxide have optical absorption in the near infrared range and their spectra are shown in Figure 3. From Figure 3, it is clear that, due to the low resolution of the spectrometer used, there is a strong spectral interference between methane and carbon dioxide. Methane has approximately ten times higher peak absorbance than carbon dioxide. The strongest absorption band of carbon dioxide (near 1400 nm) is completely overlapped by methane band spanning from ~1200 to 1400 nm. The wavelength range 900 to 1700 nm has several advantages over longer mid infrared wavelengths for analysis of mixtures of hydrocarbons and carbon dioxide [1].

As the peaks in a spectrum due to different absorbers overlap, it is not possible to use the absorbances measured at a few wavelengths to estimate the composition of the mixtures. This is often called the selectivity problem. The multivariate statistical methods – Principal Components Regression (PCR) and Partial Least Squares Regression (PLSR, commonly referred to as PLS) are the most powerful and almost universally accepted methods for NIR multicomponent analyses [5]. These methods also minimize the irrelevant errors due to noise in the optical spectra. The description of these methods can be found elsewhere [6-9].

In order to implement the PCR and PLS, the compositions, heating values and spectral data of predetermined producer gas-like mixtures were collected. Table 1 shows the compositions of calibration and validation mixtures. Calibration mixtures are used for building PCR and PLSR models and validation mixtures are used for validating the calibration model. The concentration ranges considered are as follows: methane 8.5 to 18%, carbon dioxide 41 to 60%, hydrogen 21 to 40%, and nitrogen 1 to 10.5%. The minimum concentrations are selected so that measurable signal is produced for each gas. For example, for carbon dioxide, the peak absorption is approximately 0.01. Thus, at very low concentrations, the magnitude of its absorption signal is very close to background noise. Methane has relatively high absorption, thus it will produce adequate signal even at relatively low concentrations. The heating values of the mixtures are in the range 5.74 MJ/m³ to 11.62 MJ/m³.

The experimental data is organized into a matrix X. The first column of matrix X represents the analog output of hydrogen sensor for a mixture. This analog output is a measure of the concentration of hydrogen in the mixture. Each subsequent column of X represents the absorbance of the mixture at a particular wavelength. Thus, each row of matrix X represents the measurements for a given mixture. Similarly, the composition and heating value of each mixture are arranged in rows in another matrix Y. The data is then processed to fit a regression model, which correlates absorption spectra of a mixture to its composition and heating value. The fitted regression model is used to estimate the properties of unknown mixtures from their measured absorption spectra. For data processing RGui software is used [10]. There are a number of other commercial softwares, such as, SAS, Unscrambler, PLS Toolbox, which provide environment for statistical computing.

Figure 3. NIR absorption spectra of pure methane and carbon dioxide at ambient pressure and temperature conditions.

RESULTS AND DISCUSSION

Figure 4 and Figure 5 show the actual and estimated properties of validation mixtures from Table 1. The PLS estimated properties have not been plotted, as they are very similar to PCR estimated properties. For both methods, four principal components/factors were used for building regression model and estimating unknown properties. It is clear that the PCR estimated concentrations and heating values are close to the actual values. Methane, hydrogen and heating value are under-predicted and carbon dioxide is over-predicted.
Table 1. Compositions and heating values of calibration and validation mixtures. The balance of the mixtures is nitrogen.

<table>
<thead>
<tr>
<th>Mix #</th>
<th>CH$_4$, %</th>
<th>CO$_2$, %</th>
<th>H$_2$, %</th>
<th>HV, MJ/m$^3$</th>
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<td></td>
<td></td>
<td></td>
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<tr>
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<td>21</td>
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<td>10</td>
<td>18</td>
<td>41</td>
<td>40</td>
<td>11.62</td>
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The root-mean-squared-error of prediction (RMSEP) is a good quantitative measure of prediction accuracy. Eq. (2) can be used to compute the RMSEP for each concentration and heating value. In Eq. (2), $y_{actual}$ and $y_{predicted}$ are actual and estimated properties of validation mixtures, $N$ is the number of validation mixtures (ten, in this case).

$$RMSEP = \left[ \frac{\sum (y_{actual} - y_{predicted})^2}{N} \right]^{1/2}$$ \hspace{1cm} (2)

Table 2 shows the RMSEP and percentage error for each concentration and heating value. From Table 2, it can be seen that methane concentration has the least RMSEP for both the methods (±0.5%). Estimated carbon dioxide and hydrogen concentrations are ±1% from the actual values, while estimated heating value are ±0.31 MJ/m$^3$ of actual values. The relative errors of gas composition measurements for the corresponding full scales of 100% will be the same as RMSEP for each gas. A full scale for heating value measurements corresponds to a pure methane case and is equal to 37.6 MJ/m$^3$. The relative error of heating value measurements estimated based on this scale is 0.8%. The accuracy in the estimated properties is adequate and can be increased further by adding more mixtures to the training data set.

Figure 4. Actual and PCR estimated composition of validation mixtures from Table 1.
Heating value, MJ/m³

Figure 5. Actual and PCR estimated heating values of validation mixtures from Table 1.

Table 2. RMSEP in PCR and PLS estimated properties.

<table>
<thead>
<tr>
<th>RMSEP</th>
<th>PCR</th>
<th>PLS</th>
</tr>
</thead>
<tbody>
<tr>
<td>CH₄, %</td>
<td>0.5</td>
<td>0.5</td>
</tr>
<tr>
<td>CO₂, %</td>
<td>1</td>
<td>1</td>
</tr>
<tr>
<td>H₂, %</td>
<td>1</td>
<td>1</td>
</tr>
<tr>
<td>HV, MJ/m³</td>
<td>0.31</td>
<td>0.31</td>
</tr>
</tbody>
</table>

It is clear from above results that mixtures having compositions similar to producer gas can be accurately characterized using multivariate statistical methods. We have a mix of several interfering signals here. Methane and carbon dioxide have strong spectral interference in the selected wavelength range. Also, despite cross-sensitivity of hydrogen sensor to methane, the PCR and PLS methods are able to extract accurate compositional information from the experimental measurements.

For measuring carbon monoxide, the considered wavelength range can be extended to the mid infra red region. With extension of the wavelength range, it is expected that accuracy in the predicted properties will be higher, as in the mid infrared range, methane, carbon dioxide and carbon monoxide have higher absorption and distinct absorption bands. However, it is required that other experimental parameters, such as, pressure, temperature, optical path length and compositions should be selected such that a measurable absorption signal is produced. For example, with high methane concentrations at elevated pressures, the gas may become completely opaque. The measured absorption of carbon monoxide can be utilized as one of the variables and the concentration of carbon monoxide can be estimated using similar approach. Alternatively, an off-the-shelf carbon monoxide sensor can also be used. The data analysis principle remains the same. Accuracy of the methods will not be affected when a wider wavelength range and/or multiple gas sensors are used. The gas sensors may or may not be cross sensitive to each other.

This sensing approach (method) can potentially be used to mitigate the cross sensitivity problem and utilize low cost sensors for real time monitoring of hydrogen, oxygen, carbon monoxide and hydrocarbons in producer gas type mixtures. The sensor technology will be evaluated for analysis of fuel mixtures containing oxygen, hydrogen, carbon monoxide, hydrocarbons such as fuel biomass gasification gas, coke oven gas, etc as an alternative to GC.

CONCLUDING REMARKS

The composition and heating value sensor system is developed for real-time characterization of producer gas. Spectral and non-spectral measurements are collectively processed using PCR and PLS methods to obtain a correlation between the measurements and fuel properties. Reasonable accuracy has been achieved in the PCR/PLS estimated properties despite strong interference among measurements from different sources. The method can be extended to more complex mixtures composed of more number of components.

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REFERENCES


