Final Report for NETL: Real-Time BTU Sensor for Natural Gas Applications

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Abstract

The natural gas industry seeks automation of pipeline processes and distribution. The development of an inexpensive monitoring device for gas heating value is desirable for pipeline system analysis and gas accounting. To meet this need, a fuel-quality sensor system is under development through collaboration between General Electric and Sandia National Laboratories. This effort, supported in part by NETL, is directed towards real-time monitoring of the heating value of natural gas and syn-gas fuels. This report describes advances made in the development of the basic microfabricated components, their assembly into a prototype field-portable instrument, and includes a brief market analysis to provide insight into where such systems may find use upon commercialization.

Background

Sandia's patented micro-hotplate platform has been developed into a microcalorimeter for determining BTU (British Thermal Unit) values of natural gas and other fuel gas streams. A thin catalyst layer deposited on the calorimeter surface catalytically combusts the fuel, premixed with air. The heat of combustion is measured directly from a feedback circuit powering the sensor. This sensitive and rapid sensor provides a direct measurement of the BTU content of the fuel. When combined with a density measurement, the Wobbe Index[1] can be determined, which is an important fuel property used to aid combustion control in systems such as gas turbines. The

[1] The Wobbe Index is the ratio of the heating value of a gas to its density, commonly given in units of megaJoules per cubic meter of gas.

sensor has been field tested at natural gas and syn-gas facilities in conjunction with General Electric.

Sandia has parallel and complementary research programs to develop microfabricated components for portable gas chromatography (GC) applications. A two-year internally funded program focused on using fast micro-GC for natural gas applications has just been completed. The microcalorimeter above serves as the detector. Separations were performed using microfabricated GC columns packed with custom and commercially available separation materials. The combination of the micro-GC components with the microcalorimeter has made it possible to assemble a truly field-portable microGC instrument operating with air as a carrier gas.

Characterization of the individual constituents of natural gas samples enables precise determination of the BTU content of the samples. Our expectations are that this simple instrument will fill niches in the natural gas industry where more information about gas content is needed and where the cost of full GC instrumentation is currently prohibitively high. Potential monitoring sites include smaller pipeline switching stations, large industrial consumer locations, and remote natural gas production wells where sample tanks are filled in a time-integrated manner and typically analyzed on a monthly schedule. The use of air as the carrier gas for truly field-portable gas chromatography is a feature that distinguishes Sandia's research from other research institutions.

Market Analysis

A market analysis was performed to assess the interest of natural gas end users in a portable gas chromatography-based instrument for determining natural gas composition. As natural gas is sold by the BTU, improved analysis will produce more equitable trade between buyers and sellers by reducing unaccounted for (UAF) gas content. A 10% improvement in UAF gas accounting through improved sampling and analysis will benefit the gas transport industry by approximately $45 million annually.[2] Industrial users will benefit through continuous feedback of physical gas properties during consumption, in particular with gas turbine engines used for power and electricity generation. A further complication arises during gas transfers between wholesale or commercial entities along the gas supply chain when both gas volume and heating value indices can be used in the transaction. Discrepancies between the two can result in billing errors or lost revenues. A gas transfer system based solely on heating value and made possible by a low-cost microtechnology approach would be beneficial to the natural gas industry.

For market acceptance of an advanced monitoring system, there is a trade-off between cost, performance (accuracy), and sensor lifetime. Utilities currently charge residential and small industrial customers based on a volumetric meter reading. This type of metering device has a typical maintenance schedule of 11 to 17 years. A new technology would not only need to meet this lifetime, but could not cost more than $20. From a cost stand-point, a micro-GC in every home is not practical. However, the stand-alone microcalorimeter system may fall into this performance and cost range, though more frequent maintenance would be required. The accuracy of the microcalorimeter is +/-5% BTU when heating values vary over a wide range, though little speciation information is obtained. This may be sufficient for many users. When variations in the composition of the natural gas fall within a narrow range, accuracy with our sensor has been

[2] Thermo-ONIX, 2003

shown to increase to +/-1.2% BTU. A potential customer base for this system is medium- to large-volume natural gas consumers who desire continuous knowledge of gas characteristics as it is delivered, and/or confirmation data of their consumption independent from the utility metering and billing systems.

For many users, including gas transfer/mixing stations and electricity generating turbines, accuracy of 0.1% BTU is required.[3] For pipelines and turbines, speciation is necessary to obtain the hydrocarbon dew point.[4] The dew point is defined by a combination of gas temperature and gas pressure where unwanted condensation of natural gas components begins to take place.[5] For medium-sized utilities just seeking to improve energy utilization, the cost trade-off for a sensor system is lower, with a threshold cost of $2000 per instrument. Where large quantities of natural gas are consumed (medium-size or larger switching stations, gas-turbine electricity generators), and all fuel properties need to be known, widespread implementation of advanced monitoring techniques would occur at a threshold cost of approximately $5000. It is anticipated that a competitive manufacturer could build the instrument under development at Sandia and meet this cost threshold (cost plus profit) in production runs of 1000+ units per year by using microfabricated analytical components. Through economies of scale, this unit cost could be further reduced, by as much as 50%. No data exists for annual maintenance costs, which will depend on many external factors. We expect that field testing of the sensor system will provide much of this needed information.

Technical Accomplishments

While the funding provided to Sandia through FEW04-012425 was focused on a market study and accelerated production of the prototype instrument, other technical accomplishments made during this time are also presented here.

The larger project as a whole encompassed three major tasks in concurrent development. The first task tailored a microfabricated gas chromatography (GC) column to separate injections of natural gas. The second task experimented with micro-hotplate calorimeters to respond to natural gas compounds, with emphasis placed on rapid response to chromatographic exposures. Third, a complete field-portable gas chromatographic instrument was fabricated using these and other commercially available components.

Natural gas separations were performed using Sandia's packable chromatography columns microfabricated from silicon and glass. The columns were packed with various chromatographic materials commonly used in natural gas separations. The performance of the columns, their separation ability, and the analysis time were then determined under various temperatures and pressures. HayeSep polymers (Supelco, Inc.) were found to produce the best performance. A 19-cm column with HayeSep B completely separated all of the constituents of a natural gas calibration standard by carbon number, and nearly separated the higher carbon number isomers. Analysis time was two minutes for complete elution of pentane. A 15-cm column with HayeSep D can separate all of the constituents by carbon number with little isomer

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3 ASTM D 3588 "Standard Practice for Calculating Heat Value, Compressibility Factor, and Relative Density of Gaseous Fuels" requires precision of 1 part in 1000 at a single lab, but only +/-5% for analyses between labs.

4 NYSEARCH, 1-20-2005

5 "Gas Processing Effects on Gas Quality," AGA Engineering Technical Note, draft 04/04/04, provided by NYSEARCH (Northeast Gas Association's research branch).

separation in less than one minute (Figure 1). Thermal ramping of the low-mass silicon column speeds the run time considerably while maintaining excellent resolution. Partial separation of the isomers produces a maximum 0.009% error in the BTU (heating) value for each one percent of C4+ hydrocarbon in the mixtures – well within industry requirements and sufficient for most applications. The chromatography packing showed no degradation after 500 analyses with air carrier and thermal cycling from 80 to 120 degrees Celsius, and excellent reproducibility of peak position from run-to-run was observed (Figure 2).

Experiments also were conducted to understand the mechanisms of catalytic combustion for the microcalorimeter sensor, and to optimize combustion behavior during chromatography. This involved optimizing combustion efficiency by optimizing flow rate, dead volume of the sensor, and sensor temperature during static hydrocarbon exposures. Sensor temperature is inversely related to lifetime of the supporting membrane. An average surface temperature of 480 degrees Celsius was determined to maximize combustion while providing lifetimes of weeks or longer. Total dead volume did not seem to affect the combustion percent, though it does cause spreading of chromatography peaks. After flow rate optimization in the range of 30 to 40 mL/min, it was determined that combustion efficiency does not exceed 35% at this time, though the combustion percent for each compound is highly reproducible under a given set of experimental conditions. Future work will address the issue of incomplete combustion, which will increase the sensitivity and lifetime of the sensor. Some work was also performed on sulfur poisoning of the catalyst material. While carbon disulfide is found to poison the catalyst, the effect can be reversed through continuous exposure to hydrogen at combustion-level temperatures.

As a critical step to bridging laboratory research to field application, hardware and circuits from the stand-alone BTU analyzer and micro-chromatography system have been assembled into a field-portable GC instrument (Figure 3). A commercially available pneumatic injection valve is included to inject microliter sample volumes into the system for analysis. A custom electronics board provides independent PID (proportional-integral-derivative) temperature control of the microGC column and microcalorimeter fixture. A second custom board provides thermal control of the microcalorimeter. The board also incorporates a reference sensor and has voltage outputs that are proportional to the input power of the sensor. The active heaters on the microcalorimeter have a temperature coefficient of resistance, which is used to maintain the micro-hotplate temperature at a desired set point using an active feedback circuit. The input power to the microcalorimeter is dynamically controlled to maintain constant electrical resistance of the heating element, and thus a constant temperature on the hotplate. External heating from hydrocarbon combustion and cooling from gas flow dynamically modify the hotplate temperature, and thus the resistance of the heating element. The feedback circuit modifies input power to maintain the desired resistance, and thus constant temperature. The magnitude of these fluctuations about a baseline power constitutes the measured signal of the sensor. These two boards are controlled and read through a commercially available data acquisition board. The board and all instrument functions are controlled through custom LabVIEW™ programs. These components are fixed inside a travel-size suitcase, which also holds a small laptop. The only external component is a small tank containing 2 cubic feet of zero-air, enough for 100 hours of continuous operation. Existing air supplies can be plumbed through the same port. As this instrument has only recently reached final assembly, it has yet to be tested in its entirety at this writing.

Next Steps

The next steps in this program involve further testing, expanding our capabilities, and commercialization. We are actively negotiating a proposal with a consortium of natural gas utilities. The goal is to expand the analysis capability of the current GC prototype to analyze natural gas samples for constituents up to C10. This will involve further characterization of the microcalorimeter for heavier compounds, and development of hardware and protocols for simultaneously analyzing light and heavy compounds. For improved durability, the microcalorimeter sensor will be further ruggedized. In addition, a foundry has been identified to produce the sensor in bulk. Our collaboration with General Electric has strong potential to develop into a commercialization partnership. During this process, field-testing of the prototype GC instrument will yield data on maintenance requirements, long-term accuracy and precision, and other important marketing information.

Conclusion

We have performed a market study to gauge interest of potential consumers in a low-cost, portable, gas chromatography based BTU analyzer, and have assembled a prototype BTU monitoring instrument using existing and modified microfabricated components that can address market niches for efficient natural gas transfer at key points in the national gas distribution network. In conjunction with a commercial injection valve, the instrument uses a silicon microfabricated, packed, gas chromatography (GC) column. A microfabricated calorimeter with a reference element serves as the detector. The microcalorimeter senses combustion at its catalytic surface through monitoring the power required to keep the device at a constant, elevated temperature. Batch microfabrication techniques will allow these components to be manufactured in production quantities at a low cost in order to meet industry requirements for cost, lifetime and performance. The market study reveals that the current system may be suitable for large commercial users, as well as niche applications. An order of magnitude improvement in the sensor’s measurement capability will make it appropriate for custody transfer applications and gas turbines. Proposals to meet these and additional goals have been submitted to NETL and the Northeast Gas Association.

Figures

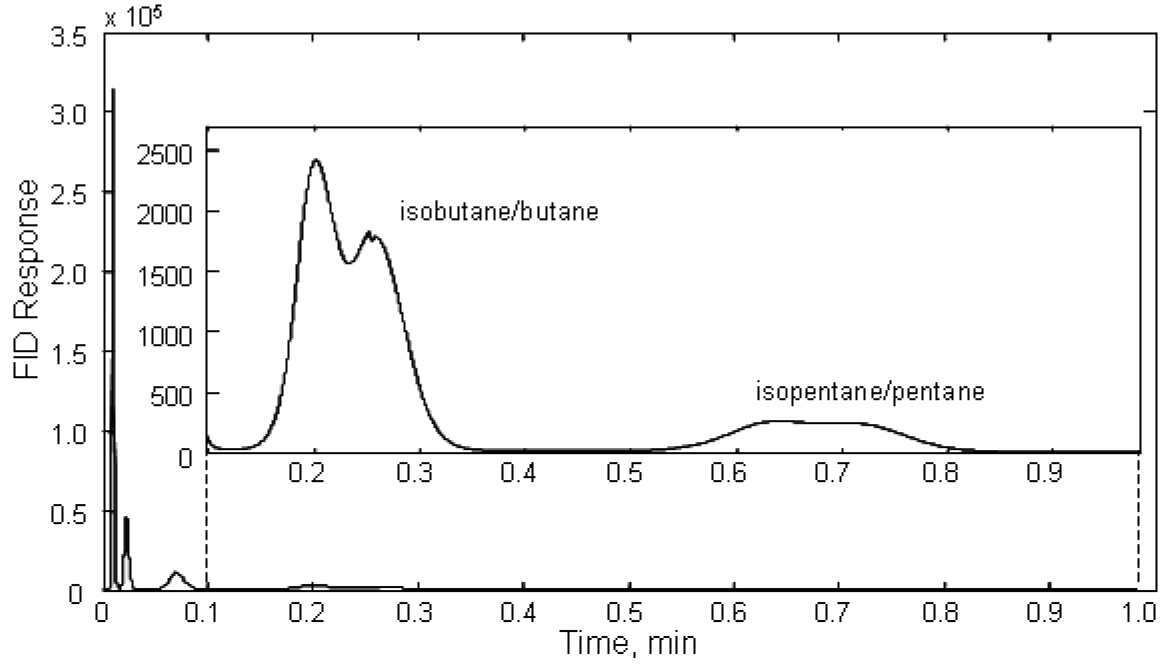

Figure 1. Separation of 5 μL natural gas injection using 15 cm packed micro-column, 20 p.s.i. air carrier, temperature ramp from 80 to 120°C at 40°C/min. Inset is magnified 100X.

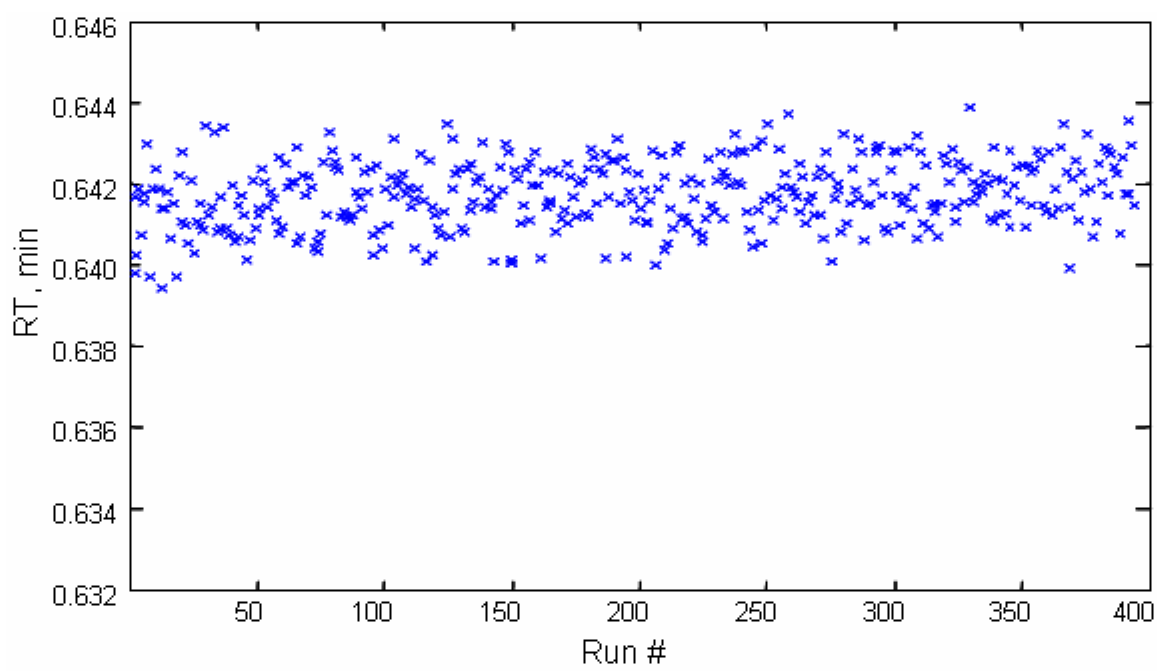

Figure 2. Retention time stability of pentane is 0.05 seconds absolute standard deviation, or 0.1% drift on 39sec retention time.

Figure 3. Field-portable natural gas analysis instrument. An air tank with 2 cubic feet capacity straps to the side of the instrument. Chromatography hardware is visible to the right of the computer. Electronics boards are located under the computer. LabVIEW program on computer controls instrument and acquires data. A 12VDC battery or 120VAC is required.