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Application Note

MKS FTIR Analysis for the Reforming of Hydrocarbons

PROBLEM

Recent climate change concerns have heightened the interest in proton exchange membrane (PEM) fuel cells for transportation and other energy applications. These cells are powered by hydrogen (H_2) that is produced primarily by high temperature, catalyzed processes that reform fossil fuels. This hydrogen source presents a variable matrix of contaminants that can range in concentration levels from ppm to percentage, depending upon the conditions and catalyst used in the process. The analytical methods that are employed for quality assurance and process control or optimization in reforming and purification of the H_2 fuel must provide simultaneous and accurate analytical data for all of these contaminants. Both Gas Chromatography (GC) and Flame Ionization Detector (FID) instrumentation have been used, but they are unable to provide either real time analysis of the gas stream (grab sample is required) or speciation (all components lumped together as a Total Hydrocarbon number) which can be used to control and adjust the reaction parameters in real time.

BACKGROUND

Hydrocarbon reforming processes are the dominant industrial technology for the production of hydrogen. Steam methane reforming (SMR) of natural gas accounts for about 50 per cent of the world's hydrogen; other fossil fuels can also be used. SMR reacts natural gas with steam at 750-850°C and high pressure in the presence of a metal (typically nickel) catalyst to produce CO and H_2[1, 2] according to:

$$CH_4 + H_2O \rightarrow CO + 3H_2 \quad \text{Methane Reforming} \quad (1)$$

This is followed by a lower temperature water-gas shift reaction that produces more H_2 from CO and additional H_2O in the form of steam.

$$CO + H_2O \rightarrow CO_2 + H_2 \quad \text{Water Gas Shift} \quad (2)$$

Alternative processes for the production of hydrogen include partial oxidation (POx) and autothermal reforming of hydrocarbons[3] (the combination of endothermic SMR and exothermic POx).

$$CH_4 + \tfrac{1}{2}\, O_2 \rightarrow CO_2 + 4H_2 \quad \text{Partial Oxidation Reaction} \quad (3)$$

Like SMR, these are catalyzed, high temperature, high pressure processes yielding similar product mixes. Reforming technologies can produce hydrogen from a variety of hydrocarbon sources, including methanol, ethanol, gasoline, diesel and various petroleum fractions.

The product of these hydrocarbon reforming processes is crude hydrogen that is mixed with multiple byproducts and contaminants; the contaminants may be present at broad and varying concentrations. Before it can be used in fuel cell applications, the hydrogen must be purified to at least 99.9995% in order to avoid power degradation in the fuel cell and shortening fuel cell life through catalyst poisoning[4]. Accurate chemical analysis under these circumstances represents a unique challenge. The analysis must simultaneously determine concentrations for multiple contaminants at levels ranging from low ppm up to 30% or more for some components. Table 1 lists typical species concentration ranges found in the reformate product gas streams.

Component	Typical Product
Hydrogen (H_2)	20%-80%
Oxygen (O_2)	0 -1%
Nitrogen (N_2)	0 -10%
Hydrogen Sulfide (H_2S)	0 – 300 ppm
Carbon Monoxide (CO)	0 - 30%
Carbon Dioxide (CO_2)	0 - 30%
Water (H_2O)	25 - 40%
Methane (CH_4)	0 - 1000 ppm
Non-methane Hydrocarbons	0 - 1000 ppm
Nitric Oxide (NO)	Low ppm
Nitrogen Dioxide (NO_2)	Low ppm
Sulfur Dioxide (SO_2)	Low ppm

Table 1. Typical Crude Hydrogen Concentration Profile

SOLUTION

The MKS MultiGas™ 2030 gas analyzer is an effective solution providing simultaneous and accurate analysis of complex multi-component mixtures such as those found in reformate gas, as well as real time data acquisition during the process run. Figure 1 shows the FTIR spectrum of the product from an Ethanol Reforming process, as determined using the MultiGas 2030 gas analyzer. Color coded infrared bands clearly identify the spectra of unreacted hydrocarbons such as ethanol (red), methane (light blue), acetaldehyde (yellow), methylacetate (blue), propane (brown) propylene (salmon) even in the presence of high methane, CO, CO_2 and moisture. Non-infrared active species such as O_2, H_2, Ar and N_2 are not detected by the analysis.

The white dashed sample spectrum seen in Figure 1 was obtained using an electropolished, nickel-plated aluminum gas cell having a path length of 5.11 meters, maintained at 150°C (which also may be run at 191°C if needed to keep reactants in the vapor phase). A 16µ broad band, LN_2 cooled MCT detector, capable of accurate determinations at concentrations ranging from high ppb to %, produces a linearized response over the entire concentration range. The spectrometer system was configured with both a heated cell and heated sampling lines (both of which can run at 150°C or 191°C) to ensure that any moisture in the sample remained in the vapor phase. This allows the analysis of all of the production products to be performed wet, without the need to remove moisture. The high resolution of spectra obtained using the MultiGas 2030 gas analyzer (0.5 cm^{-1}) permits excellent speciation of CO, CO_2, hydrocarbons, etc. It also allows for low level analysis even in the presence of high levels of moisture (in particular, for SO_2 and NOx).

The MultiGas 2030 FTIR analyzer provides real time reaction monitoring. Component concentration versus time plots are shown in Figure 2 below. Figure 2a is a plot of the percent level concentrations of CH_4 – white, CO_2 – green, CO – red, and H_2O – blue versus time, while Figure 2b is a plot of the high ppm level components such as ethanol – green, ethane – white, ethylene – red, methylacetate – blue, propane – yellow-green, and propylene – purple, all showing changes as the reaction proceeds in time. The MultiGas 2030 gas analyzer can be used to monitor real time reaction process changes allowing for quick response to out of control reactions or for monitoring unwanted reaction products.

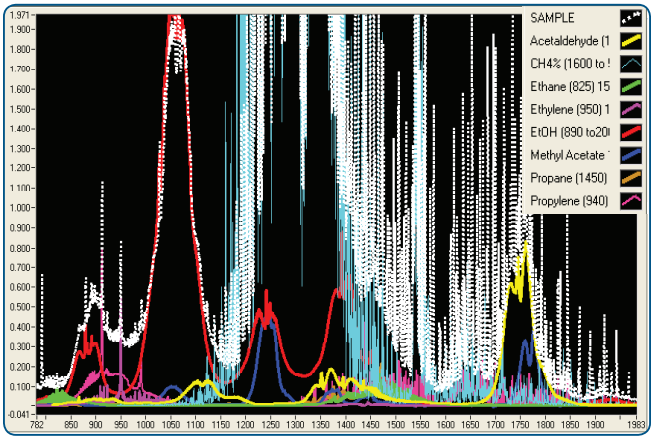

Figure 1 - FTIR spectra of ethanol reforming reaction products

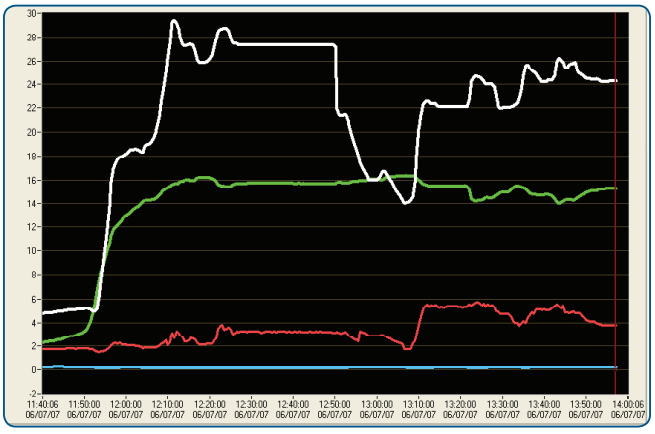

Figure 2a - Timeline plot of the percent level reactants (CH_4, CO_2, CO and H_2O)

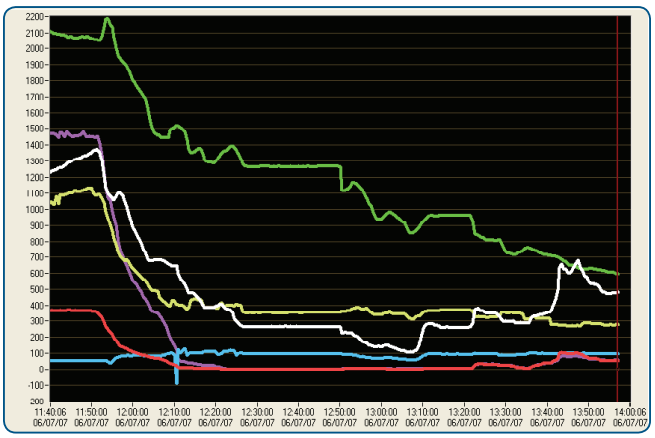

Figure 2b - The higher ppm level reactants of an ethanol reforming reaction initiating just as the reaction starts until just before the reactor is shut off.

BENEFITS

MultiGas 2030 analyzer provides benefits to monitoring reforming reaction by-products including:

- Low cost, state-of-the-art solution for continuous process monitoring
- Single analytical tool which can analyze and display over 30 gas species including unburned fuel (and H_2 Fuel Cell specified criteria contaminants), substantially reducing the space and cost of conventional rack systems containing multiple single gas analyzers
- The ability to monitor contaminants, such as formaldehyde, NOx, SOx and ammonia, with one single instrument instead of multiple instrumentation
- Continuous on-line feedback for reactor tuning, resulting in lower energy use and improved reaction monitoring which is based upon real time data and not grab samples
- The 2030 does not require moisture removal from the sample stream, eliminating the need for sample conditioning and the corresponding maintenance
- Unlike FID and GC analysis, no expensive calibrations gases are needed to run the instrument on a daily basis

REFERENCES

1. I. Wender, “Reactions of synthesis gas”, Fuel Processing Technology, 48, 189 (1996).
2. S. Sonsoni and F. Vigano, “Decarbonized hydrogen and electricity from natural gas”, Int. J. Hydrogen Energy, 30, 701 (2005).
3. A. Ersoz, H. Olgun and S. Ozdogan, “Reforming options for hydrogen production from fossil fuels for PEM fuel cells”, J. Power Sources, 154, 67 (2006).
4. J. Han, I-S. Kim and K-S. Choi, “High purity hydrogen generator for on-site hydrogen production”, Int. J. Hydrogen Energy, 27, 1043 (2002).systems containing multiple single gas analyzers

For further information, call your local MKS Sales Engineer or contact the MKS Applications Engineering Group at 800-227-8766.
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App. Note 05/10 - 8/10

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