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Technology for Productivity

Application Note

MKS FTIR Analysis for Syngas Reactions

PROBLEM

The rising cost of fossil fuels and the worldwide need for reduction in green house gases have sparked renewed interest in alternative fuel sources that require less energy to produce. Gasification of biomass, coke and other residuals from petroleum, coal, municipal and industrial wastes can produce synthetic gas or "syngas". Syngas can be used directly as fuel; as well, it can be used to produce hydrocarbon fuels, hydrogen for fuel cells, and chemical feedstocks such as methanol. The analytical methods employed for quality assurance in syngas production must provide simultaneous and accurate data on mixtures of contaminants in the presence of high CO and CO_2 content. The contaminant levels in syngas range in concentration from high ppm to % levels, depending upon the final product required.

BACKGROUND

Gasification breaks hydrocarbons and other carbon-containing materials down into a mixture of hydrogen and carbon monoxide (CO) in which the relative ratio of hydrogen to carbon monoxide depends on the H/C ratio in the starting material. This product is then purified and the final CO and H_2 gas mixture is separated or further converted to other products.

The process uses a gasifier that converts carbon-containing solid feedstocks into ash and syngas at high temperature (650°C up to 1400°C) and pressures using the exothermic water-gas shift reaction:

$$C + H_2O \rightarrow CO + H_2 \qquad \text{Water Gas Shift - Steam} \qquad (1)$$

After the coke bed cools, the exothermic reaction no longer occurs and oxygen or air is added to remove CO_2. This produces two further reactions that complete the production cycle of syngas to CO and H_2:

$$C + O_2 \rightarrow CO_2 \qquad (2)$$

$$C + CO_2 \rightarrow 2CO \qquad (3)$$

The final fuel matrix contains % level concentrations of CO (up to 40%) in H_2. When this mixture is analyzed at elevated temperatures, accurate analysis of low level hydrocarbon and sulfur impurities is very difficult.

Depending on the final product requirements, the H_2/CO ratio in syngas needs to be adjusted and monitored. Since the gasification of hydrocarbon sources produces crude hydrogen as a mixture with multiple byproducts and contaminants at varying concentrations, accurate chemical analysis of the syngas processes represents a unique challenge. This analysis of the gas mixture must simultaneously determine concentrations for multiple components having contaminant levels that range from low ppm to 40%. Table 1 lists the typical species concentration ranges found in Syngas product gas streams.

Component	Typical Product
Hydrogen (H_2)	50%-90%
Carbon Monoxide (CO)	0 - 50%
Carbon Dioxide (CO_2)	0 - 30%
Water (H_2O)	25 - 45%
Methane (CH_4)	0 - 15%
Non-methane Hydrocarbons	0 - 5%
Ammonia (NH_3)	0 – 4000 ppm
Hydrogen Sulfide (H_2S)	0 - 800 ppm

Table 1 - Typical Crude SynGas Concentration Profile

SOLUTION

The MKS MultiGas™ 2030 provides an effective solution for the simultaneous and accurate analysis of multicomponent mixtures such as those found in the syngas process. Figure 1 shows the FTIR spectrum of a syngas calibration gas standard as determined using the MultiGas™ 2030. Color coded infrared bands due to 13% carbon monoxide, 8% carbon dioxide, 1.5% methane and ppm levels of water are apparent in the spectrum.

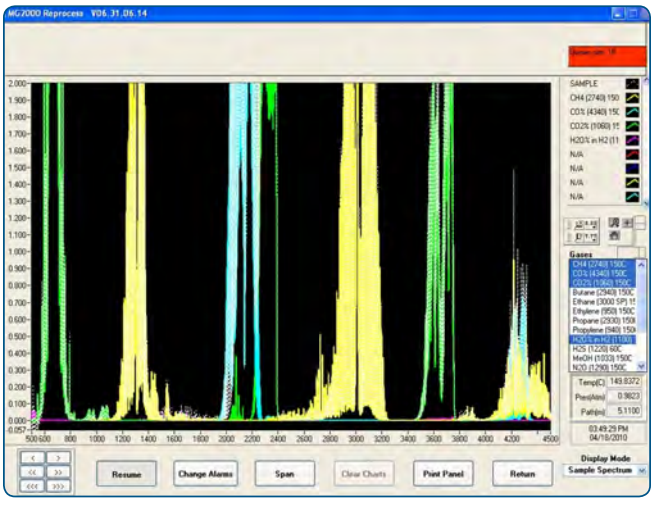

Figure 1 - Syngas Standard 1.5% CH_4 (Yellow), 13% CO (Blue), 8% CO_2 (Green), balance H_2

The dashed sample spectrum shown in white in Figure 2 was obtained using an electropolished nickel-free stainless steel gas cell with a 5 meter path length. The cell was heated to 150°C but can be heated to 191°C if higher vapor pressure components are present to prevent them from condensing in the sample line. The system sampling lines were also heated to ensure that any moisture in the sample remained in the vapor phase. This allows analysis of all production products to be performed without the removal of moisture.

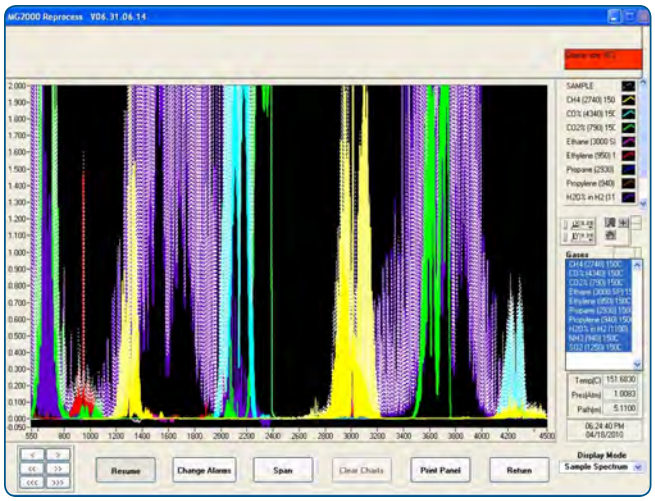

Figure 2 - Syngas product spectrum CH_4 (Yellow), CO (Blue), CO_2 (Green), Ethane (Pink), Ethylene (Red), Propane (Dark Blue), Moisture (Purple) in a balance H_2

A 16µ broad band, LN_2 cooled detector, capable of accurate determinations at concentrations ranging from high ppb to %, provided a linearized response over the entire concentration range. If quantification of low levels (ppb to low ppm) of impurities is not required then the MultiGas 2030 can be configured with a 2 cm stainless steel gas cell. This provides a minimum detection limit from 250 to 500 ppm (depending upon the component) up to 100% for all components as well as provides very rapid response times due to the 10 cm^3 internal volume of the gas cell. For the analysis of syngas the MultiGas™ 2030 FTIRs are configured with a heated, highly polished nickel-free stainless steel gas cell (either 2 cm or 5.11 m) to avoid any chance of producing toxic Ni(CO)4 through exposure of nickel plating to high CO levels at 150°C or 191°C.

The high resolution (0.5 cm^{-1}) of the spectra obtained using the MultiGas™ 2030 permits excellent speciation of like molecules, with the instrument capable of separate analyses for such similar species as butane, propane, ethane and methane. It also allows for low level analysis even in the presence of high levels of moisture (in particular, for SO_2 and NOx).

For further information, call your local MKS Sales Engineer or contact the MKS Applications Engineering Group at 800-227-8766.
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