Applications of GC with Sulfur and Nitrogen Chemiluminescence Detection in the Production of Ultra Clean FT Fuels
Randy Shearer, Ph.D., Rentech, Inc., Denver, Colorado, USA in collaboration with Agilent Technologies, Inc., Wilmington, Delaware, USA.

Introduction
Rentech Inc. is an alternative fuels company whose mission is to deliver clean energy solutions through its patented Fischer-Tropsch (FT) technology. The fundamental FT process is well established and involves catalytic conversion of synthesis gas into hydrocarbons. This process is attractive for a number of reasons. FT fuels are particularly clean because contaminants, many of which are FT catalyst poisons, are removed in the purification of the synthesis gas whether it is derived from natural gas, biomass, coal, petroleum coke and even municipal solid wastes. The resultant FT fuels contain ultra-low levels of sulfur, nitrogen, and aromatics. The diesel fuel, in particular, is of premium quality because of this and also because it has a high cetane value. Consequently, FT diesel burns more cleanly than petroleum derived diesel. In addition, it is possible to capture carbon dioxide formed in the FT process for sequestration or other uses, such as enhanced oil recovery. Furthermore, FT fuels represent another alternative in an environment of dwindling and high-cost petroleum. The source of synthesis gas is unimportant provided that it is cleaned appropriately. The conversion of wastes and non-food renewable biomass avoids the negative impact of fuel production competing with food production. This avoids problems of limited available fertile crop land and the rising cost of food that can result, as is being seen with conventional biofuels.

The application of gas chromatography is extremely important throughout the entire Rentech FT process, from feed characterization, process operation and optimization, through quality control and quality assurance of finished products. The application of gas chromatography with sulfur and nitrogen specific detection is particularly important in the operation of the FT process, and especially so for catalyst protection. Using GC with the sulfur and nitrogen chemiluminescence detectors, it is possible to linearly detect trace sulfur and nitrogen species down to ppb levels with little or no interference using large-bore thick-film capillary columns. Other column choices are more appropriate for trace detection of heavier species in fuels and intermediate streams.

Key Attributes
FOR SCD
- High sulfur selectivity over carbon
- Little or no quenching
- Linear and equimolar response
- Simultaneous serial FID response is available
- Fast amplifier response, e.g. for GC X GC

FOR NCD
- High nitrogen selectivity over carbon
- Little or no quenching
- Linear and equimolar response
- Simultaneous serial FID response is available
- Fast amplifier available for comprehensive GC X GC
- Integral selective nitrosamines detection option

Principles of Operation

Nitrogen Chemiluminescence Detector
- Direct column connection for greatest nitrogen sensitivity, column outlet under vacuum
- FID adapter for simultaneous NCD and FID detection (Ar/O2 in place of air to FID)
- Linear and equimolar response
- Simultaneous serial FID response is available
- Fast amplifier available for comprehensive GC X GC
- Integral selective nitrosamines detection option

Sulfur Chemiluminescence Detector
- Direct column connection for greatest sulfur sensitivity, column outlet under vacuum
- SCD with high speed amplifier and FID adapter is the only sulfur detector suited for comprehensive GC X GC

Block Diagrams

FOR SCD
- High sulfur selectivity over carbon
- Little or no quenching
- Linear and equimolar response
- Simultaneous serial FID response is available
- Fast amplifier response, e.g. for GC X GC

FOR NCD
- High nitrogen selectivity over carbon
- Little or no quenching
- Linear and equimolar response
- Simultaneous serial FID response is available
- Fast amplifier available for comprehensive GC X GC

Application

Ultra Clean Fischer-Tropsch Fuels

Fischer-Tropsch products contain very little sulfur since sulfur is removed during synthesis gas purification, although some sulfur can be introduced into products upon catalytic hydro-cracking or from contamination. The following chromatograms illustrate low level sulfur sensitivity and compare NIST 2723 with an ultralow sulfur diesel (~ 0.6 mg/kg total sulfur). The chromatograms were obtained using a 30m, 0.32 mm ID, HP-5 with a 0.25 μm film programmed from 60˚C hold for 1 min to 350 ˚C at 10 ˚C/min.
The injection volume was 1 μL split 1:10. This type of analysis is especially useful for determining the contribution of individual sulfur peaks to total sulfur and for evaluating comingle of products that contain different levels or types of sulfur species.

Summary

The NCD and SCD assist in the analysis of sulfur and nitrogen containing species important in the FT process and products. In the process, these detectors can be used to measure the presence of catalyst poisons and to verify proper unit operations. In the products, one can measure trace species as part of quality assurance or for troubleshooting purposes. In either case, the attributes of the SCD and NCD contribute to the successful production of these important alternative fuel and chemical sources.