Introduction

Ethanol fuels made from renewable biomass are finding markets worldwide as producers scale up production and automobile manufacturers develop ethanol capable vehicles. The key feedstock for these fuels is denatured fuel ethanol, composed of 92 to 98 percent ethanol denatured with hydrocarbons. Final commercial fuels contain 20 to 85 percent ethanol with the balance of natural gasoline. To meet engine requirements and environmental regulations, both the denatured ethanol and the various ethanol-based blends must meet key specifications in regards to the content of ethanol, methanol, benzene and toluene. Industry consensus organizations such as ASTM have specified two GC methods to measure these components, D5501 and D5898. These methods require two instruments with specific columns and valve configurations resulting in long analysis times. Multidimensional capillary GC (MDGC) offers the possibility of combining several individual measurements into a single run. Additionally, using short, orthogonal columns a MDGC separation is often faster than a single long capillary column. As applied to a simple analysis of denatured ethanol, this concept was demonstrated by the author using a Deans switch system in 2003.[1] This poster presents a MDGC system for industrial applications.

Improvements Using Heart-Cutting Multi-Dimensional GC

Heart-Cutting Multidimensional GC (MDGC) was used to speed the analysis of ethanol fuels. Two 15-meter columns of different polarity were installed in the Deans switch as shown above. The overall cycle time for the analysis was also improved by using isothermal column oven conditions, thus eliminating the need for cool-down between runs. Since the ethanol and methanol elute quickly from the non-polar HP-1 column, a single heart-cut was used to transfer the alcohol and co-eluting hydrocarbons to the polar HP-Innowax column. 

Heart-Cutting MDGC Analysis of Ethanol and Methanol in Fuel Ethanol

Heart-cutting MDGC method was optimized to achieve only marginal separation of methanol from isobutane. For another GC to completely measure key components resulting in long analysis times. Multidimensional capillary GC (MDGC) offers the possibility of combining several individual measurements into a single run. Additionally, using short, orthogonal columns a MDGC separation is often faster than a single long capillary column. As applied to a simple analysis of denatured ethanol, this concept was demonstrated by the author using a Deans switch system in 2003.[1] This poster presents a MDGC system for industrial applications.

Combining Multiple Analyses on a Single Instrument

- Alcohol analysis time reduced from 45 minutes to 3.5 minutes
- isothermal temperature eliminates cycle time between runs
- complete resolution of methanol from light hydrocarbons
- Benzene and toluene content must also be measured in these fuels.

ASTM GC Methods for Ethanol Fuel Analysis

Column 1 – after heart cut
no back flush

Column 2 – after heart cut
back flush

ASTM method D5011 is designed to measure ethanol and methanol in ethanol fuels. A 150-meter PVM column is needed to resolve the alcohols from the light hydrocarbons. An oven temperature program is used to elute the heavy hydrocarbons from this column. The method has two drawbacks. First, the analysis time is quite long. Second, the column flows and GC conditions must be carefully optimized to achieve only minimal separation of methanol from isobutane.

ASTM method D3529 is specified for the measurement of benzene in ethanol fuels. This method uses a 15-port valve and two columns to separate benzene from the ethanol and hydrocarbons in the sample. While this method works quite well, it does require a lab to have another GC to completely measure key components in ethanol fuels.

Improving Speed, Accuracy, and Productivity For Renewable Bio-Ethanol Fuel Analysis

Commercial ethanol fuels are made by blending denatured fuel ethanol with various ratios of petroleum gasoline. The ethanol, methanol, benzene and toluene content must also be measured in these fuels.

Compared favorably with the ASTM method.

Ten runs of a commercial denatured fuel ethanol were each made using both the MDGC method and the standard ASTM D5501 method. This results show excellent precision for the MDGC method. The results also compare favorably with the ASTM method.

Summary and Conclusion

- Improved Speed, Accuracy, and Productivity For Renewable Bio-Ethanol Fuel Analysis
- Alcohol content reduced from 20-25% to 1.5% in a single run
- heart-cutting MDGC using short, orthogonal columns
- complete resolution of methanol from light hydrocarbons
- back flush capability to reduce run time to 3.5 minutes
- isothermal temperature eliminates cycle time between runs
- Benzene and toluene analysis easily adds to MDGC method eliminates the need for a second GC

Analysis of Other Commercial Ethanol Fuels Using Heart-Cutting MDGC

Commercial ethanol fuels are made by blending denatured fuel ethanol with various ratios of petroleum gasoline. The ethanol, methanol, benzene and toluene content must also be measured in these fuels. Two samples of commercial ethanol fuels, E25 and E85, were denatured and run along with the denatured fuel ethanol using this MDGC method. Three consecutive runs were made for each sample. The table below shows excellent precision for each sample.