Coal-to-Chemical Process Gas Analysis Using Agilent J&W HP-PLOT Q PT and HP-PLOT U PT

Application Note

Energy & Fuels

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Abstract

Agilent J&W HP-PLOT Q PT and HP-PLOT U PT GC columns were evaluated for coal-to-chemical process gas analysis by GC/TCD and GC/MS detection. HP-PLOT U PT columns provided excellent peak shapes for the target compounds, especially for polar compounds such as methanol and hydrogen sulfide, although performance for resolving certain hydrocarbon isomers was limited. HP-PLOT Q PT columns were well able to separate polar and nonpolar compounds. GC/MS with an HP-PLOT Q PT column is a useful system for further research of process monitoring or catalyst evaluation.

Introduction

The chemical industry traditionally uses petroleum as its basic raw material, but the use of coal as a feedstock is becoming more attractive as oil prices continue to rise, especially in countries where coal is abundant. Coal-to-olefins (CTO) processes are of particular interest because of the high demand for propylene and ethylene. The first commercial CTO plant in China was started up by the Shenhua Coal to Liquid and Chemical Company at the end of 2010, and at least 10 additional CTO plants are projected to come on stream by 2016 in China. In a typical CTO process, methanol from coal or natural gas is first dehydrated to dimethyl ether (DME). The equilibrium mixture is then converted to light olefins [1]. Current research in this area is focused on developing high-efficiency catalysts and optimizing process conditions for improving yield of olefins [2,3].

GC/MS is a useful tool for analysis of product components after methanol-to-olefins (MTO) reaction or factors affecting catalyst deactivation. Traditional PLOT columns are seldom used for GC/MS analysis, primarily because the stationary phase layer is not mechanically stable and can lead to particle shedding. The Agilent J&W HP-PLOT Q PT and HP-PLOT U PT columns are stabilized with integrated particle trapping technology on both ends of the column to virtually eliminate particle shedding. This allows the columns to be used for valve switching, online, and MS applications [4]. This application note evaluated HP-PLOT Q PT and HP-PLOT U PT GC columns for use in the analysis of coal-to-chemical process gas by GC/TCD and GC/MS.

Experimental

Analyses were performed on an Agilent 7890A GC equipped with a thermal conductivity detector (TCD) and a 7890A GC combined with an Agilent 5975 Series GC/MSD. Sample introduction consisted of a 6-port gas-sample valve connected directly to the split/splitless inlet. A point-of-use gas blending system controlled by auxiliary EPC was used for preparation of low level samples.

The gas mixture was obtained from Beijing AP BAIF Gases Industry Company. The composition of the mixture was referenced to typical coal-to-chemical process gas. To test the performance of the columns, hydrogen sulfide was added to the samples. Table 1 lists the original compounds and concentrations. The concentrations were modified by a point-of-use gas blending system. During analysis, the possibility of air leaking into the sample loop may also have contributed to slight variability in concentration.

Conditions

GC/TCD

Columns:	Agilent J&W HP-PLOT Q PT, 30 m × 0.53 mm, 40 µm (p/n 19095P-QO4PT)
	Agilent J&W HP-PLOT U PT, 30 m × 0.53 mm, 20 µm (p/n 19095P-UO4PT)
Carrier:	Hydrogen, constant flow mode, 40 cm/s, 32 °C
Oven:	32 °C for 5 min, 32 °C to 70 °C at 30 °C/min, 70 °C for 5 min, 70 to 160 °C at 10 °C/min
Injection:	170 °C, split ratio 5:1, 250 µL gas sampling loop
Detector:	TCD at 250 °C

GC/MSD

Columns:	Agilent J&W HP-PLOT Q PT, 30 m × 0.32 mm, 20 µm (p/n 19091P-QO4PT)
	Agilent J&W HP-PLOT U PT, 30 m × 0.32 mm, 10 µm (p/n 19091P-UO4 PT)
Carrier:	Helium, constant flow mode, 35 cm/s, 32 °C
Oven:	32 °C for 5 min, 32 °C to 70 °C at 30 °C/min, 70 °C for 5 min, 70 to 160 °C at 10 °C/min
Injection:	170 °C, split ratio 5:1, 250 µL gas sampling loop
Instrument:	Agilent 7890A GC with gas blending system
MS:	EI, Scan/SIM
Transfer line:	180 °C
MS temperature:	230 °C (source), 150 °C (quad)
Scan mode:	Mass range (10 to 100 amu)

Table 1. Coal-to-chemical process gas sample.

Compound	Concentration (% mol)
Carbon monoxide	19.94
Carbon dioxide	0.81
Methane	1.08
Ethane	0.40
Ethylene	0.43
Propane	0.25
Propylene	0.25
Butane	0.27
Butylene	0.26
Hydrogen sulfide	0.47
Methanol	0.48
Dimethylether	0.94
Hydrogen	Balance gas

Results and Discussion

The conversion of methanol to olefins over a catalyst takes place through a complex network of chemical reactions. In general, at lower temperatures methanol reacts to form dimethyl ether. At higher temperatures, the desired products (olefins) are produced and the selectivity for DME decreases. The variety of components in coal-to-chemical process gas requires the separation of polar and nonpolar compounds.

The gas mixture was analyzed using the GC/TCD system with an HP-PLOT Q PT column and HP-PLOT U PT columns. Figures 1 and 3 show that all polar compounds, such as methanol and hydrogen sulfide, were well separated from hydrocarbons using HP-PLOT Q PT and U PT, but the HP-PLOT Q PT column provided better resolution of hydrocarbon isomers. There were two pairs of coeluting compounds on the HP-PLOT U PT column, namely propylene and propane, and 2-butylene and butane. Since HP-PLOT U PT is a more polar phase, it demonstrated improved inertness and provided better peak shape and response for very polar compounds such as methanol (500 ppm, Figure 3) and hydrogen sulfide (500 ppm, Figure 3), which indicate lower detection limits for these compounds.

The same analytical results were obtained using GC/MS. Figures 2 and 4 show the total ion chromatograms of HP-PLOT Q PT and HP-PLOT U PT GC columns.

Many investigations have been devoted to the study of the effect of reaction conditions on the activity and selectivity of catalysts, or examination of the MTO reaction mechanism. Sometimes the real sample is more complex than the standard gas mixture used in this application note during the MTO reaction. GC/MS is a useful tool for further qualitative and quantitative study. Since the upper temperature limit is quite low (190 °C), backflushing hydrocarbon compounds heavier than C7 is necessary when using HP-PLOT U PT for such investigations. HP-PLOT Q PT is more suitable for use with GC/MS for further identification of unknowns or confirmation of components in process byproducts. This column can elute up to C14 and provide good resolution of polar and nonpolar compounds.

Peak identification for all figures

1. CO/air
2. Methane
3. Carbon dioxide
4. Ethylene
5. Ethane
6. Hydrogen sulfide
7. Propylene
8. Propane
9. Dimethyl ether
10. Methanol
11. Butylene
12. Butane

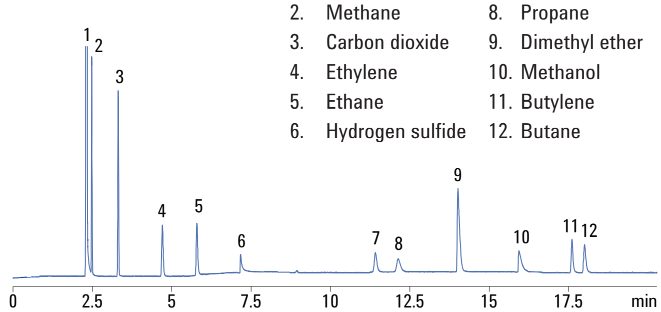

Figure 1. Chromatogram of a gas mix using an Agilent GC/TCD system and Agilent J&W HP-PLOT Q PT column.

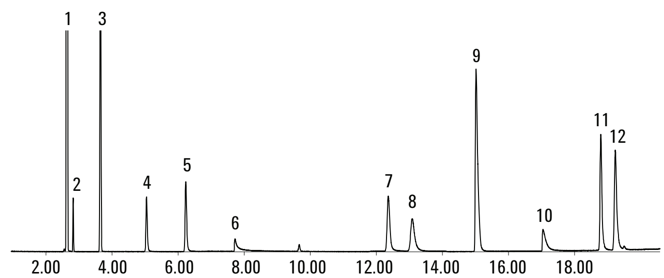

Figure 2. TIC of gas mix using an Agilent GC/MSD system and Agilent J&W HP-PLOT Q PT column.

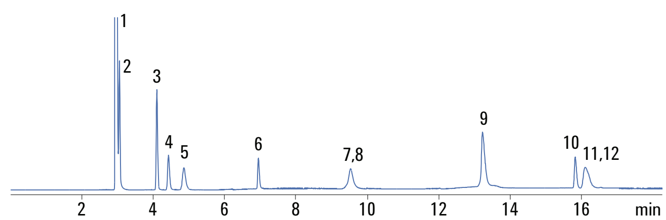

Figure 3. Chromatogram of a gas mix using an Agilent GC/TCD system and Agilent J&W HP-PLOT U PT column.

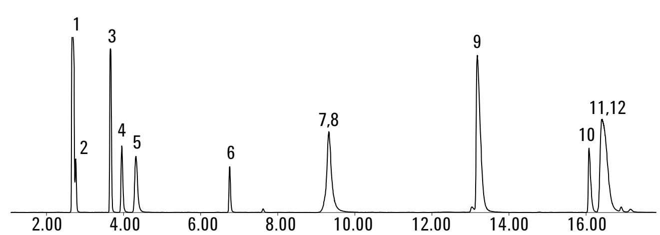

Figure 4. TIC of gas mix using an Agilent GC/MSD system and Agilent J&W HP-PLOT U PT column.

Conclusions

Agilent J&W HP-PLOT Q PT and HP-PLOT U PT columns were evaluated for coal-to-chemical process gas analysis with GC/TCD and GC/MS detection. HP-PLOT Q PT and HP-PLOT U PT columns with integrated particle trapping technology enable worry-free operation with valves and MS detection. HP-PLOT U PT can provide excellent peak shape for even very polar compounds, such as methanol and hydrogen sulfide, but resolution of some hydrocarbon isomers is not as effective as with HP-PLOT Q PT. This Q-type column can provide good resolution for polar and nonpolar compounds and is suitable for GC/MS catalyst evaluation or analysis of the composition of coal-to-chemical process gas.

References

1. C. D. Chang, A. J. Silvestri. *J. Catal*. 47, 249 (1977).

2. H. Q. Zhou, Y. Wang, F. Wei, D. Wang, Z. Wang. *Appl. Catal. A*. 348, 135 (2008).

3. M. Stocker. *Micropor. Mesopor. Mat.* 29, 3 (1999).

4. Anon. Protect your GC system from PLOT column phase shedding. Agilent Technologies, Inc., Publication Number 5991-1174EN (2012).

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