

Agilent J&W PoraBOND Q PT Analyzes Oxygenates in Mixed C4 Hydrocarbon Streams by GC/FID and GC/MSD

Application Note

Energy & Fuels

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Abstract

Even trace amounts of oxygenates can cause catalyst poisoning, so monitoring the level of oxygenates in mixed C4 streams is very important in the production of propylene. This application note demonstrates the analysis of trace oxygenates in mixed C4 streams using an Agilent J&W PoraBOND Q PT column with GC/FID and GC/MS detection. The auxiliary qualitative and quantitative analysis by GC/MS allows more effective and reliable process control.

Introduction

Mixed C4 streams, containing butadiene, butenes, and butanes, are coproduced by steam cracking processes [1]. C4 hydrocarbons are used as feedstock for industrial chemicals, rubber, and plastics. Due to the presence of harmful impurities, only a small proportion of valuable components are extracted from the mixed C4 streams and subsequently processed into usable products, while the majority of remaining C4 by-products are flared or used as low-quality, low-value additives. Maximizing the yield of the mixed C4 stream is a major objective for most petrochemical companies. The key to processing C4 streams into value-added products is accurately monitoring impurities.



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Based on the mechanism of 2-butene and ethylene disproportionation [2], the process for the production of propylene is one of the effective ways of improving the chemical utilization value of mixed C4. This advanced production technology is mature with good economic returns. The technology can be used with a variety of C4 streams, including mixed C4 produced in steam cracking, raffinate C4 mixtures from MTBE, or butadiene extraction [3]. Fresh C4, plus C4 recycle, are mixed with ethylene and sent through a guard bed to remove trace impurities from the mixed feed. It is crucial that the oxygenate impurities, including dimethyl ether (DME), methanol (MeOH), ethanol (EtOH), methyl tertiary butyl ether (MTBE), and ethyl tertiary butyl ether (ETBE) are thoroughly monitored because trace oxygenates can lead to catalyst poisoning, halting reactions, or lowering yields [4].

Agilent Lowox or GS-OxyPLOT GC columns are designed specifically for the accurate analysis of mg/L or µg/L level oxygenates in complex matrixes [5,6]. They are used successfully to control product quality by GC/FID analysis. However, for process control, the matrix of mixed C4 feed from various routes is sometimes quite complex and will interfere with the qualification analysis of some oxygenates by GC/FID. The alternative GC/MS analysis can offer more identification possibilities but is seldom combined with PLOT columns because the particle layer is not mechanically stable. In this application note, an Agilent J&W PoraBOND Q PT column was used to analyze oxygenates in mixed C4 streams by GC/FID and GC/MS for process monitoring. PoraBOND Q PT columns, with integrated particle traps on both ends, offer greater stability than conventional PLOT columns and enable worry-free operation with MS detection [7].

Experimental

Analyses were performed on an Agilent 7890 Series GC equipped with a flame ionization detector (FID) and a 7890 Series GC combined with an Agilent 5973 Series GC/MSD.

GC/FID conditions

Column:	Agilent J&W PoraBOND Q PT, 30 m × 0.32 mm, 5 µm (p/n CP7351PT)
Sample:	50-100 mg/L oxygenates in mixed C4
Carrier:	Helium, constant flow mode, 35 cm/s, 45 °C
Oven:	45-90 °C at 6 °C/min, 90-240 °C at 15 °C/min, 240 °C for 10 min
Injection:	200 °C, split ratio 30:1, 200 µL gas sampling valve
Detector:	FID at 250 °C
GC:	Agilent 7890A Series

GC/MSD conditions

Column:	Agilent J&W PoraBOND Q PT, 30 m × 0.32 mm, 5 µm (p/n CP7351PT)
Carrier:	Helium, constant flow mode, 39 cm/s, 48 °C
Oven:	48-90 °C at 6 °C/min, 90-240 °C at 15 °C/min, 240 °C for 10 min
Injection:	200 °C, split ratio 5:1, 200 µL gas sampling valve
GC:	Agilent 7890A Series GC
MS:	EI, Scan/SIM
Transfer line:	280 °C
MS temp:	230 °C (source), 150 °C (quad)
Scan mode:	Mass range (10-200 amu)
SIM mode:	See Table 1

Table 1. Typical quantitation ions for target oxygenates.

No.	Compound	CAS no.	Molecular form	Target ion
1	Methanol	67-56-1	CH ₄ O	31
2	Dimethyl ether	115-10-6	C ₂ H ₆ O	45
3	Ethanol	64-17-5	C ₂ H ₆ O	31
4	Methyl tert-butyl ether	1634-04-4	C ₅ H ₁₂ O	73
5	Ethyl tert-butyl ether	637-92-3	C ₆ H ₁₄ O	59

Results and Discussion

Normally, highly polar stationary phases, such as GS-OxyPLOT and Lowox, are used for the separation of oxygenates in light hydrocarbons with oxygenates eluting well behind the C4 hydrocarbon matrix compounds. This allows these components to be measured accurately at low levels.

The presence of dimers or higher polymers in some mixed C4 streams, however, can interfere with the quantitation of DME by GC-FID. The monitoring of DME is critically important in the production cycle of propylene. Two methods are discussed here. One approach is the choice of a selective column to promote interference-free elution of oxygenates from hydrocarbons.

Figure 1 shows that hydrocarbons are separated according to carbon number on the PoraBOND Q PT column; dimer, such as C8, elutes far from C4. Target oxygenates, including DME, methanol, ethanol, MTBE, and ETBE, achieve good resolution from hydrocarbons. Figure 2 is a chromatogram overlay. Although the content of C3 hydrocarbons is normally not very high in mixed C4 streams, even at the level of 80% C3 hydrocarbons, this does not interfere with the qualitative and quantitative determination of DME. DME can be well resolved from C3 and C4 hydrocarbons.

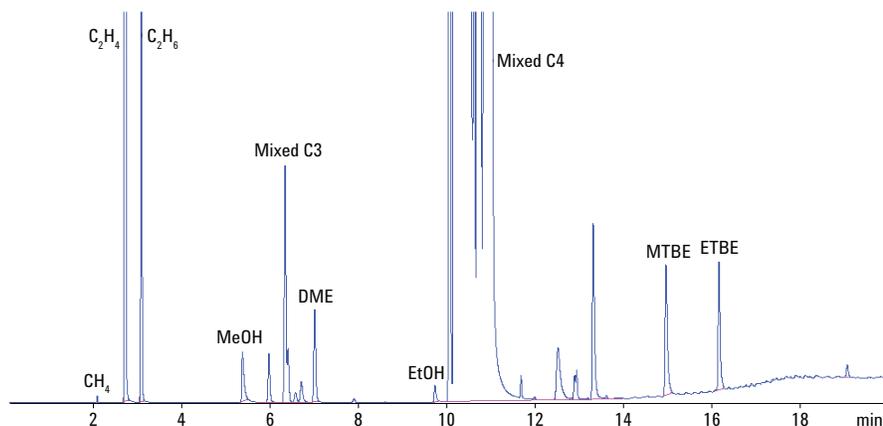


Figure 1. Chromatogram of mixed C4 streams from an etherification process using an Agilent GC/FID system and Agilent J&W PoraBOND Q PT column.

Another solution is the use of highly sensitive and selective GC/MS for identification purposes, as this avoids the detection interference of hydrocarbons. GC/MS is a useful tool for further qualitative and quantitative study on mixed C4 streams. However, 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 as a result. The new PoraBOND Q PT column is stabilized with integrated particle trapping technology on both ends of the column to virtually eliminate particle shedding. This technology expands the applicability of PLOT columns into the MS domain.

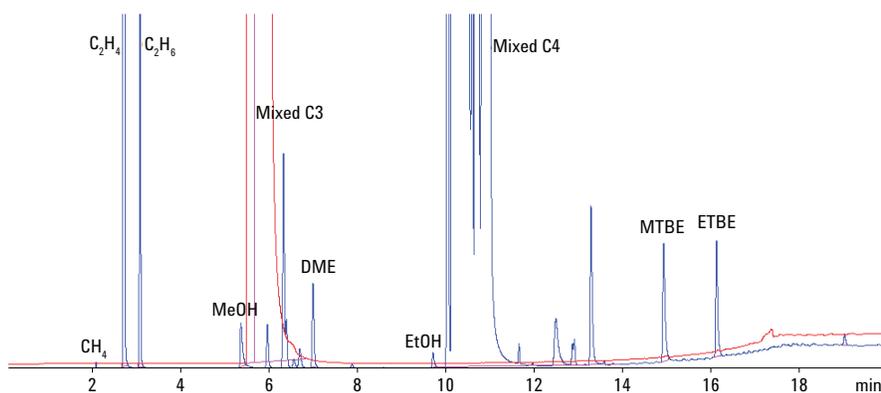


Figure 2. Chromatogram overlay of mixed C4 streams from an etherification process and 80% C3 hydrocarbons using an Agilent GC/FID system and Agilent J&W PoraBOND Q PT column.

GC/MS is a convenient and important tool for routine analysis and process control for further identification of unknowns or confirmation in C4 streams. Figure 3 demonstrates the total ion chromatogram of raffinate C4 mixtures from MTBE. Synchronous SIM/scan was used to monitor ions of interest with high-sensitivity SIM mode and to simultaneously acquire library-searchable scan data in one run. In SIM mode, the method can eliminate air and hydrocarbon interferences to allow for MS identification of the target oxygenates and achieve reliable analysis.

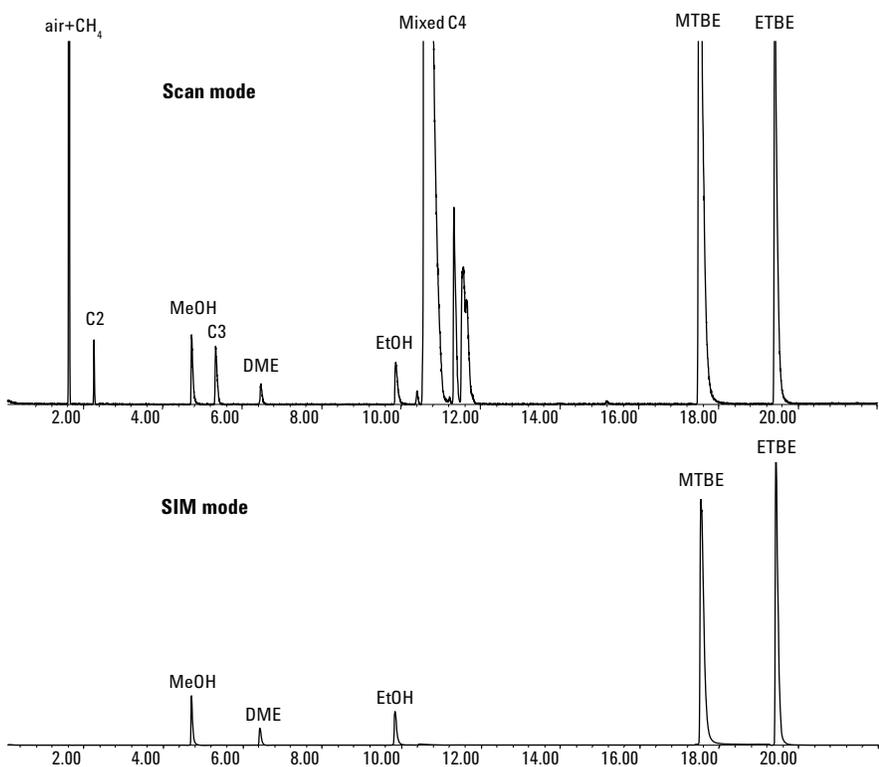


Figure 3. Simultaneous scan (top) and SIM (bottom) analysis of raffinate C4 mixtures from MTBE using an Agilent GC/MS system and an Agilent J&W PoraBOND Q PT column.

Conclusions

This application demonstrates the analysis of oxygenates in mixed C4 streams that are used as feedstock in the production of propylene. The PoraBOND Q PT column with integrated particle trapping technology proves its suitability for quantifying target oxygenates in a challenging C4 matrix using MS detection. In comparison with a standard GC/FID method, the auxiliary qualitative and quantitative analysis from GC/MS can eliminate interfering matrixes. This results in more reliable data for process monitoring or routine analysis and presents opportunities for the possible conversion of more low-value C4 streams into higher value products.

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