Agilent

Trusted Answers

Analysis of Fischer-Tropsch Syngas and Tail Gas with the Agilent 990 Micro GC

Author

Zhang Jie
Agilent Technologies
(Shanghai) Co. Ltd.

Abstract

In this application note, the Agilent 990 Micro GC was applied for the detailed analysis of syngas and tail gas during the Fischer-Tropsch (F-T) reaction process. Two types of configurations were tested and recommended according to the sample composition. The target analytes included N_2, H_2, CO, CO_2, and C1 to C8 hydrocarbons. The test results demonstrated that the 990 Micro GC can provide satisfactory qualification (RT %RSD < 0.25%) and accurate quantitation (response %RSD < 1%) to the target analytes within 4 minutes. The analysis speed was greatly improved compared to the similar analysis performed on conventional GCs.

Introduction

The F-T reaction is a process that converts syngas into hydrocarbon liquids and waxy solids based on catalytic conversion (Figure 1). Syngas is primarily a mixture of CO and H_2 gases that is often sourced from natural gas, coal, and/or biomass. The different sources can lead to the presence of small amounts of other species such as CO_2 and light hydrocarbons. During generation of syngas from feedstock, both alkenes and alkanes can be produced, and the ratio of both molecular classes can be an indicator of catalyst health and aid in planning process maintenance. The main products of the F-T reaction are heavier hydrocarbons (C10 to C20), which are typically further upgraded for fuel applications and synthesis of valuable chemicals. Some additional products such as light gases (CO_2 and C1 to C8) are also formed during the F-T reaction, and together with the unreacted syngas make up the primary components of F-T tail gas. The analysis of F-T tail gas composition can provide useful information for proper tail gas treatment and recycling, which will bring additional economic value and reduce the tail gas environmental impact.

The F-T syngas and tail gas analysis developed on a benchtop GC is usually based on a multi-valve/multicolumn configuration.[1] The system setup is complex, and the method optimization requires experienced analysts to optimize the oven temperature program and valve timing for switching the flow path between different columns to achieve an effective separation. Such analyses can take 20 to 30 minutes to finish on conventional benchtop GCs. The 990 Micro GC F-T syngas and tail gas analysis can be performed using either three or four analytical channels in parallel, depending on the compositional requirements of the user. An optional fourth channel outfitted with an Al_2O_3 column can provide users with detailed C3 to C5 alkene information, or can be omitted for a more economical solution, which mainly provides α-alkenes and n-alkanes information. Each channel of the 990 Micro GC has independent dedicated temperature and pressure setpoints, which greatly simplifies optimizing and troubleshooting the separation compared to conventional GC systems.

In this application note, the analysis of H_2, CO, CO_2, and light hydrocarbons in F-T syngas and tail gas was demonstrated on a 990 Micro GC using either a three-channel or four-channel configuration and a total analysis time of under 4 minutes.
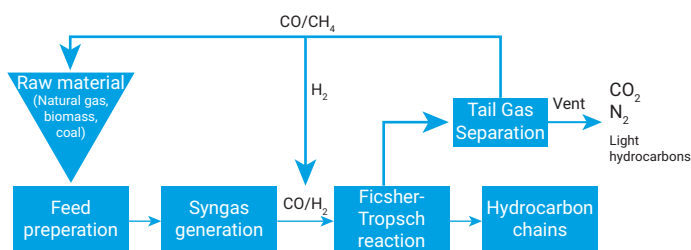

Figure 1. Fischer-Tropsch process.

Experimental

The four-channel configuration of the 990 Micro GC is equipped with a 10 m CP-Molesieve 5Å backflush channel, a 10 m Agilent J&W CP-PoraPLOT U (PPU) backflush channel, a 10 m CP- Al_2O_3/KCL backflush channel, and an 8 m CP-Sil 5CB straight channel for both syngas and tail gas analysis. The three-channel configuration replaced the PPU channel with a 10 m CP-PoraPLOT Q channel, and the Al_2O_3 channel was removed for a more economical solution. The experimental conditions of the two configurations are shown in Tables 1 and 2. The standard gas was purchased from Air Liquide Inc. Table 3 shows the standard gas composition and concentration.

Table 1. Test conditions of syngas and tail gas based on a four-channel configuration.

Channel Type	10 m Agilent CP-Molesieve 5Å, Backflush with 3 m Precolumn	10 m Agilent CP-PoraPLOT U, Backflush	10 m Agilent CP-Al_2O_3/KCL Backflush	8 m Agilent CP-Sil 5CB, Straight
Carrier Gas	Argon	Helium	Helium	Helium
Column Pressure	150 kPa	150 kPa	100 kPa	250 kPa
Injector Temperature	80 °C	80 °C	80 °C	80 °C
Column Temperature	60 °C	80 °C	100 °C	90 °C
Injection Time	40 ms	40 ms	40 ms	40 ms
Backflush Time	23 s	10 s	23.9 s	NA
Sampling Time	30 s	30 s	30 s	30 s

Table 2. Test conditions of syngas based on three-channel configuration.

Channel Type	10 m CP-Molesieve 5Å, Backflush with 3 m Precolumn	10 m CP-PoraPLOT Q, Backflush	8 m CP-Sil 5CB, Straight
Carrier Gas	Argon	Helium	Helium
Column Pressure	150 kPa	150 kPa	150 kPa
Injector Temperature	80 °C	80 °C	80 °C
Column Temperature	60 °C	120 °C	80 °C
Injection Time	40 ms	40 ms	40 ms
Backflush Time	23 s	9 s	N/A
Sampling Time	30 s	30 s	30 s

Table 3. Test standard information.

Standard Gas 1		Standard Gas 2	
Component	Concentration	Component	Concentration
H_2	58.45%	H_2	12.00%
N_2	2.36%	N_2	63.50%
CO	6.17%	CO	1.01%
CO_2	4.97%	CO_2	3.01%
CH_4	14.10%	CH_4	5.06%
C_2H_6	4.04%	C_2H_6	4.06%
C_2H_4	3.07%	C_2H_4	2.02%
C_3H_8	1.04%	C_2H_2	1.04%
C_3H_6	2.05%	C_3H_8	2.01%
$n-C_4H_{10}$	1.04%	C_3H_6	1.03%
1-Butene	1.63%	Allene	1.00%
n-Pentane	0.22%	Propyne	1.00%
1-Pentene	0.41%	$i-C_4H_{10}$	0.31%
n-Hexane	0.12%	$n-C_4H_{10}$	0.30%
1-Hexene	0.24%	1-Butene	0.30%
n-Heptane	0.03%	i-Butene	0.30%
1-Heptene	0.03%	*cis*-Butene	0.30%
n-Octane	0.02%	*trans*-Butene	0.30%
1-Octene	0.02%	1,3-Butadiene	0.30%
		i-Pentane	0.10%
		n-Pentane	0.10%
		1-Pentene	0.10%
		cis-2-Pentene	0.10%
		trans-2-Pentene	0.10%
		2-Methyl-2-butene	0.57%
		n-Hexane	251 ppm
		O_2	796 ppm

Results and discussion

Four-channel configuration

A 10 m CP-Molesieve 5Å (MS5A) channel with 3 m precolumn was used for H_2, N_2, CH_4, and CO analysis (Figure 2A). The 3 m precolumn helps separate CO_2 from the other permanent gases so that high concentration CO_2 can be backflushed before entering the analytical MS5A column. CO_2 is strongly retained by the MS5A column and is instead backflushed to the precolumn to preserve the separation performance and retention time precision of the MS5A. This is an important consideration for tail gas analysis of coal-based F-T processes, which can contain high levels of CO_2. Argon was used as the carrier gas for this channel because it yields a wider linear dynamic range for hydrogen on TCD compared to when using helium as carrier gas. Good enough sensitivity for the typical permanent gases in F-T syngas and tail gas can be achieved using argon carrier gas.

CO_2, ethane, and ethylene were separated on the CP-PoraPLOT U channel. The negative drop right before the nitrogen peak was caused by H_2 in the test sample (Figure 2B).

The Al_2O_3 channel can provide sufficient resolution of C3 to C5 alkenes and alkane isomers in both syngas and tail gas. The separation of C3 to C5 light hydrocarbons was demonstrated using standard gas 2 (Figures 2C and 2D). The normal alkanes eluted before their corresponding alkenes of the same carbon number on the Al_2O_3 channel. The peak shapes of the later-eluting compounds (C5 hydrocarbons) are not as good as those of the early-eluting C3 components due to the isothermal mode.

C6 to C8 alkanes and α-alkenes were separated on the 8 m 5CB channel. The elution order of n-alkanes and alkenes on the 5CB channel is different compared to the Al_2O_3 channel, with α-alkenes eluting right before their corresponding n-alkanes. The RT of N-octane was just under 2 minutes using the conditions shown in Table 1 (Figure 2E).

The analysis time of F-T process gas using the four-channel configuration was less than 4 minutes, with the final compound eluting at 3.05 minutes (CO).
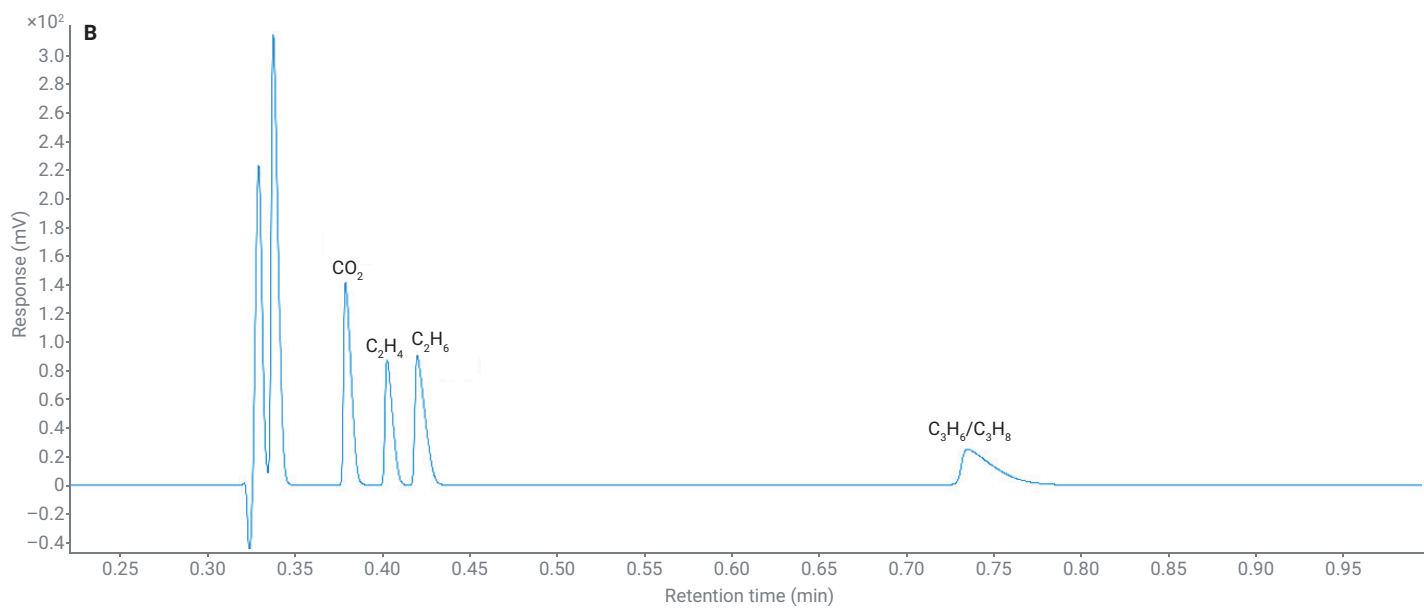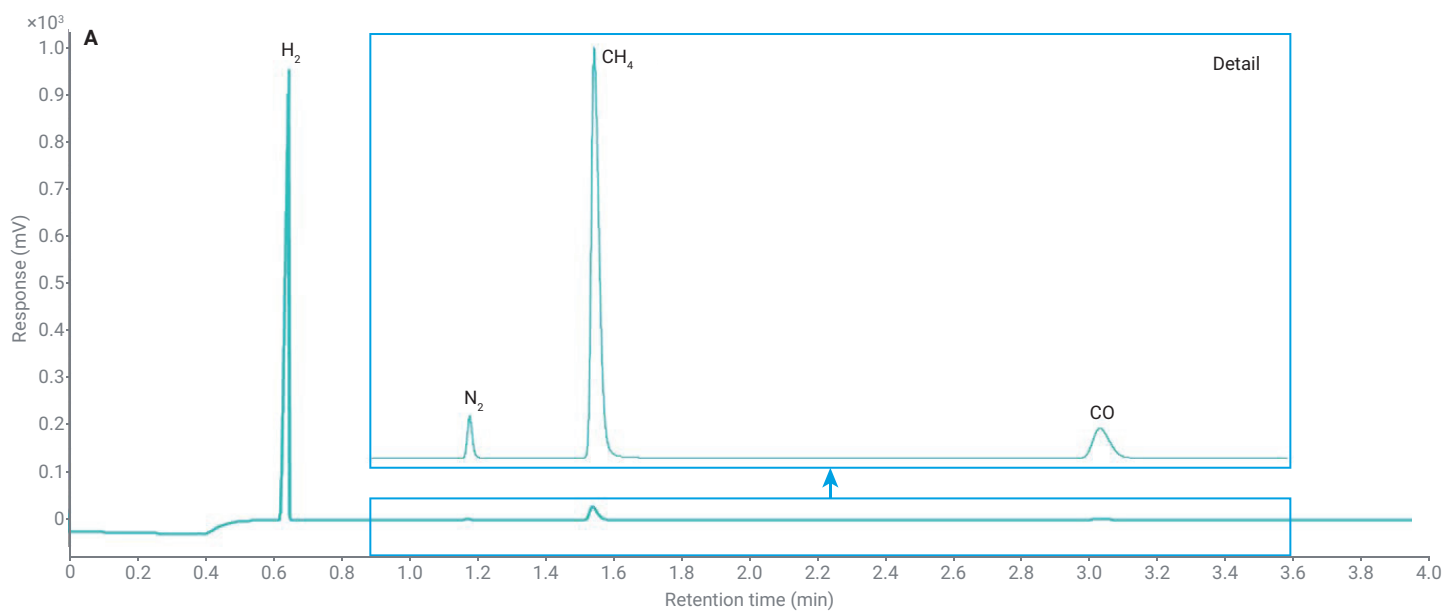
Figure 2A,B. (A) Permanent gas analysis on the MS5A BF channel (Ar as carrier gas). (B) CO_2 and C2 analysis on the PPU BF channel.
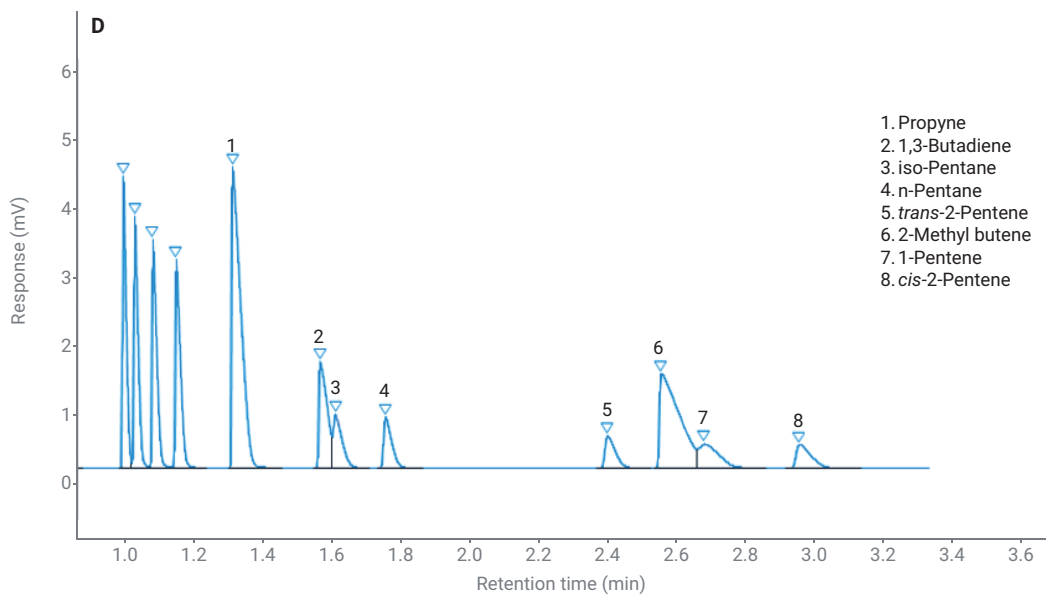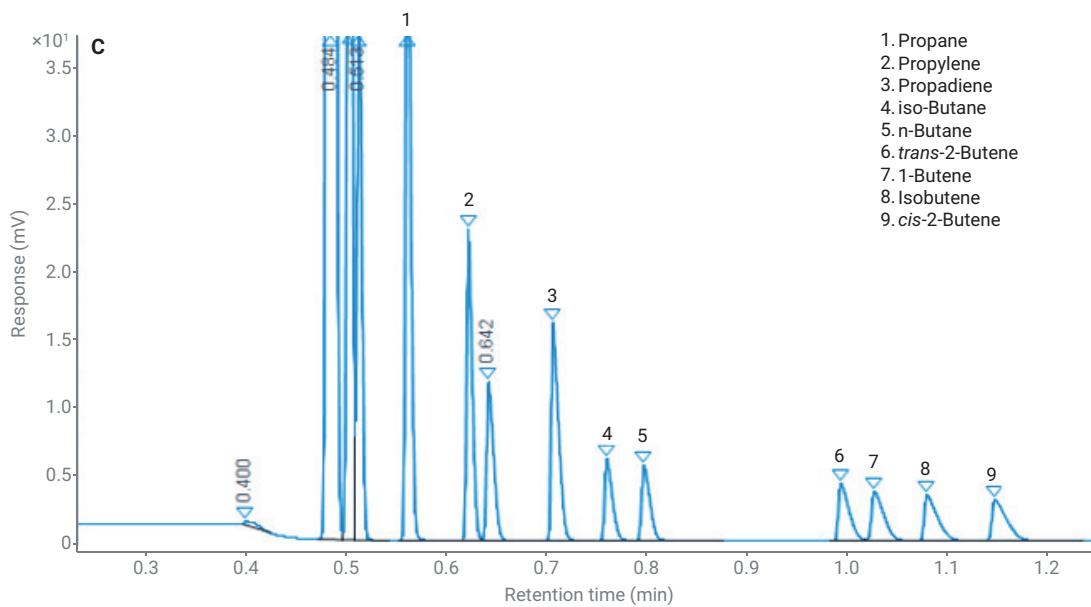
Figure 2C,D. (C) C3 to C4 light hydrocarbons on the Al_2O_3 BF channel. (D) C5 light hydrocarbons on the Al_2O_3 BF channel.
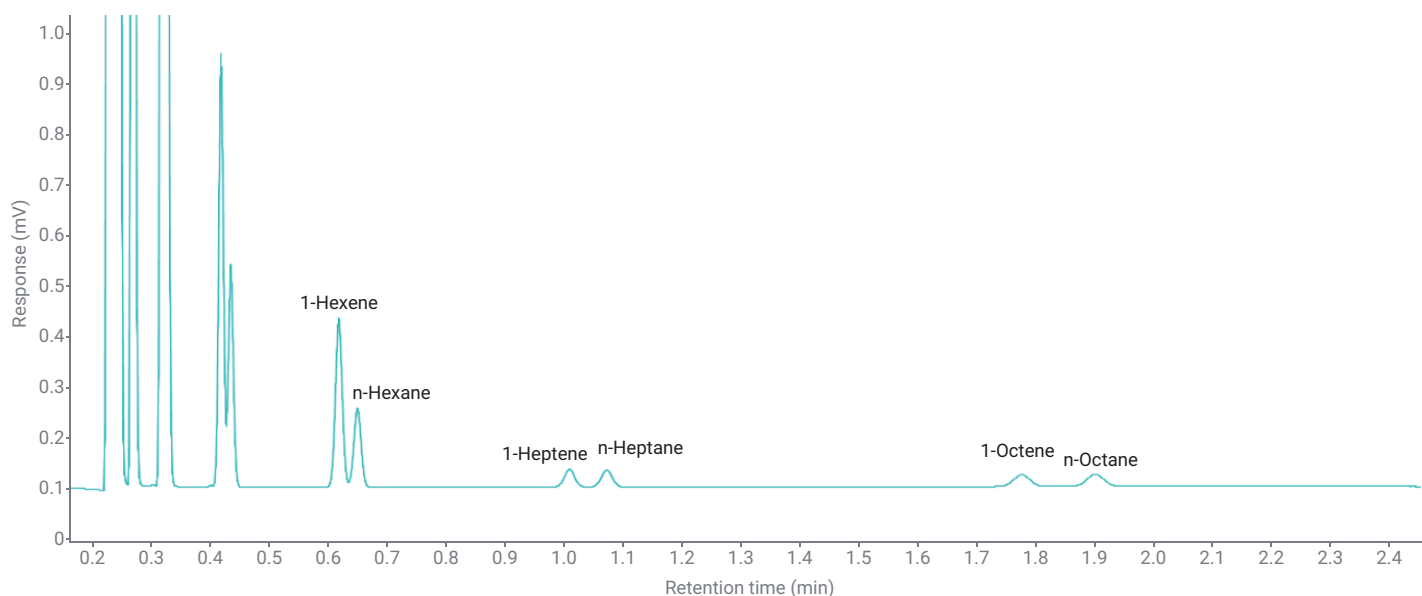
Figure 2E. C6 to C8 α-alkenes and n-alkane separated on the 8 m 5CB channel.

The method precision was assessed based on 20 consecutive analyses of standard gas 1 on the MS5A, PPU, and 5CB channels and standard gas 2 on the Al_2O_3 channel. The RT, peak areas, and corresponding %RSDs for the target analytes are tabulated in Table 4. The area %RSD was below 1% except for 1,3-butadiene with 2.5% RSD. The RT %RSD on the MS5A, PPU, and 5CB channels was less than 0.03%. The RT %RSD of the Al_2O_3 channel was from 0.02% to 0.24%. With high percent-level CO_2 in samples, the RT precision on Al_2O_3 is expected to be lower than other channels. For real sample analysis, it is recommended to keep the Al_2O_3 channel above 100 °C for better RT precision when the instrument is idle.

Table 4. Chemical performance of four-channel configuration.

Component	Conc. (%)	RT (min)	RT RSD (%)	Area (mV × s)	Area RSD (%)	Analytical Channel
H_2	58.48	0.6488	0.0082	760.6538	0.0588	MS5A
N_2	2.36	1.1736	0.0134	3.0261	0.5386	MS5A
CH_4	14.10	1.5414	0.0102	47.2165	0.1978	MS5A
CO	6.17	3.0352	0.0258	7.6785	0.7119	MS5A
CO_2	4.97	0.3788	0.0071	41.5464	0.0641	PPU
C_2H_4	3.07	0.4026	0.0069	26.169	0.0565	PPU
C_2H_6	4.04	0.4198	0.0081	36.0531	0.0358	PPU
C_3H_8	1.01	0.6215	0.0475	8.5275	0.1364	Al_2O_3
C_3H_6	2.03	0.5607	0.0238	17.6449	0.1852	Al_2O_3

Component	Conc. (%)	RT (min)	RT RSD (%)	Area (mV × s)	Area RSD (%)	Analytical Channel
Propadiene	1.00	0.7054	0.0771	7.9454	0.3863	Al_2O_3
Iso-Butane	0.31	0.7591	0.0679	3.1288	0.1734	Al_2O_3
n-C_4H_{10}	0.30	0.7962	0.0759	3.1101	0.2684	Al_2O_3
trans-2-Butene	0.303	0.9915	0.1181	3.021	0.3726	Al_2O_3
1-Butene	0.295	1.0248	0.1272	3.0014	0.2709	Al_2O_3
iso-Butene	0.307	1.077	0.1347	3.0013	0.2603	Al_2O_3
cis-2-Butene	0.306	1.1444	0.1436	2.99	0.3054	Al_2O_3
Propyne	1.01	1.3062	0.2052	7.8955	0.4847	Al_2O_3
iso-Pentane	0.104	1.5589	0.2212	2.5527	0.7041	Al_2O_3
1,3-Butadiene	0.311	1.6058	0.1309	1.3717	2.5005	Al_2O_3
n-Pentane	0.097	1.7494	0.1681	1.2179	0.455	Al_2O_3
t-2-Pentene	0.098	2.3903	0.2143	0.9948	0.471	Al_2O_3
2-methyl-Butene	0.049	2.5466	0.2096	5.4884	0.4095	Al_2O_3
1-Pentene	0.10	2.6698	0.2369	1.439	0.8108	Al_2O_3
cis-2-Pentene	0.1	2.9452	0.2417	1.0414	0.5211	Al_2O_3
1-Hexene	0.24	0.6184	0.0025	2.7232	0.0516	5CB
n-Hexane	0.12	0.6499	0.0027	1.3573	0.2337	5CB
1-Heptene	0.03	1.0092	0.0042	0.4302	0.092	5CB
n-Heptane	0.03	1.0724	0.0037	0.4386	0.1114	5CB
1-Octene	0.02	1.7758	0.0058	0.4603	0.2221	5CB
n-Octane	0.02	1.9005	0.0061	0.5017	0.2186	5CB

Three-channel configuration

For users that require only permanent gases, α-alkenes, and n-alkanes, a more economical three-channel configuration can be used. This configuration includes a 10 m MS5A BF channel, a 10 m CP-PoraPLOT Q BF channel, and an 8 m 5CB straight channel. With this configuration, C2 to C4 α-alkenes and n-alkanes can be separated on the PPQ channel and C5 to C8 counterparts can be resolved on the 5CB channel at lower column temperature and lower column head pressure in under 4 minutes (Table 5). The RT/area precision on the 8 m 5CB channel is at the equivalent level to those listed in Table 3. The performance of the PPQ channel based on 20 injections using standard gas 1 is listed in Table 5.

Table 5. Chemical performance of the PPQ channel.

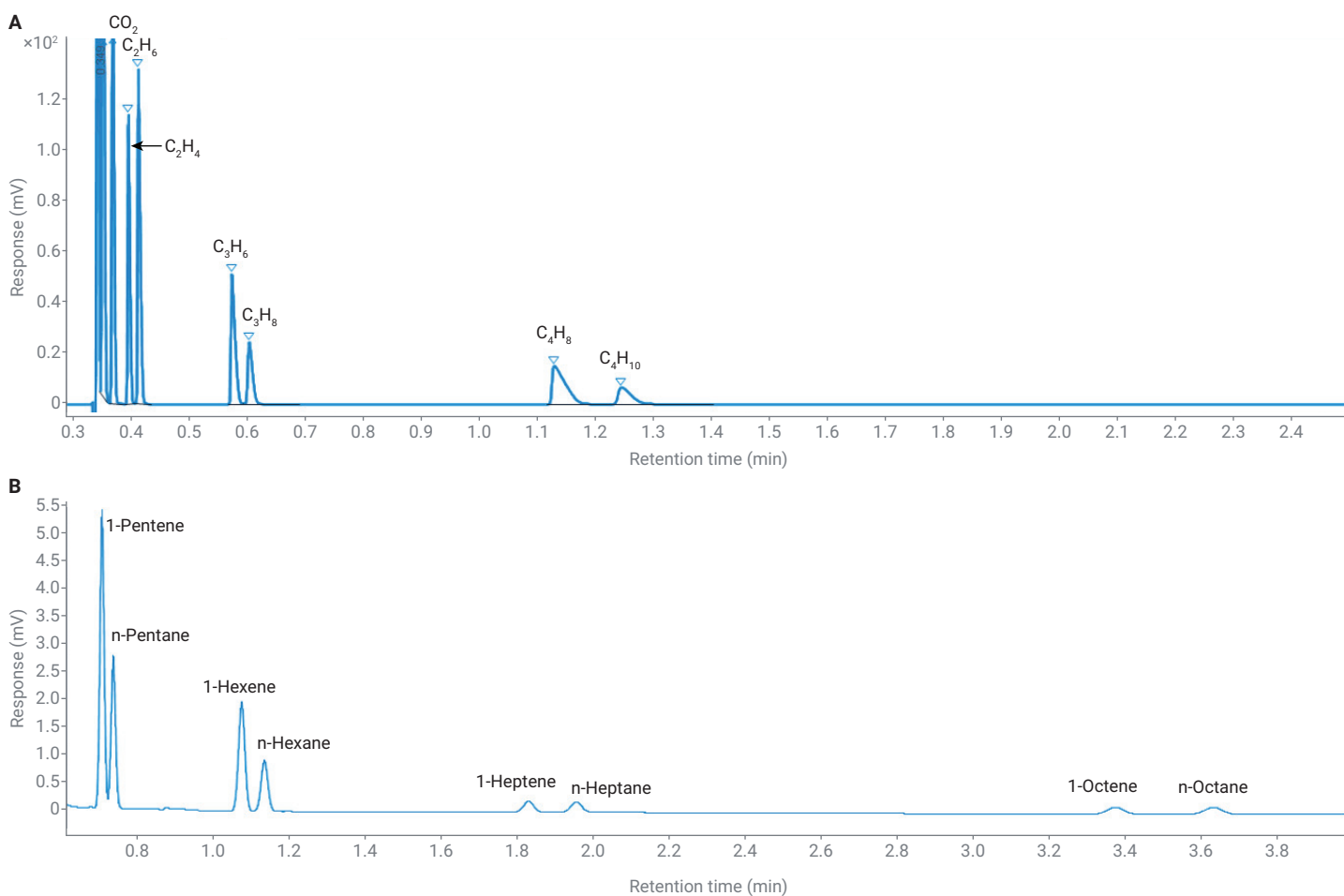| Component	Conc. (%)	RT (min)	RT RSD (%)	Area (mV × s)	Area RSD (%)	Analytical Channel
CO_2	4.97	0.3788	0.0071	41.5464	0.0641	PPQ
C_2H_4	3.07	0.3934	0.0053	29.8288	0.0513	PPQ
C_2H_6	4.04	0.4105	0.0042	41.0435	0.0499	PPQ
C_3H_8	1.01	0.6014	0.0040	13.4325	0.0196	PPQ
C_3H_6	2.03	0.5715	0.0042	24.6209	0.0265	PPQ
$n-C_4H_{10}$	1.04	1.2426	0.0037	10.4202	0.0593	PPQ
1-Butene	1.63	1.1268	0.0036	23.8581	0.0178	PPQ

Figure 3. (A) C2 to C4 α-alkenes and n-alkanes separated on the 10 m PPQ BF channel. (B) C5 to C8 α-alkenes and n-alkanes separated on the 8 m 5CB channel.

Conclusion

In this application note, an Agilent 990 Micro GC configured with four analytical channels was applied to F-T syngas generation process and tail gas analysis. Permanent gases and light hydrocarbons (C1 to C8) were separated on the described system and excellent quantitation and qualification precision was achieved in less than 4 minutes.

For F-T processes focusing on permanent gas, α-alkenes, and n-alkanes analysis, a three-channel configuration was demonstrated that reduces instrument capital investment without compromising on performance.

Reference

1. Bu, L-K; Xin, D-W; Chang, S-P; Lian, Y-C. Rapid Determination of Permanent Gas, C1 ~ C9 Olefins and Alkanes in Fischer Tropsch Synthesis Gas by GC. *Chemical Industry Management* **2021**.

www.agilent.com

Agilent

Trusted Answers