Pyrolysis of HDPE Using Hydrogen as a GC Carrier Gas

Author:

Karen Sam

Application Note
General

Abstract
This application note demonstrates the benefits of using hydrogen as a carrier gas on a Thermo GC-MS and a CDS Pyroprobe

Introduction
The choice of GC carrier gas depends on many factors, which include separation efficiency, safety, cost, and a gas suitable for the detector. The most common carrier gases are helium, nitrogen, and hydrogen. Hydrogen has the lowest viscosity and the highest velocity, producing efficient separation in the shortest time. Additionally, it is readily available, while He becomes less economical and more difficult to acquire. In this application note, pyrolysis of HDPE in Hydrogen and Helium carrier gases were compared.

Experimental Setup
Hydrogen has an auto-ignition temperature of 1,040 °F (560 °C) and a flash point of - 423 °F (- 253 °C). Ignition can occur at a volumetric ratio of hydrogen to air as low as 4%. Due to its flammability, some precautions need to be taken to prepare the room and instrumentation.

Proper air vent along with a hydrogen sensor (Eagle Eye Power Solutions HGD-2000 Hydrogen and Combustible Gas Detector) was mounted on the wall near the Py-GC-MS instrumentation and hydrogen sources. Additionally, signs banning the use of smoking or open flames were used.

The Pyroprobe has a 30μL of dead volume from the sample chamber to the injector, ensuring that only a small amount of gas is within the system at one time. Also, the built-in leak check function serves as a safety check. To further lower the operation cost nitrogen was used as a purge gas.

For the Thermo 1310 GC-MS, a Hydrogen Gas Sensor (p/n 27605006) was installed to stop the flow of hydrogen in case of a leak in the GC oven. UHP Grade 5.0 hydrogen was used, along with a Triple Stage Gas Filter for the removal of water and oxygen. Additionally, all gas lines were brand new 1/8" pre-cleaned stainless-steel tubing with appropriate gas-tight fittings. Finally, the inlet configuration was changed to hydrogen. A Hydrogen Ion Volume (p/n 1R120404-4115) in the MS was installed for improved chromatography.

Instrument Conditions

Pyroprobe 6150 Autosampler

DISC:	700°C 30 sec
Interface:	300°C
Transfer Line:	325°C
Valve Oven:	300°C
Leak Check:	ON
Purge Flow :	N_2, 25mL/min

Thermo Trace 1310 ISQ GC-MS

Column:	5% phenyl (30m x 0.25mm)
Carrier:	He 1.25mL/min, H_2 1.6mL/min 75:1 spl
Injector:	360°C
Oven:	40°C for 2 minutes
	10°C/min to 320°C (20min)
Ion Source:	230°C
Mass Range:	35-550amu

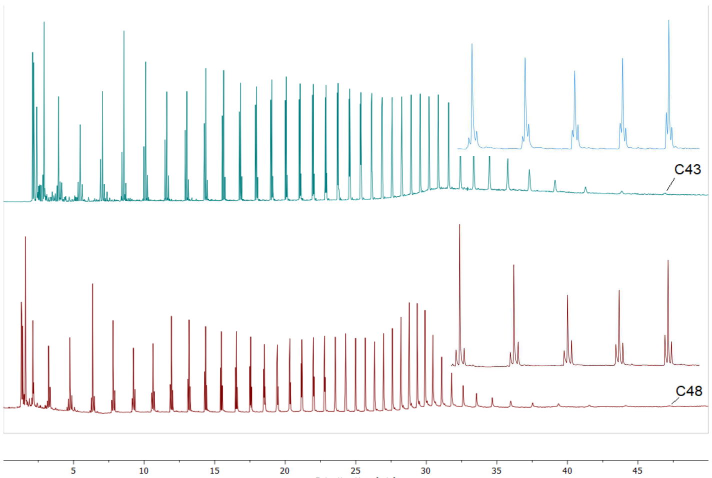

Figure 1. HDPE in Helium(top) and Hydrogen (bottom).

	RecordId	Score	Polymer Name
1	11	984	Polyethylene,
2	8	909	Polypropylene
3	3	801	Nylon 6,6

	RecordId	Score	Polymer Name
1	11	989	Polyethylene,
2	8	889	Polypropylene
3	3	793	Nylon 6,6

Figure 2. Py database hit results in Hydrogen(top) and Helium (bottom).

Results and Discussion

Figure 1 compares HDPE run in helium (top), and hydrogen (bottom). A series of aliphatic hydrocarbon peaks with a triplicate structure are present between both chromatograms, a pattern known for polyethylene which breaks apart via the random scission mechanism, so the pyrolysis pattern of HDPE is unchanged. Additionally, because hydrogen has a lower viscosity and the higher velocity, elution of the triplicate peaks occurs more rapidly with hydrogen when compared to helium. In the same GC oven program, a C48 chain length was seen in hydrogen, compared to C43 with helium. Additionally, the resolution between the alkane, alkene and diene peaks has improved. Therefore, a more efficient separation and more productive analysis was achieved.

When performing pyrolysis in hydrogen, hydrogenation reactions often occur, such as formation of alkanes from alkene and diene pyrolysis products in polyethylene, and these reactions are more pronounced with the presence a catalyst. Even the HDPE sample that is used in this application note is manufactured with metal catalysts[1], no hydrogenation products were observed, potentially due to shorter reaction time in the DISC chamber due to high flow and low dead volume.

Even though the Py-GC-MS database is composed of datasets using helium as a carrier gas, a database search with Mestrelab's Mnova MsChrom and DB plugins came up with polyethylene as a top hit with a 984 match quality (Figure 2), indicating that library search results are minimally influenced by a change in carrier gas when using the Pyroprobe.

Conclusion

The choice of GC carrier gas depends on many factors, which include separation efficiency, safety, cost, and a gas suitable for the detector. As hydrogen is inexpensive and readily available, it is often chosen as a GC carrier gas. As hydrogen is flammable, safety precautions must be taken into account. The Pyroprobe's low sample path volume plus leak check function can be used to prevent a hydrogen gas leak. In this application note, the possibility of hydrogenation during pyrolysis was studied on HDPE which found to have negligible effect on the pyrolysis results. Additionally, hydrogen was proven to provide more efficent separation.

References

1.Clifton L. Wagner, Tianning Diao, in Comprehensive Organometallic Chemistry IV, 2022, 8.05.7.3 Olefin polymerization catalysts