Characterizing Waste Plastic Pyrolysis Oils using a Pyrolysis GC-MS

Application Note
Energy

Abstract
This application note demonstrates characterization of plastic pyrolysis oils using Evolved Gas Analysis coupled with Multi-Step Pyrolysis GC-MS.

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Introduction
As the global production of polymers continues to rise, the demand to recycle plastic waste has increased. Besides traditional mechanical recycling, petrochemical companies are investing in chemical recycling technologies. Among various chemical recycling, techniques such as methanolysis and hydrolysis can be used to recycle PET and nylon, respectively. However, polyolefins such as polyethylene and polypropylene resist this type of depolymerization due to strong carbon-carbon bonds. For these plastics, pyrolysis as a method of chemical recycling is preferred. Superficially, the operation may seem simple: apply elevated temperatures in an inert atmosphere to break down plastics into smaller molecules. However different polyolefins decompose at different temperatures, affecting the nature and quality of the resulting pyrolysis oil. Additionally, unwanted plastics such as PET and PVC, can yield oxygenated and chlorinated compounds, contaminating the output. Therefore, the output needs to be analyzed for adjustment of conditions or post pyrolysis processing as needed[1].

The most widely applied technique to determine the composition of plastic pyrolysis oil is GC-MS[2]. However, certain fractions of the output may be too heavy, containing un-volatile fractions which would remain in the GC injection port. These complex samples would have to undergo lengthy sample preparation steps before GC analysis, and the non-volatile portion would still be left un-analyzed by GC. In these cases, evolved gas analysis (EGA) coupled with multi-step pyrolysis (MSP) GC-MS can be a viable method. Evolved Gas analysis, which will chart a sample's gases which evolve versus temperature, is used for the temperature selection in multi-step pyrolysis (MSP). Then MSP can then be used to gain detailed chromato- graphic information on the types of compounds present, based on evaporation and decomposition temperatures. In this application note EGA + MSP was applied to two pyrolysis oil outputs which could not be analyzed by traditional GC methods,to examine the oil quality.

Experiment Setup
Plastic pyrolysis oils from two locations of the pyrolysis stream were evaluated. "A," had a semi-solid consistency, "B" was a solid. 100µg of samples were added to Drop-In-Sample Chamber (DISC) tubes, each for EGA and MSP.

EGA

Pyroprobe 6150 Autosampler
Initial: 50°C
Final: 1000°C
Ramp Rate: 100°C per min
Interface: 300°C
Transfer Line: 325°C
Valve Oven: 300°C

GC-MS
Column: Fused silica (1m x 0.10mm)
Carrier: He1.25mL/min 75:1 spl
Injector: 360°C
Oven: 300°C
Ion Source: 230°C
Mass Range: 35-600amu

Multi-Step Pyrolysis

Pyroprobe 6150 Autosampler

DISC:
300°C 60 sec
450°C 60 sec
520°C 60 sec

Interface: 300°C
Transfer Line: 325°C

GC-MS

Column:
5% phenyl (30m x 0.25mm)
Carrier:
He 1.25mL/min, 75:1 spl
Injector: 360°C
Oven: 40°C for 2 minutes
12°C/min to 320°C

Results and Discussion

Figure 1 contains the EGA runs of both samples overlaid. The semi-solid sample (A) shows one peak of evolved gases at 290 °C, while the solid sample in green (B) shows two regions, a thermal decomposition region at 290°C, and a decomposition region at 520 °C.

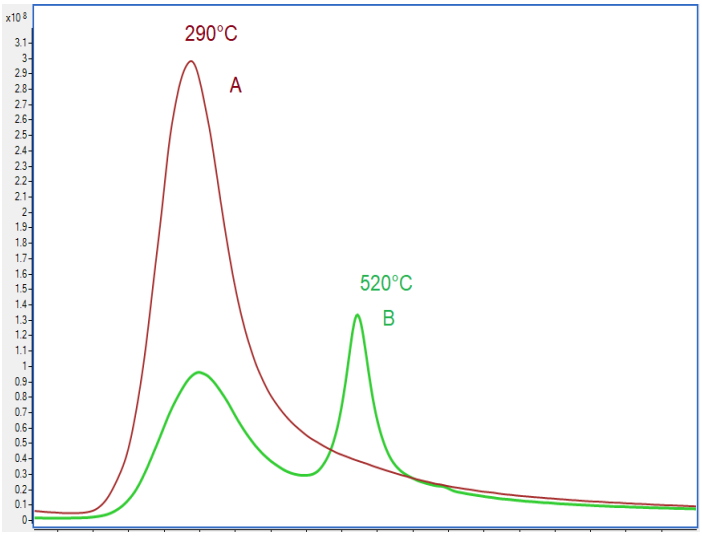


Figure 1. EGA Overlay of 2 Plastic Pyrolysis Oils.

Information gathered from these EGAs was used to determine setpoint temperatures for MSP. Since A contained one region of outgassing at 290°C, a single temperature, just past the peak apex, 300 °C, was chosen for characterization.

At 300 °C, strong carbon-carbon bonds of polyolefins remain intact, so the oil product simply volatilizes to the gas chromatograph via thermal desorption. The chromatogram exhibits a series of straight alkanes from 14 carbons to 37 carbons (Figure 2). Closer inspection reveals other characteristics. For example, there is a hump in the baseline populated with tiny peaks, otherwise known as an unresolved complex mixture, which is often seen in crude oils[3]. Secondly, a second series of peaks, alkenes, are seen between the range of 16 carbons and 24 carbons (Figure 3).

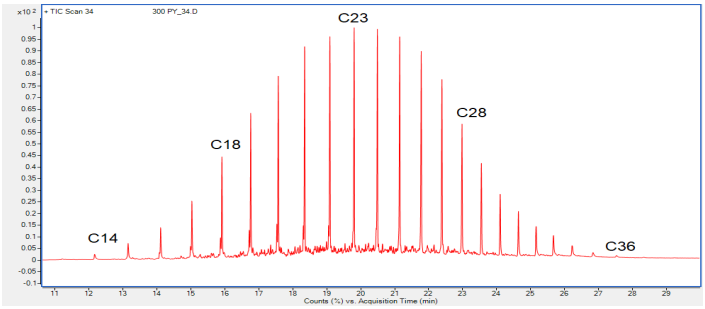


Figure 2. A at 300 °C.

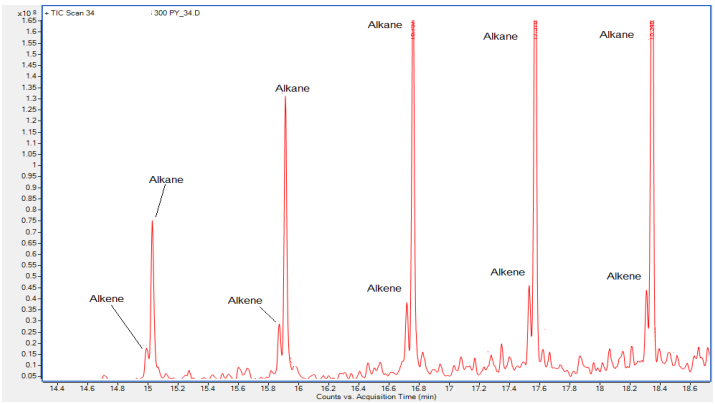


Figure 3. Close-up of A at 300°C, showing doublet peaks.

As opposed to A, the EGA of B instead contains two regions of outgassing, 290°C and 520°C. To fully characterize this oil, 3 temperatures were chosen, 300°C, 450°C, and 520°C, representing both the peaks and the valley of the EGA. Figure 4 contains a stack of 3 chromatograms, representing increasing pyrolysis temperatures, 300°C, 450°C, and 520°C from top to bottom.

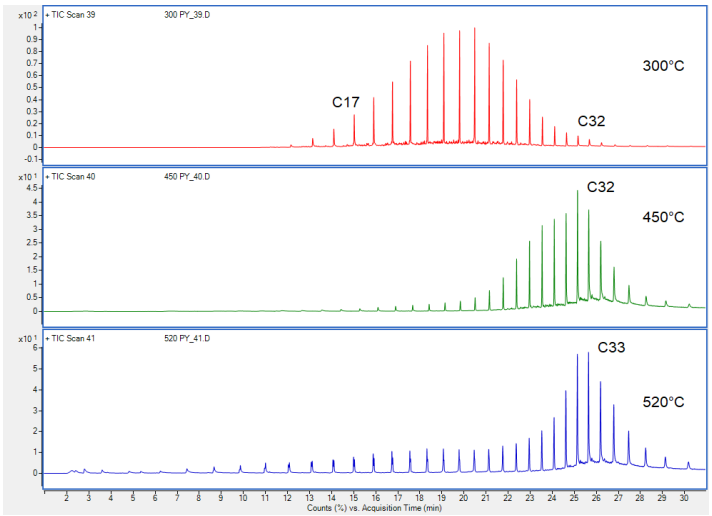


Figure 4. Multi-step pyrolysis of B.

At 300 °C, the chromatogram is similar to A in that it exhibits a series of alkanes. At 450°C, the remainder of the alkanes continue to outgas. At 520 °C, pyrolysis breaks apart the non-volatile portion of the oil into smaller volatile fragments which travel to the GC-MS (Figure 5). These pyrolysates appear as a series of two peaks, alkenes, and alkanes, as a fragment of a larger hydrocarbon breaks via random scission and stabilizes by hydrogen abstraction to create an alkane, or beta-scission for an alkene.

Chlorinated and oxygenated species indicate unwanted plastics such as PET and PVC in the pyrolysis recycling stream. For example, hydrochloric acid and chlorinated compounds from PVC promote pipeline corrosion[4]. Benzoic and terephthalic acids and other oxy- genated aromatics from PET are also corrosive and can clog pipes[5]. When peaks from the chromatograms were searched against the NIST library, no benzoic or terephthalic acids from PET, or chlori- nated species from PVC were seen, indicating the pyrolysis inputwas of high purity.

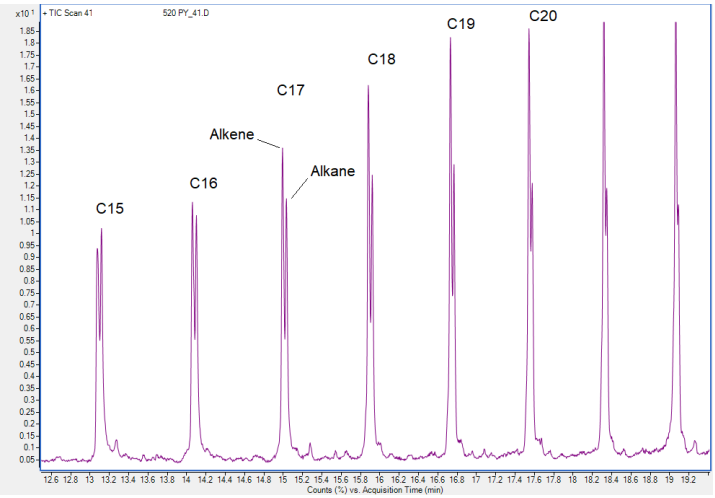
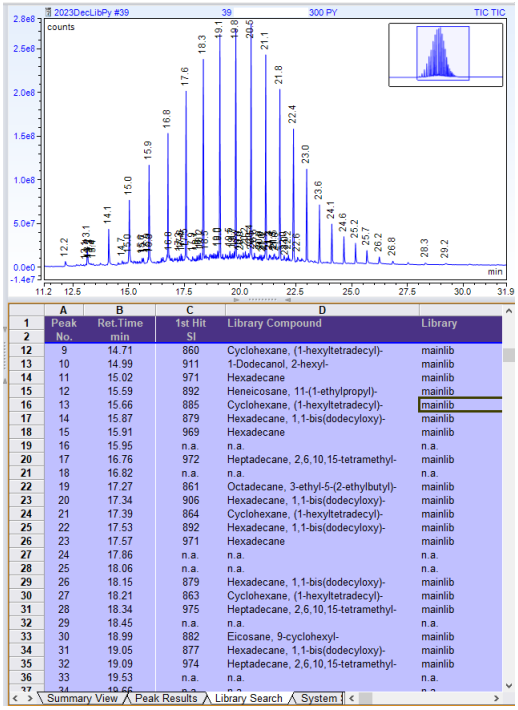


Figure 5. Close-up of B at 520°C.



	A	B	C	D	
1	Peak	Ret.Time	1st Hit	Library Compound	Library
2	No.	min	SI		
12	9	14.71	860	Cyclohexane, (1-hexyltetradecyl)-	mainlib
13	10	14.99	911	1-Dodecanol, 2-hexyl-	mainlib
14	11	15.02	971	Hexadecane	mainlib
15	12	15.59	892	Heneicosane, 11-(1-ethylpropyl)-	mainlib
16	13	15.66	885	Cyclohexane, (1-hexyltetradecyl)-	mainlib
17	14	15.87	879	Hexadecane, 1,1-bis(dodecyloxy)-	mainlib
18	15	15.91	969	Hexadecane	mainlib
19	16	15.95	n.a.	n.a.	n.a.
20	17	16.76	972	Heptadecane, 2,6,10,15-tetramethyl-	mainlib
21	18	16.82	n.a.	n.a.	n.a.
22	19	17.27	861	Octadecane, 3-ethyl-5-(2-ethylbutyl)-	mainlib
23	20	17.34	906	Hexadecane, 1,1-bis(dodecyloxy)-	mainlib
24	21	17.39	864	Cyclohexane, (1-hexyltetradecyl)-	mainlib
25	22	17.53	892	Hexadecane, 1,1-bis(dodecyloxy)-	mainlib
26	23	17.57	971	Hexadecane	mainlib
27	24	17.86	n.a.	n.a.	n.a.
28	25	18.06	n.a.	n.a.	n.a.
29	26	18.15	879	Hexadecane, 1,1-bis(dodecyloxy)-	mainlib
30	27	18.21	863	Cyclohexane, (1-hexyltetradecyl)-	mainlib
31	28	18.34	975	Heptadecane, 2,6,10,15-tetramethyl-	mainlib
32	29	18.45	n.a.	n.a.	n.a.
33	30	18.99	882	Eicosane, 9-cyclohexyl-	mainlib
34	31	19.05	877	Hexadecane, 1,1-bis(dodecyloxy)-	mainlib
35	32	19.09	974	Heptadecane, 2,6,10,15-tetramethyl-	mainlib
36	33	19.53	n.a.	n.a.	n.a.

Summary View | Peak Results | Library Search | System

Figure 6. Example Search Results using Chromeleon 7.2.7

Conclusion

EGA and MSP are two powerful tools in polymer identification. The first tool can quickly screen pyrolysis oils based on temperature, whereas the second tool can provide more detailed information. These two oils were proven to be a complex mixture of hydrocarbons, dominating in alkanes.

References

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