Effluent Monitoring by Repetitive Injection Gas Chromatography—Mass Spectrometry

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Abstract

A small volume gas chromatograph (GC) oven and interface that permits repetitive separation and mass spectrometric analysis of effluents are described. Volatile products formed during the thermal analysis of solid samples are separated and identified by employing repetitive temperature program capillary GC with mass spectrometric (MS) detection. Thermal analysis effluent sampling intervals of a few minutes are achieved by using liquid nitrogen to cool the GC column between separations. A filtering algorithm that extracts MS information for selected species from multiple GC–MS chromatograms is also described. The algorithm simplifies the task of finding chromatographic peaks that correspond to the same eluent. After species-specific peaks are identified, they are integrated to create evolution temperature profiles that reflect changes in the effluent component concentrations.

Introduction

The resolution trade-off required to achieve fast gas chromatographic (GC) separations has been known for some time (1). The availability of high-efficiency capillary columns now makes it feasible to sacrifice chromatographic resolution to facilitate rapid complex mixture analyses (2,3). Analysis techniques that incorporate solute focusing have been developed and can yield a baseline separation of several mixture components in a matter of seconds (4–6). High-speed chromatographic separations typically require rapid sample introduction and necessitate the use of detectors that can provide effluent measurements on a time scale of milliseconds (7). However, even without techniques for solute focusing and the use of high-speed detectors, it is possible to employ GC to separate mixtures in a few minutes. For some applications, repetitive analyses on this time scale are sufficient to permit effluent monitoring. By combining repetitive GC separations with the mass spectrometric (MS) detection of separated components, it is possible to monitor concentration variations for effluent mixture components.

Thermal analysis (TA) techniques are routinely employed for characterizing solid-state materials. Bulk property information provided by thermal analysis can be augmented by evolved gas analysis (EGA) when volatiles are produced as a result of heating solid samples. Species-specific evolution temperature profiles can be obtained using EGA when analyzer signals can be uniquely ascribed to particular substances entrained in purge gas effluent. MS and infrared (IR) spectrophotometry are common evolved gas detectors that provide structural information regarding volatiles generated during thermal analyses (8,9). However, the structural information provided by MS and IR spectrophotometry EGA is typically comprised of overlapping contributions from mixture components. Consequently, species-specific spectral features may not be available. Alternatively, chromatographic separation coupled with structure-specific detection can provide species-specific information. GC separations were first used to separate TA effluent components that were cryogenically trapped during analyses. Species-specific evolution temperature profiles were difficult to obtain by this method, because it was difficult to repetitively trap and separate volatiles during a single analysis. More recently, McClennen et al. (10) described TA-GC–MS and TA-GC–IR analysis systems incorporating automated vapor sampling and short chromatographic columns that provided both satisfactory GC separations and species-specific evolution profiles. Species-specific evolution profiles can be quite helpful when attempting to elucidate thermal decomposition mechanisms (11–14). Chromatographic separations could be repeated at 1-min intervals by using their apparatus. However, their systems were limited to isothermal chromatographic separations, column flow rates were not easily varied, and sample injection was not readily adapted for the analysis of standard mixtures. The TA-GC–MS analysis system described here provides rapid temperature program GC analyses and permits repetitive effluent sampling during a single thermal analysis. One goal in the design of this apparatus was to facilitate rapid column heating and cooling within a well-insulated small-volume GC oven. For TA-GC–MS analyses, chromatographic

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conditions that provided the most rapid separations possible in which most mixture components were baseline resolved were selected.

Experimental

The TA-GC–MS system consisted of a quartz tube within a Carbolite (Watertown, WI) model MTF tube furnace connected to a Hewlett-Packard (Palo Alto, CA) 5985 quadrupole MS via a heated interface and a small-volume GC. A diagram of the interface and GC is shown in Figure 1. The TA-GC–MS interface was contained within a 12- × 10- × 6-inch oven that was used to heat a Valco Instruments (Houston, TX) 4C8T 8-port injection valve and an SGE (Austin, TX) MCVT-1-50 effluent splitter valve to prevent the condensation of TA effluent. Two 100-µL sample loops were attached to the injection valve. TA effluent passed through one of the sample loops, and the GC carrier gas passed through the other. During injection, the TA effluent trapped in the first sample loop was directed into the GC column, and the second sample loop was switched to the TA effluent stream to collect the next sample. The interface oven was heated by two 3- × 10-inch, 500-watt strip heaters, and the oven temperature was maintained at 220–300°C (depending on the sample analyzed) by an Omega (Stamford, CT) CN76000 temperature controller. An SGE UNI-K10 on-column capillary GC injector was mounted to the top of the interface oven and could be used to inject standards into the GC column. The injector was connected to the 8-port injection valve by a short length of 0.332-mm o.d. uncoated fused-silica tubing. Figure 2 shows the gas flow paths through the injection valve in each of its 2 positions. Helium carrier gas (2 mL/min) from the on-column injector entered the 8-port injection valve, passed through a 100-µL stainless steel sample loop attached to the valve, and then passed into a 10-m × 0.25-mm-i.d. capillary GC column with a 0.25-µm dimethyl polysiloxane stationary phase film thickness. The capillary column was contained in a 8- × 6- × 6-inch GC oven placed beneath the interface oven. The GC incorporated a 1100-watt nichrome wire heating element and a fan to achieve column heating rates as high as 300°C/min. A Grainger (Oklahoma City, OK) liquid nitrogen solenoid valve (not shown in Figure 1) was mounted to the front of the chromatograph oven. The solenoid valve was attached to a liquid nitrogen dewar using insulated ¼-inch-o.d. copper tubing. The capillary column can be cooled at a rate of about 600°C/min when the solenoid valve is opened. The chromatograph oven temperature was maintained using an Omega CN3202 heating/cooling temperature controller that varied the heating element current and energized the liquid nitrogen solenoid valve to heat or cool the oven to the temperature setpoints. The GC capillary column exit was connected to the MS ion source through the SGE effluent splitter in the interface oven. During TA-GC–MS analyses, the effluent splitter valve was opened until the column flow rate (measured at the exit port on top of the interface oven) was reduced to nearly zero. This established a nearly direct couple connection between the capillary GC column and the MS ion source.

The TA furnace quartz tube extended into the interface oven and was connected to the 8-port injection valve by 1/16-inch-o.d. stainless steel tubing. Helium and hydrogen at flow rates of

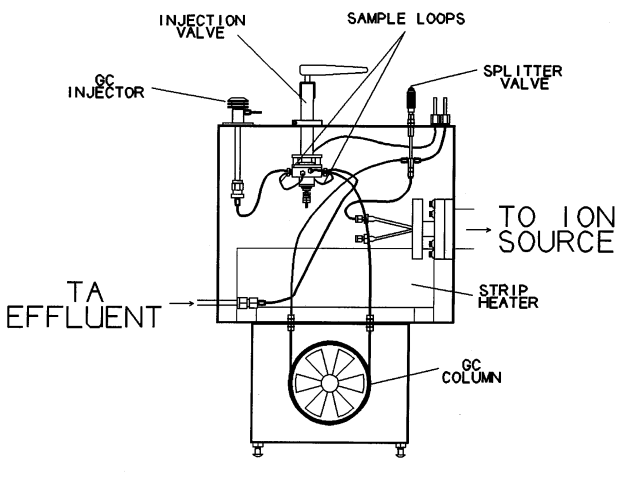

Figure 1. Diagram of the TA-GC–MS interface.

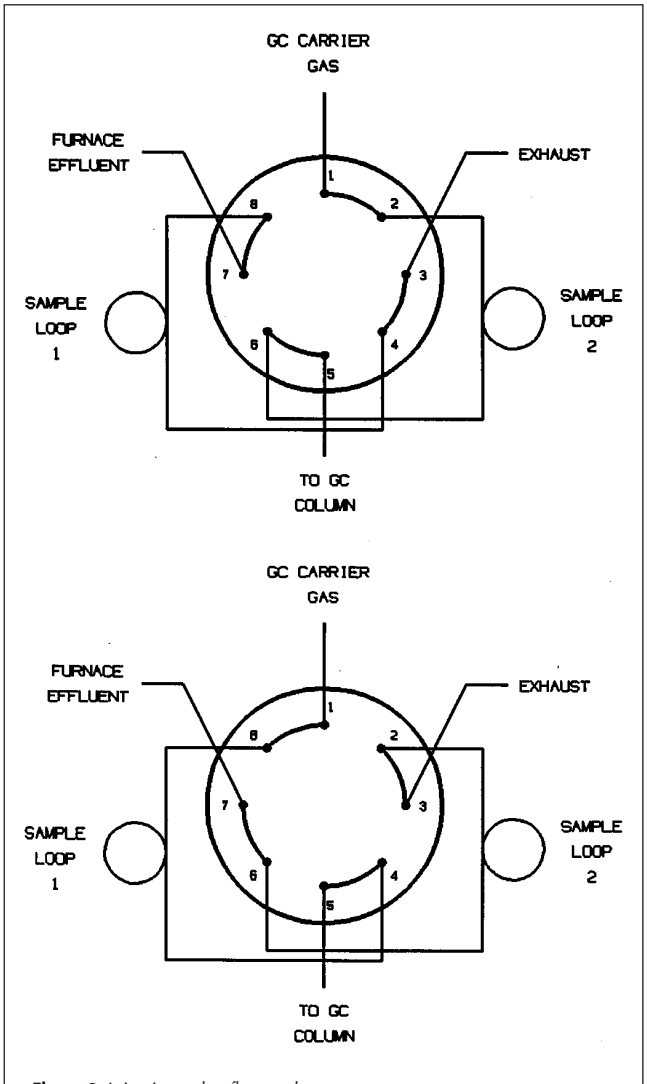

Figure 2. Injection valve flow paths.

25 mL/min were employed for the TA sample purge gas. As shown in Figure 2, TA effluent entering the 8-port valve passed through a 100-µL stainless steel sample loop attached to the valve and then through 1/16-inch-o.d. stainless steel tubing to an exit at the top of the interface oven. During TA-GC–MS analyses, TA effluent was injected into the GC column by rotating the 8-port injection valve, switching the 100-µL sample loop containing TA effluent to the GC carrier gas stream. At the same time, the 100-µL sample loop that had been in line with the GC column was switched to the TA effluent stream.

The quadrupole MS was operated in electron impact ionization mode (70 eV) with an ion source pressure of about 1 × 10–5 torr. Mass spectra were acquired at rates of 0.3–0.4 s/scan depending on the mass range employed. Eluent identifications were made with the aid of a 36,218-spectra NBS mass spectral library.

Results and Discussion

The first step in creating species-specific evolution profiles from repetitive injection GC–MS data is to identify the substances responsible for selected chromatographic peaks. This is usually accomplished by comparing retention times and mass spectra of known materials with those associated with unknown chromatographic eluents. After the substance responsible for a chromatographic peak is identified, information regarding the concentration of this species in TA effluent can be obtained by computing the total ion current (TIC) chromatographic peak areas. To generate species-specific evolution temperature profiles, chromatographic peaks representing the same substance in successive TA-GC–MS gas chromatograms must be integrated. A profile is generated by plotting the TIC peak areas for a particular substance against the sample temperatures at which the chromatographic injections were made. TA-GC–MS data sets may contain 20,000–30,000 mass spectra and consist of 15–30 chromatograms, each containing 30–50 peaks. Commercially available GC–MS software is designed for manipulating single chromatograms; therefore, each species-specific TA-GC–MS peak must be located and integrated manually when these data reduction tools are employed. Consequently, the task of generating species-specific evolution profiles using commercially available GC–MS data reduction software can be very time-consuming. To simplify TA-GC–MS data reduction procedures, a filtering algorithm that compares structure-specific mass spectral patterns to determine which chromatographic peaks represent selected eluents was employed.

The chromatogram peak extraction algorithm compares all TA-GC–MS mass spectra with a target mass spectrum and extracts chromatogram segments from the data set when mass spectra match the target spectrum. After isolating the chromatogram peaks representing a selected eluent, their areas are computed and plotted as a function of the sample temperature at the time of chromatographic injection. The mass spectrum filter employs a spectral comparison method that has been used for library searching (15) and is supplied with many MS data systems. In this method, mass spectra are represented as multidimensional vectors. Vector dimensionality is determined by the number of ions scanned to obtain the spectrum (i.e., the mass range). The orientation of a mass spectral vector in multidimensional space is determined by relative ion signal abundances and is therefore dependent on the structure of the substance that produced the mass spectrum. Angles between the vectors derived from TA-GC–MS mass spectra and a target mass spectrum are obtained by computing vector dot products. Small angles are obtained when mass spectra are similar, whereas large angles result when a poor match is obtained. An operator-specified threshold angle is employed to determine which chromatogram segments are extracted from the original data set. With the appropriate choice of a threshold angle value, the chromatogram peaks derived from mass spectra that closely resemble the target mass spectrum are selected from the TA-GC–MS data set.

Thermal desorption studies of the hydrocarbons formed as a result of olefin reactions with catalyst acid sites can be used for catalyst characterization (12). The magnitude of the TA-GC–MS data reduction problem for these types of analyses is illustrated by the data shown in Figure 3. Figure 3A shows successive chromatograms obtained while thermally desorbing hydrocarbons from a solid acid catalyst surface. Fifteen capillary gas chromatograms were obtained over a 70–280°C temperature range, and 70 mg of sulfated zirconia catalyst that had been exposed to 1-butene at 50°C was heated at a rate of 2°C/min in helium. One axis indicates the sample temperatures at which the TA effluent was injected into the capillary GC column. Many peaks in the

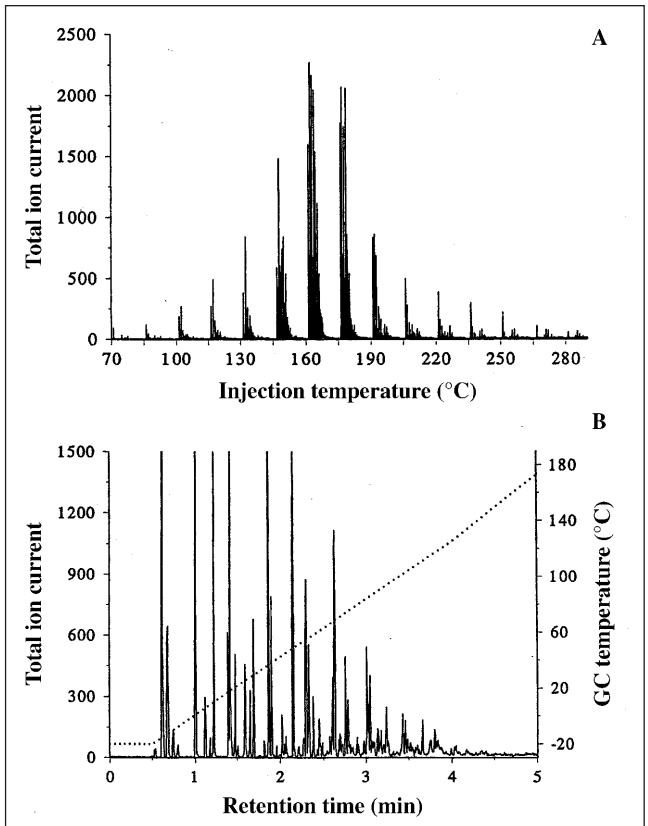

Figure 3. TA-GC–MS successive chromatograms representing hydrocarbons desorbing from sulfated zirconia (A), and the chromatogram obtained by injecting purge gas effluent into the GC when the sulfated zirconia temperature reached 160°C (B).

TA-GC–MS chromatograms represent species with more than 4 carbons, suggesting that 50°C was sufficient for 1-butene oligomerization on the catalyst surface. Figure 3B shows the gas chromatogram obtained by injecting the TA effluent into the column when the catalyst temperature reached 160°C. The dotted line in this plot represents the GC oven temperature program employed to separate volatile products. Subambient temperatures were required at the beginning of the temperature program to separate low-boiling-point hydrocarbons such as propene, butenes, and butanes. After a 30-s isothermal period at –20°C, the GC temperature was increased to 125°C at a rate of 40°C/min, and then it was increased to 220°C at a rate of 50°C/min. The GC temperature program required approximately 6 min. Cooling the GC oven back to –20°C required less than 30 s. By allowing a 1-min equilibration period at –20°C before the start of the next injection, chromatograms were obtained at 7.5-min intervals, corresponding to 15°C catalyst temperature intervals. The chromatograms in Figure 3 contain more than 50 eluent peaks, many of which are baseline resolved. Mass spectra obtained during TA-GC–MS analyses confirmed that the most evolved products were hydrocarbons in the C_3–C_{10} range. Although the majority of the volatile products were saturated hydrocarbon isomers, unsaturated species and aromatics were also detected.

The chromatographic peaks shown in Figure 4A were extracted from those in Figure 3 using the mass spectrum filtering algorithm and a 2-methylbutane target mass spectrum. With the appropriate choice of a vector angle threshold value, the chromatographic peaks attributed solely to 2-methylbutane elutions were extracted from the TA-GC–MS data. Figure 4B shows the 2-methylbutane species-specific evolution temperature profile generated from the chromatogram peak areas. Figure 5 shows the results obtained when mass spectrum filtering was applied to the TA-GC–MS data set shown in Figure 3 with a pentene target mass spectrum. Figure 5A shows the peaks that were extracted. Comparing the peaks in Figures 4 and 5 reveals that the pentene evolution temperature profile was different from the 2-methylbutane profile. Although not apparent in the chromatogram peaks shown in Figure 5A, more than one peak was extracted from some of the chromatograms. Figure 5B shows the species-specific evolution temperature profiles representing 3 pentene isomers derived from the closely spaced chromatographic elutions. Because the mass spectra representing these eluents were virtually indistinguishable, it was not possible to restrict mass spectrum filtering to a single component. The 3 evolution profiles in Figure 5 span different temperature ranges, with the lowest-yield pentene isomer exhibiting the most narrow temperature range. This phenomenon is largely due to the effects of mass spectral noise on the filtering algorithm. Mass spectral noise results in orientation changes in multidimensional vectors. The magnitude of this random effect depends on spectral signal-to-noise ratio. As a result, evolution profiles are truncated when the target spectrum matches are insufficient for chromatogram segment extraction because of low spectral

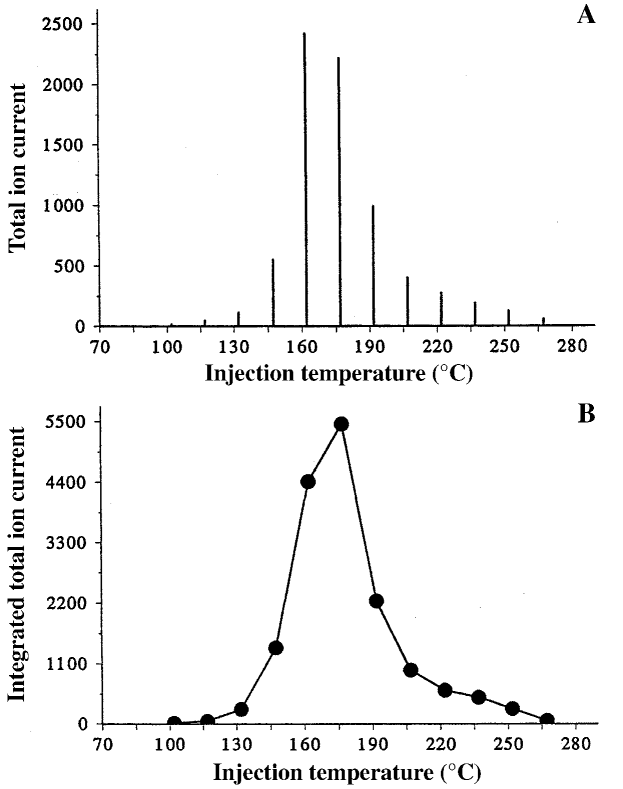

Figure 4. 2-methylbutane specific chromatogram segments extracted from the data set shown in Figure 3 (A), and the 2-methylbutane evolution temperature profile (B).

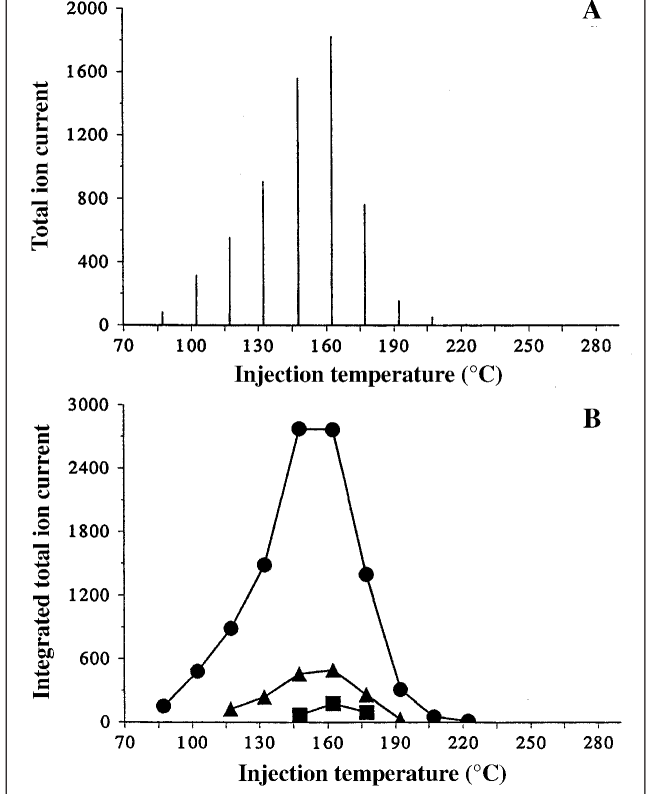

Figure 5. Pentene specific chromatogram segments extracted from the data set shown in Figure 3 (A), and the pentene evolution temperature profiles (B).

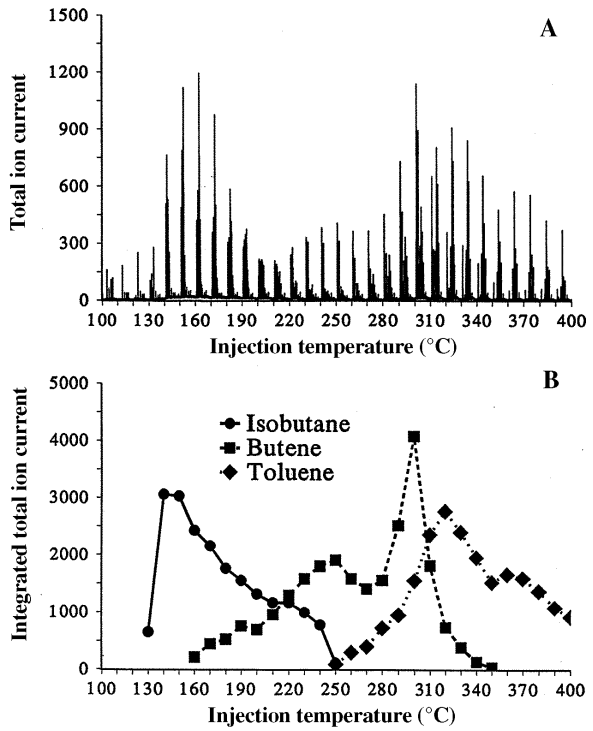

Figure 6. TA-GC–MS successive chromatograms representing volatile products derived from poly(ethylene) cracking (A), and species-specific evolution temperature profiles (B).

signal-to-noise ratios.

TA-GC–MS has also been employed to investigate polymer cracking mechanisms (13,14). Acid-catalyzed cracking is a potential new recycling method for plastic wastes. Figure 6 shows the TA-GC–MS results obtained by heating a sample containing HZSM-5 cracking catalyst mixed with approximately 2% (w/w) poly(ethylene) at a rate of 2°C/min from 100 to 400°C. Separations began by maintaining the GC oven at –20°C for 30 s followed by a ramp to 150°C at 50°C/min. The TA effluent was sampled at 5-min intervals, corresponding to 10°C sample temperature increments. More than 30,000 mass spectra are represented in Figure 6. Changes in the 29 chromatograms shown in Figure 6A suggest that poly(ethylene) cracking processes varied substantially with temperature. The 3 species-specific evolution temperature profiles shown in Figure 6B were obtained by applying the mass spectral filtering algorithm to the data set shown in Figure 6A. Differences in temperature-dependent volatile species yields are readily apparent from these evolution profiles. An inspection of other species-specific TA-GC–MS evolution temperature profiles revealed that the profiles for isobutane, butene, and toluene shown in Figure 6 were characteristic of saturated, unsaturated, and alkyl aromatic volatile products, respectively.

TA-GC–MS evolution temperature profile shapes are determined by thermal processes, such as desorption and decomposition, that yield volatile products when solid samples are heated. Consequently, solid-state thermal processes can be characterized by TA-GC–MS. TA-GC–MS was employed to investigate the differ-

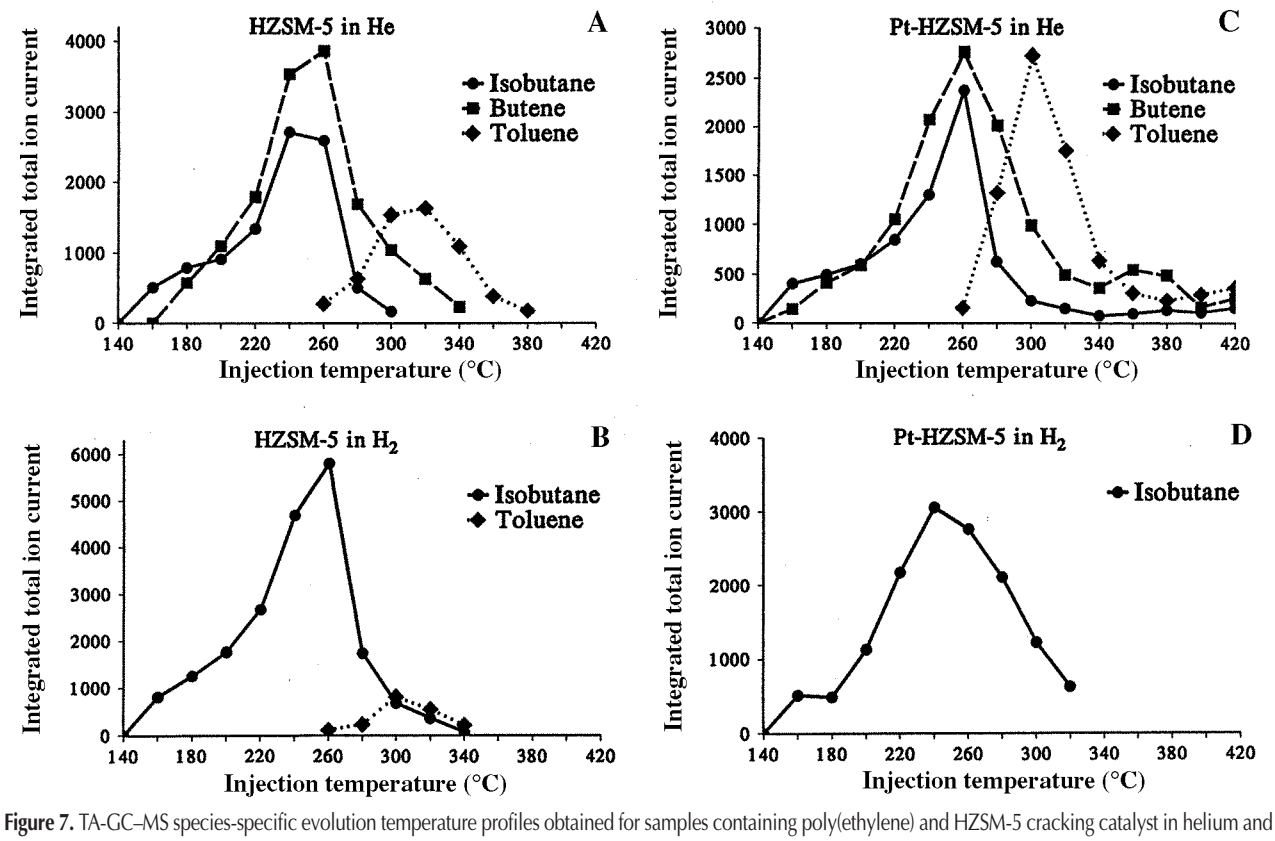

Figure 7. TA-GC–MS species-specific evolution temperature profiles obtained for samples containing poly(ethylene) and HZSM-5 cracking catalyst in helium and hydrogen. Plots denoted by Pt-HZSM-5 indicate that platinum had been added to the solid acid catalyst. HZSM-5 in He (A), HZSM-5 in H_2 (B), Pt-HZSM-5 in He (C), Pt-HZSM-5 in H_2 (D).

ences in polymer cracking mechanisms resulting from variations in the cracking catalyst and purge gas compositions. The species-specific evolution temperature profiles in Figure 7 were obtained by TA-GC–MS analyses of samples containing HZSM-5 cracking catalyst and approximately 10% (w/w) poly(ethylene). Samples were heated at 5°C/min, and the chromatograms were obtained using a temperature program beginning at –20°C for 20 s followed by a ramp to 80°C at 65°C/min and then to 280°C at 200°C/min. Chromatograms were obtained at 4-min intervals, permitting TA effluent sampling at 20°C sample temperature increments. As in Figure 6, the evolution profiles for isobutane, butene, and toluene in Figure 7 were found to be representative of saturated, unsaturated, and alkyl aromatic volatile products, respectively. Interestingly, TA-GC–MS results for the poly(ethylene)–HZSM-5 sample in helium were significantly different from those shown in Figure 6. The larger quantity of polymer in the 10% (w/w) poly(ethylene) sample may have led to more rapid catalyst deactivation during thermal analysis. This would account for the shift in evolution profiles to higher temperatures for the 10% (w/w) poly(ethylene)–HZSM-5 sample in comparison with the 2% sample. As shown in Figure 7, when the poly(ethylene)–HZSM-5 sample was heated in hydrogen, butene was not detected, and the toluene (alkyl aromatics) yield was significantly reduced. However, when compared with the results obtained in helium, the positions and widths of the evolution temperature profiles for isobutane and toluene were not significantly different. This suggests that catalytic cracking processes did not change when the purge gas was switched from helium to hydrogen. Rather, the unsaturated species formed by catalytic cracking were simply hydrogenated prior to detection by TA-GC–MS. Olefin hydrogenation in catalytic systems is facilitated by employing catalyst formulations that contain small amounts of platinum that serve as hydrogenation catalysts. Two of the evolution profiles in Figure 7 were derived from samples containing HZSM-5 with added platinum. The profiles for the poly(ethylene)–Pt-HZSM-5 sample obtained with helium purge gas are similar to those obtained with the HZSM-5 catalyst, except that the relative yield of toluene (alkyl aromatics) was increased when platinum was incorporated into the catalyst. When the poly(ethylene)–Pt-HZSM-5 sample was heated in hydrogen, only the saturated volatile products were detected. Figure 7 shows that the isobutane evolution temperature profile for this analysis is somewhat broader than those obtained from the other analyses. The broader volatile product profile likely occurred because some of the saturated volatile products that evolved at a high temperature resulted from the hydrogenation of initially formed unsaturated species. Alkyl aromatics were not detected when the poly(ethylene)–Pt-HZSM-5 sample was heated in hydrogen, because unsaturated species (which are precursors for aromatic rings) were hydrogenated soon after they were formed.

Conclusion

Although TA effluent analysis is emphasized here, repetitive GC–MS analysis can be employed to monitor any suitable effluent stream. A tremendous amount of structure-specific information regarding the volatile products can be obtained by using repetitive injection GC–MS evolved gas analysis. Information regarding the thermal events derived from TA-GC–MS far exceeds that provided by TA-MS and TA-IR, because the effluent mixture components can be both separated and identified. The TA-GC–MS species-specific evolution profiles shown here illustrate the utility of mass spectrum filtering data reduction. Unfortunately, evolution profiles cannot be obtained by this method when the eluent peaks overlap, because mass spectra obtained for overlapping eluents are often significantly different from the target mass spectra. However, modifications of the current algorithm that incorporates overlapping elution deconvolution should extend species-specific data extraction to include partially resolved chromatogram segments.

The frequency with which a TA effluent is sampled depends on the time required for chromatographic separation. For the studies described here, solid sample heating rates of 2–5°C/min were required to facilitate the generation of species-specific evolution temperature profiles. By taking advantage of solute focusing and high-speed time-of-flight MS detection, it should be possible to reduce separation times and permit increased thermal analysis heating rates, which would decrease the time required for thermal analyses.

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