Rapid analysis of pyrolysis oil using blank tube-FI method and GC-EI/FI method of JMS-T2000GC

Product used: Mass Spectrometer (MS)

Introduction

In the blank tube-FI (Field Ionization) method, a sample is introduced into the GC injection port, passed through a blank tube, and then detected using the soft ionization FI method. It is possible to detect molecular ions in less than one minute. When measuring a mixture of hydrocarbons such as oil, a complex mass spectrum containing multiple molecular ion peaks is obtained. Even in this case, qualitative information can be easily obtained by KMD analysis. The main components hydrocarbons related ion peaks can be classified based on carbon number and DBE (degree of unsaturation), and other ion peaks can be estimated their composition formulas. Although it is difficult to obtained the structural formula using the blank tube-FI method alone, it is possible to obtain it efficiently by using the GC-EI/FI method in combination.

In this MSTips, we will introduce the analysis results of pyrolysis oil using the above methods. Pyrolysis oil is an oil obtained from waste plastic and rubber products. It is used as an alternative fuel to petroleum and as a raw material for recycled plastics. So, it is one of the important technologies related to the circular economy.

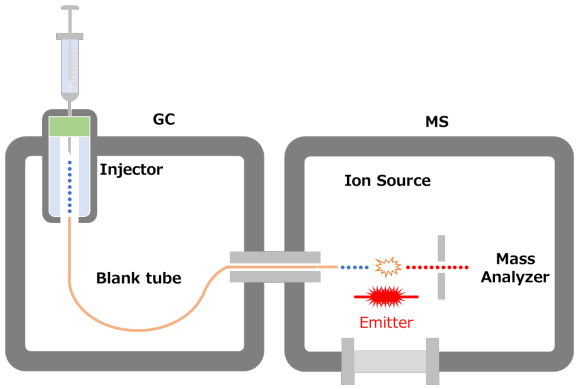

Figure 1 Schematic of blank tube-FI method

Experiment

A commercially available pyrolysis oil made from waste plastic was used as a sample. This sample was measured using the JMS-T2000GC blank tube FI method and analyzed using msRepeatFinder. The same sample was also measured using the GC-EI/FI method and analyzed using msFineAnalysis AI.

Table 1 Measurement conditions

	GC-EI	GC-FI	Blank tube-FI
Sample			
Injection volume	1µL		
GC conditions			
Column	ZB-5MS, 60 m length, 0.25 mm i.d., 0.25µm thickness (Phenomenex, Inc.)		Blank tube, 5m length, 0.25mm i.d.
Split	20:1		
Inlet temperature	300°C		
Oven temperature	40°C (1 min hold) – 5°C/min – 300°C (30 min hold)		300°C (isothermal)
Carrier gas	He, 1mL/min		He, 3mL/min
MS conditions			
Ionization	EI (70eV)	FI	
Mass range	*m/z* 35-800		

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Results

Figure 2 shows the TIC chromatogram and mass spectrum of the blank tube-FI method. The sample introduced into the GC injection port reached the MS in about 10 seconds. Since it was a soft ionization method without chromatogram separation, multiple molecular ions were detected from one mass spectrum.

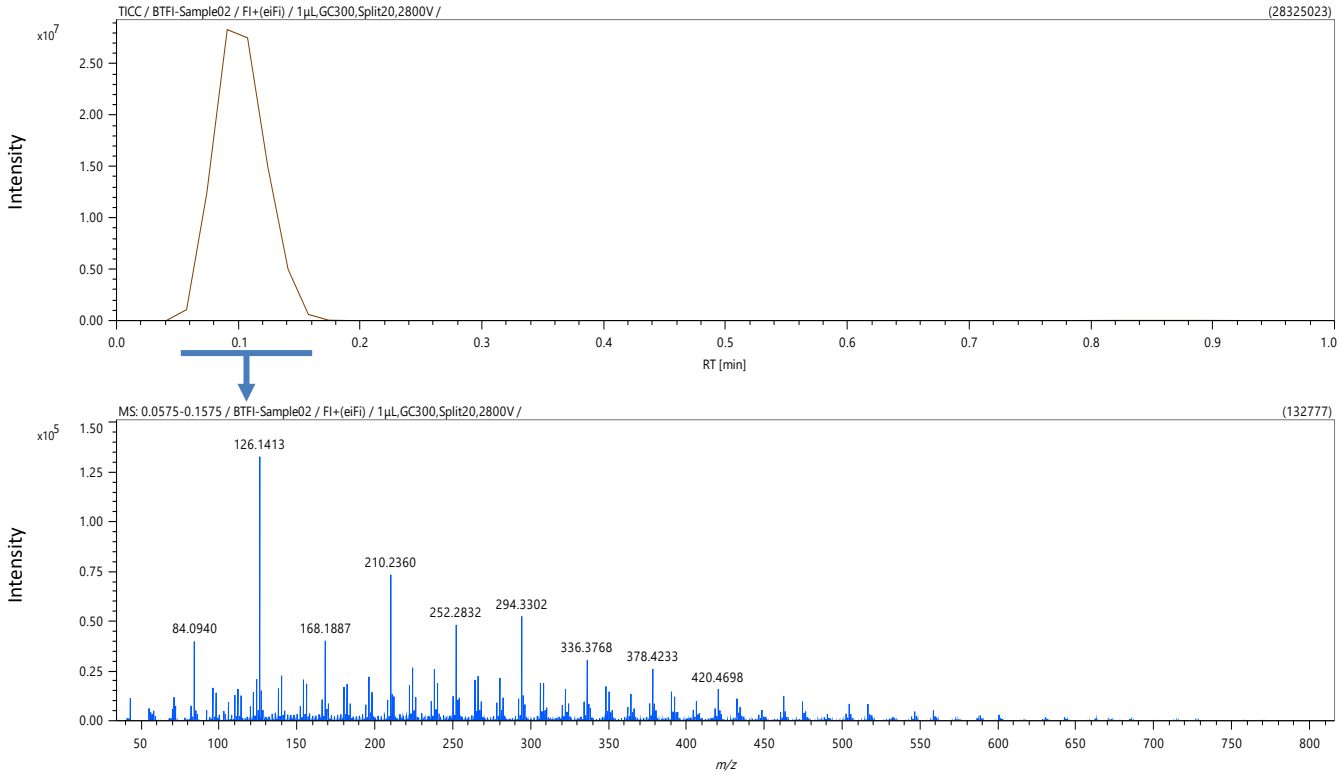

Figure 2 TIC chromatogram and mass spectrum of blank tube-FI

Figure 3 shows the KMD plot created from the above mass spectrum. In version 7 of msRepeatFinder, a new function has been added to search ion peaks of composition formulas registered in the list. Using this function, it is possible to automatically group hydrocarbons as blue/green, additives as red, and others as black. In this result, oxide of phosphorus-based antioxidant (CAS 31570-04-4) was detected as an additive.

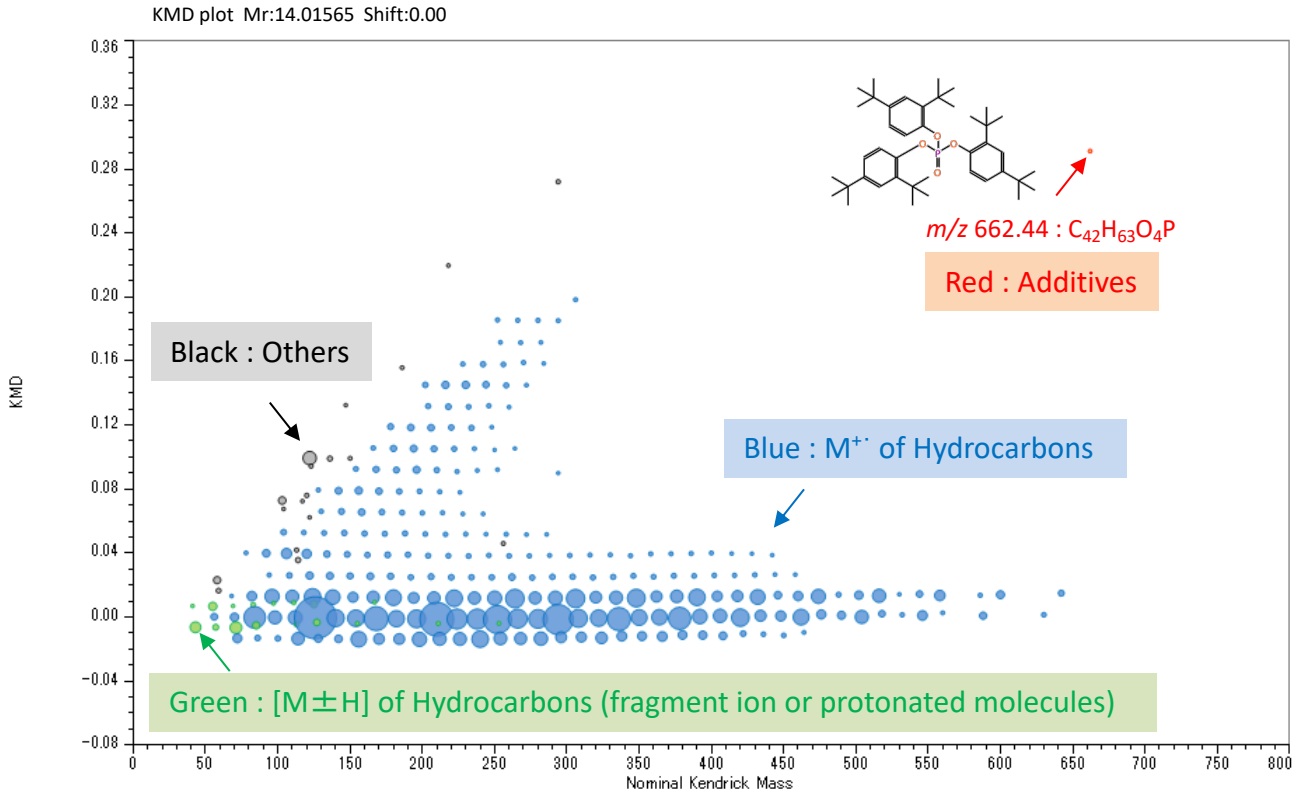

Figure 3 KMD plot of all components

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Figure 4 shows a KMD plot of the M+· of hydrocarbons only. Each ion peak is plotted with carbon number on the horizontal axis and DBE (=degree of unsaturation) on the vertical axis. It is possible to visualize and evaluate the characteristics of the oil. It is also possible to quantitatively evaluate oil characteristics by calculating strength ratios, average molecular weights, etc.

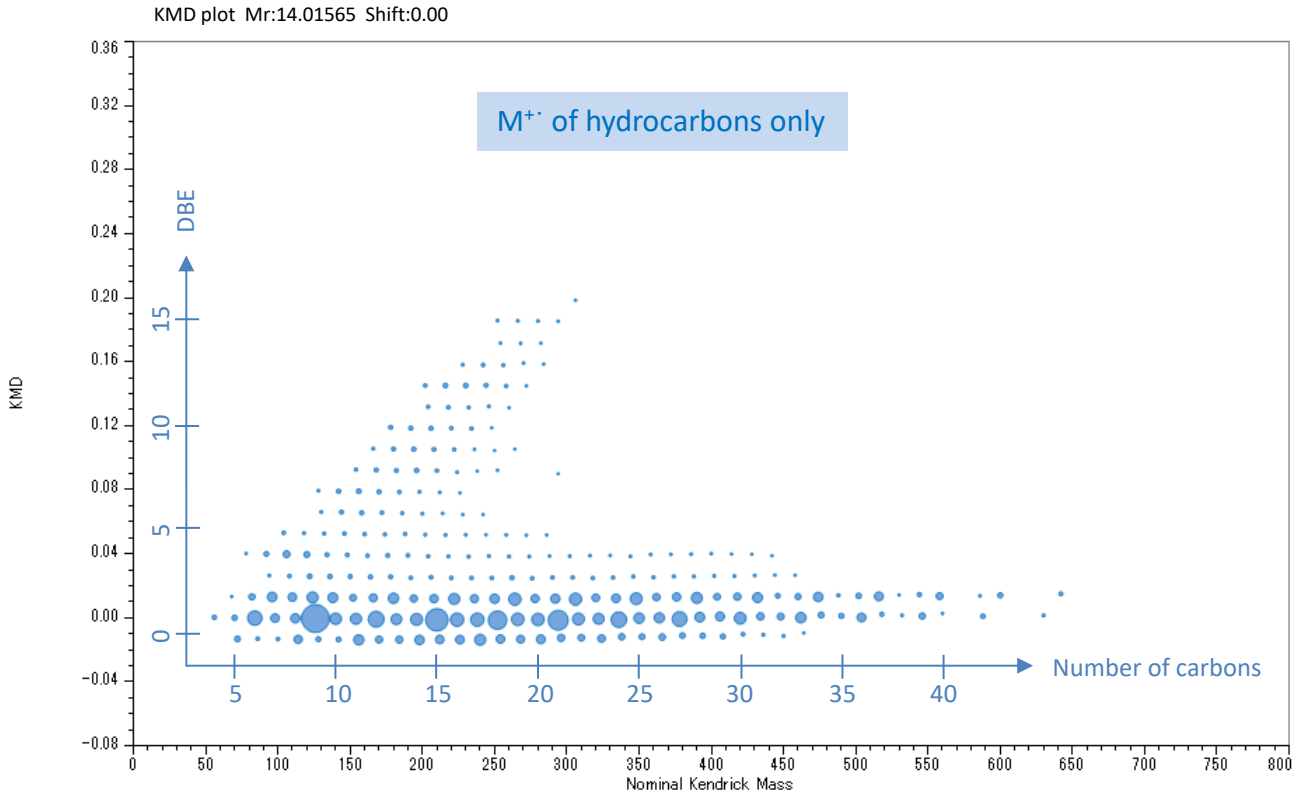

Figure 4 KMD plot of the M+· of hydrocarbons only

Figure 5 shows a KMD plot of "others" only. Each peak has accurate mass number information, and it is possible to estimate the composition formula. In this result, in addition to oxygen and nitrogen compounds, sulfur compounds, which affect oil quality, were also detected.

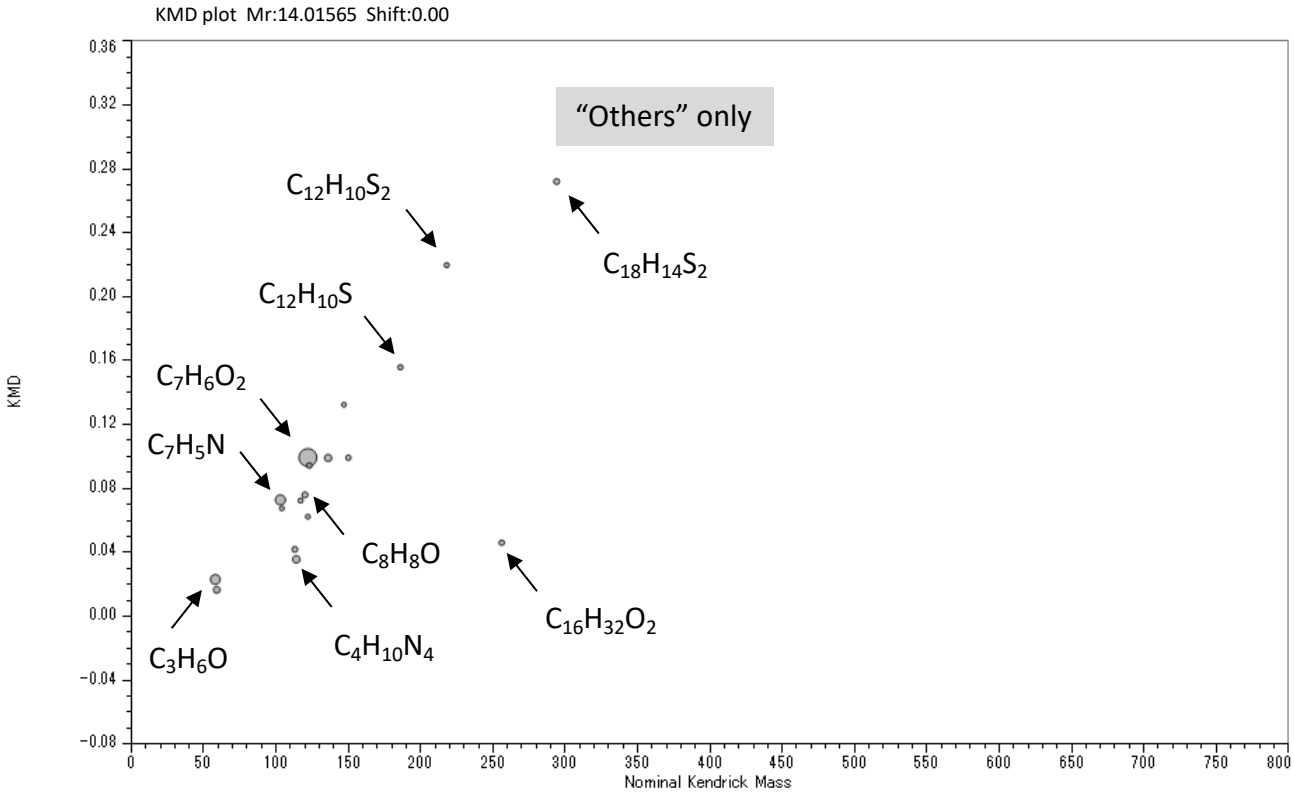

Figure 5 KMD plot of "others" only

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Figure 6 shows the analysis results of the GC-EI/FI method using msFineAnalysis AI, and Figure 7 shows the KMD plot with the resulting structural formula. The strongest component was benzoic acid ($C_7H_6O_2$), which is a thermal decomposition product of some plastics such as polyethylene terephthalate (PET). The sulfur compounds were assumed to be a thermal decomposition products of polyphenylene sulfide (PPS) based on their structural formulas. Furthermore, it is also possible to confirm the structural formula of each hydrocarbon by using the same procedure.

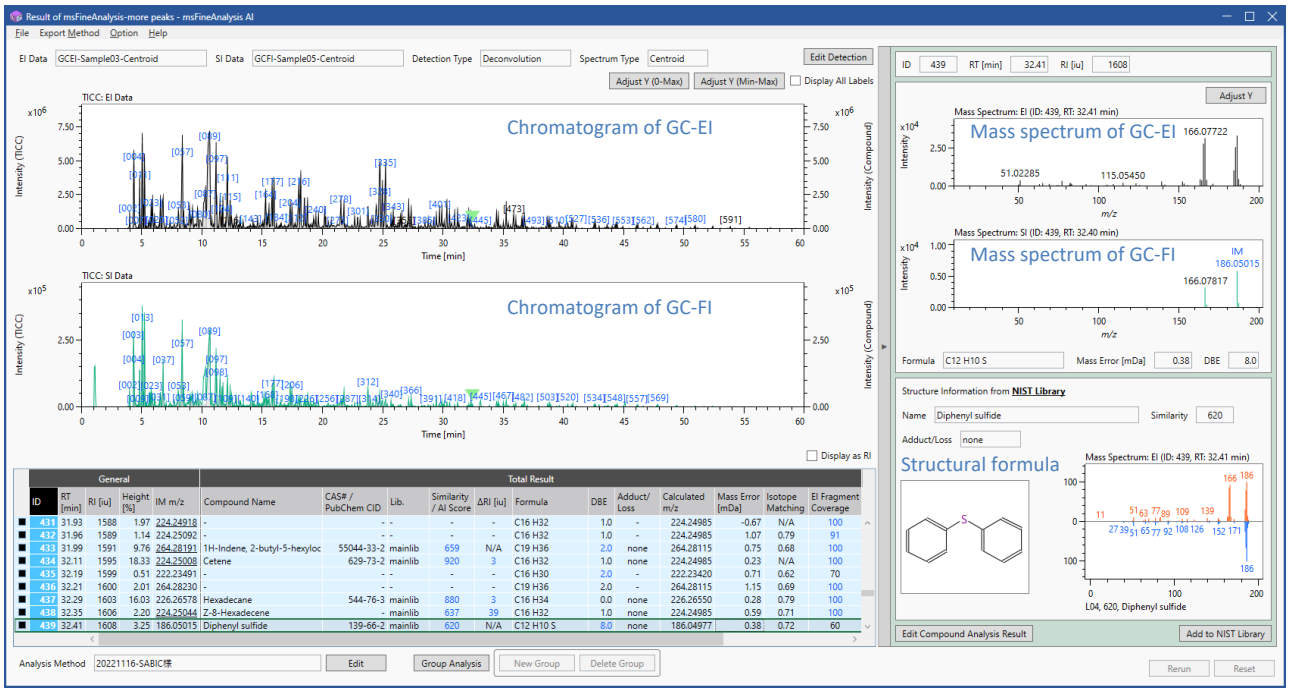

Figure 6 GC-EI/FI analysis result using msFineAnalysis AI

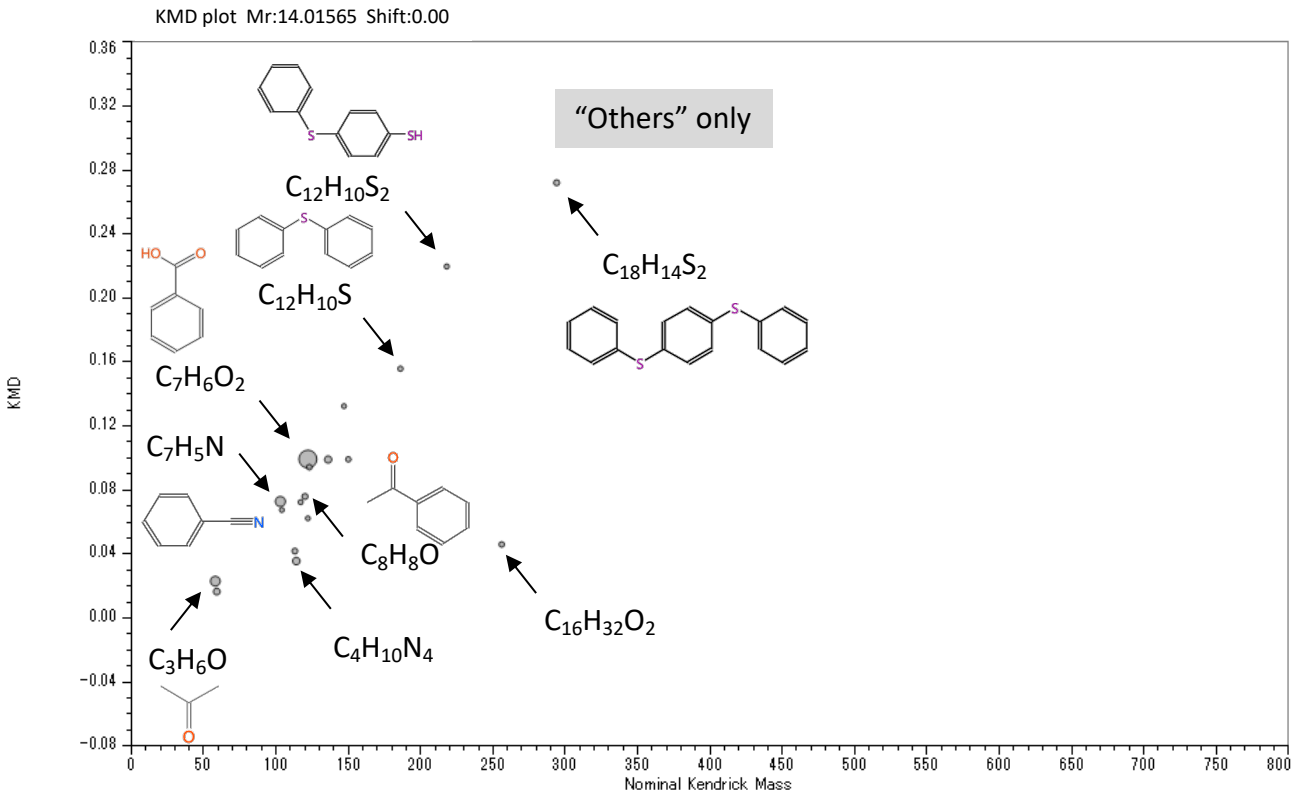

Figure 7 KMD plot with structural formulas

Conclusion

Using the blank tube-FI method and KMD analysis, we were able to visually and quantitatively evaluate hydrocarbons, which are the main components of pyrolysis oil. Furthermore, we were able to detect phosphorous antioxidants and sulfur compounds that affect oil quality, and by comparing them with the analysis results of the GC-EI/FI method, we were able to confirm their structural formulas.

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