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# Influence of Heating Rate on Pyrolysis Process of Paraffin oil for Rocket Fuel

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## Abstract

This study aims to investigate the influence of heating rate on pyrolysis behavior of paraffin oil, which is a main component of Low-melting-point-thermoplastic used for hybrid rocket fuel. This tests used two types of IA/MS devices to detect the pyrolysis products under different heating conditions. Under fast heating condition, the paraffin oil has unique spectra pattern that depends on pyrolysis temperature. No remarkable change on mass pattern was detected with increased temperature in slow heating test. The comparison of these results revealed that influence of heating rate of paraffin oil is agree with that of conventional sample, polyethylene.

## 1. Introduction

The solid fuel surface of a hybrid rocket is heated rapidly to high temperatures above $10^4$ °C $s^{-1}$. Under the effect of an external heat flux, the fuel undergoes a rapidly heating and decompositions into gases. An investigation of these phenomena is important to elucidate the degradation process of polymeric fuels.

The method of evolved gas analysis with mass spectrometry (EGA/MS) was used to evaluate qualitatively and quantitatively, the gaseous species that were generated by heating a sample, mainly below $10^2$ °C $min^{-1}$. To investigate the pyrolysis process under rocket operation condition, several decomposed test have been performed. Arisawa and Brill [1] pyrolyzed hydroxyl-terminated polybutadiene (HTPB) at 600 °C $s^{-1}$ heating rate, and analyzed its evolved gases by temperature-jump/Fourier-transform infrared (T-Jump/FTIR) spectroscopy in near real-time. Because this method is disadvantageous for accurately discriminating the gaseous products, six major products—butadiene, 4-vinyl-l-cyclohexene, trans-butadiene oligomers, ethylene, 1,5-hexadiene, and cyclopentene—and seven minor products were chosen and evaluated. Chiaverini et al. [2] pyrolyzed pure HTPB and HTPB mixtures with Al-powder fuels using a hot-cylinder conductive heating method to represent the conditions in a hybrid rocket motor. The pyrolyzed products were analyzed by gas chromatography-mass spectrometry (GC/MS). In addition, Gascoin et al. [3] heated a polyethylene sample at 20 000 °C $s^{-1}$, and then analyzed it with a GC/MS device and flame-ionization detector. The GC/MS analysis enables the precise identification of gaseous species, more accurately than the FTIR analysis. However, Tsugoshi [4] recently reported that the styrene monomer and small amounts of the dimer are detected during the thermal decomposition of polystyrene using pyrolysis-ion attachment mass spectrometry (Py-IA/MS) using skimmer interface system [5]. The trimer shows another pattern of evolution, which means the trimer is not due to the thermal decomposition but by synthesis from the monomers on the inner wall of the GC column.

The pathways and products of the process of pyrolysis at high heating rates differ from those at slow heating rates. For example, polyethylene ($M_W$ ~100 000) forms light alkanes, preferably at higher heating rates, whereas the heavier alkanes are unaffected. However, the effect of the heating rate on a polymer of low molecular weight such as paraffin oil ($M_W$ ~1000) under different conditions is not yet established.

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This study investigates the relationship between the heating rate and pyrolysis process of paraffin oil. The sample polymer was compounded in a thermoplastic fuel of low melting point, which is a thermoplastic elastomer softened by paraffin oil and used as a hybrid rocket fuel or binder for solid propellants [6].

## 2. Material and methods

### 2.1 Paraffin oil

Paraffin oil, which is a main component of LT fuel, was chosen as a sample to evaluate the chemical composition of pyrolysis products. The LT fuel sample was provided by Katazen Corporation, Japan. The fuel is a thermoplastic elastomer based on 49.4 mass% paraffin oil and 13.1 mass% styrene block polymer with 2-methyl-1,3-butadiene and 1,3-butadiene, hydrogenated. The styrene block copolymer plays some important roles in the fuel's mechanical properties [7]. Six-point-two mass% stearic acid was used to control the melting property of the LT fuel and 31.3 mass% alkylphenol-modified xylene resin was used to improve the adhesive property [7].

### 2.1 Curie-point pyrolyzer with IA/MS using capillary interface system

A Curie-point pyrolyzer (Japan Analytical Industry, JCI-22) used the pulse heating method with induction heating. The paraffin oil sample was wrapped in pyro-foil made of ferromagnetic metal. It was heated rapidly, within 0.2 s, to its specific Curie-point temperature. Pyrolysis temperatures of 485, 590, 764, 920, and 1040 °C (maximum heating rate: 6400 °C $s^{-1}$) were selected to simulate the temperature profile during combustion in the condensed phase. The flash pyrolyzer was connected to a mass spectrometer (Canon Anelva, L-250G-IA) with a fused silica capillary tube (0.15-mm diameter, 0.47-m length) heated to 523 K. The reaction gas was transferred to the detector and ionized by the IA with lithium ions. A mass-to-charge (*m/z*) ratio of the spectrum corresponds to a $[M + Li]^+$ ion. Nitrogen was used as a carrier gas with a constant flow rate of 50 ml $min^{-1}$.

### 2.2 Py-IA/MS using skimmer interface system

The unique Py-IA/MS equipment has been developed to detect the pyrolysis products which generated on burning fuel surface under typical rocket operation conditions. Figure 1 shows the apparatus, which consists of infrared image furnace, gas sampling system, and quadrupole mass spectrometer. The gas sampling system, which called skimmer interface structure, is comprised of two concentric quartz tubes with orifices for continuous and immediate sampling of the gases generated from the heated samples. It connects the two devices at atmospheric and vacuum pressures. A first orifice places between an intermediate pressure-reduced chamber and the sample heating chamber, while the second one place between the intermediate pressure-reduced chamber and the MS chamber. The gases decomposed from the samples are enriched after the second orifice, in consequence of the principle of a jet separator, and introduced into the MS chamber. They perform the more sensitive and precise gas analysis [4][5]. The sample was heated at 139 °C $min^{-1}$. The MS detects the *m/z* range of 10 – 150. Nitrogen was also used as the carrier gas.

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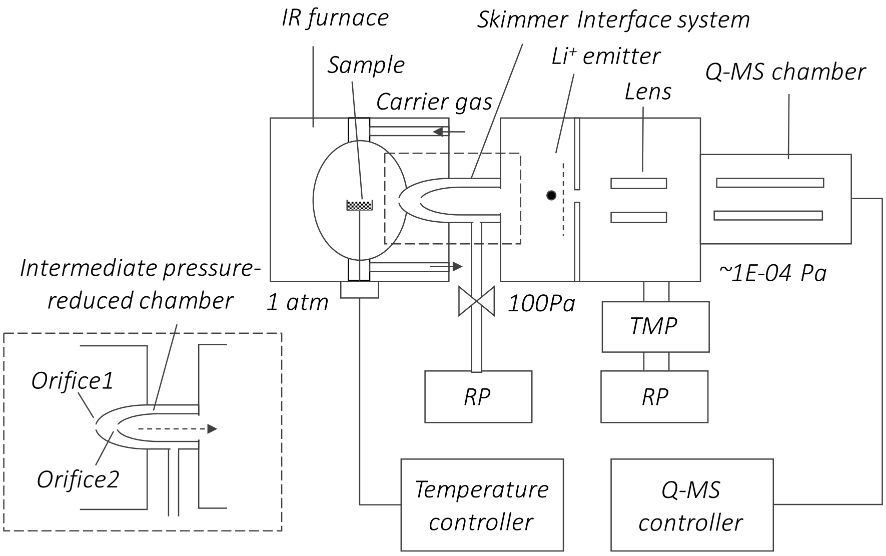


Figure 1: Schematic diagram of Py-IA/MS using skimmer interface system. Rotary pump, RP; Turbo molecular pump, TMP.

## 3. Results and discussions

### 3.1 Pyrolysis behaviour under fast heating condition

The pyrolysis products of the paraffin oil under fast heating condition were surveyed with the Py-IA/MS using capillary interface system. Figure 2 shows the Py-MS spectra at each pyrolysis temperature from 485 to 1040 °C. The mass data point corresponds to a [M + Li]+ ion. Under each temperature condition, the paraffin oil produced a unique Py-MS spectrum. Mass spectrum patterns at 485 and 590 °C indicated over a wide range, while a marked increase in the detection of peaks less than 85 was observed at 1040 °C. Our experiment reveals that the peak number was lower in the higher temperature regions because of the pyrolysis reaction. The mass spectrum patterns indicate alkene compounds (CnH2n) at lower temperatures and alkane compounds (CnH2n+2) at higher temperatures.
In addition, the mass spectra contained three large peaks at ion masses 85, 99, and 113 at 764 and 920 °C. Ion masses of 85, 99, and 113 seemingly represent the spectrum peaks of benzene, toluene, and styrene, respectively. The formation of aromatic conpoungly was agree with the results that decomposed products of marine fuel oil is aromatized and carbonized at 800 °C [8].

### 3.2 Pyrolysis behaviour at slow heating rate 139 °C min$^{-1}$

The pyrolysis products of the paraffin oil at lower heating rate, 139 °C min$^{-1}$, were investigated by the Py-IA/MS using skimmer interface system. Py-MS. Figure 3 shows the Py-MS spectra at each pyrolysis temperature from 400 to 1000 °C. Alkane compounds were detected in all of temperature range. At 1000 °C, alkene compounds also generated. No remarkable change on mass pattern was detected with increased temperature. *m/z* = 25 and 28 is $H_2O$ and $N_2$, respectively. Note that this detector has mass range of *m/z* ~ 150 even though the heavy components over *m/z* 150 might are included in gases. This study discussed the difference of type of decomposition products between fast and slow heating rate.

### 3.3 Comparison of spectrum pattern under different heating condition

The alkenes were formed under fast heating condition, while the lower heating rate generated the alkane compounds. The result agree with the pyrolysis test using polyethylene under different heating conditions [3]. The other hand, no aromatic compounds were detected in slow heating rate at higher temperature.

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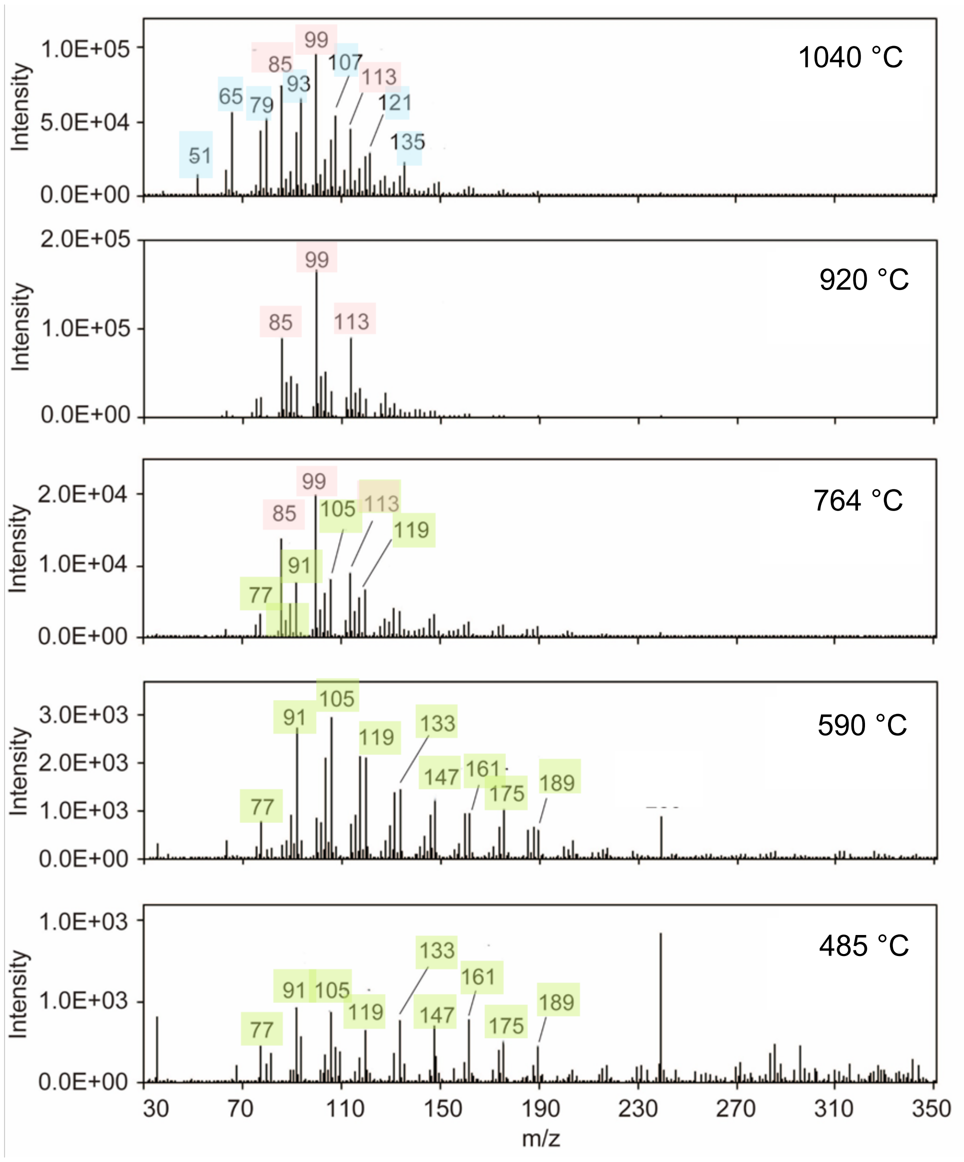
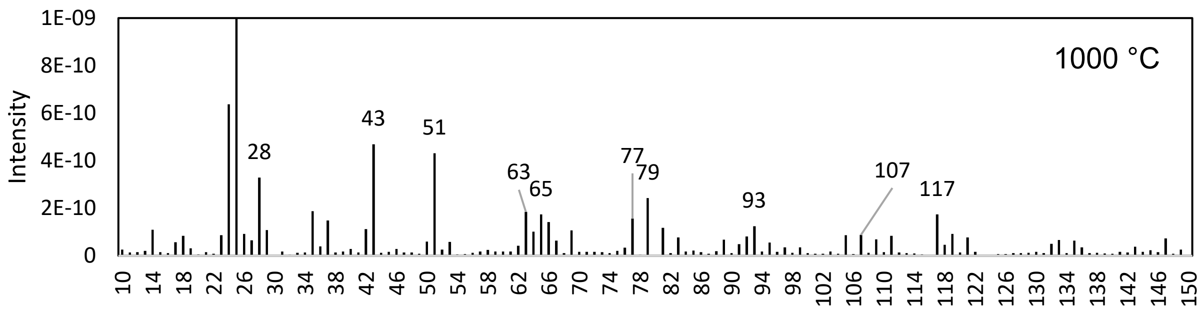



Figure 2: The mass spectra of paraffin oil obtained by Py-IA/MS using capillary system under fast heating condition. Green highlight, $C_nH_{2n}$ Alkene compounds; Red highlights, Aromatic compounds; Blue highlights, $C_nH_{2n+2}$ Alkane compounds.



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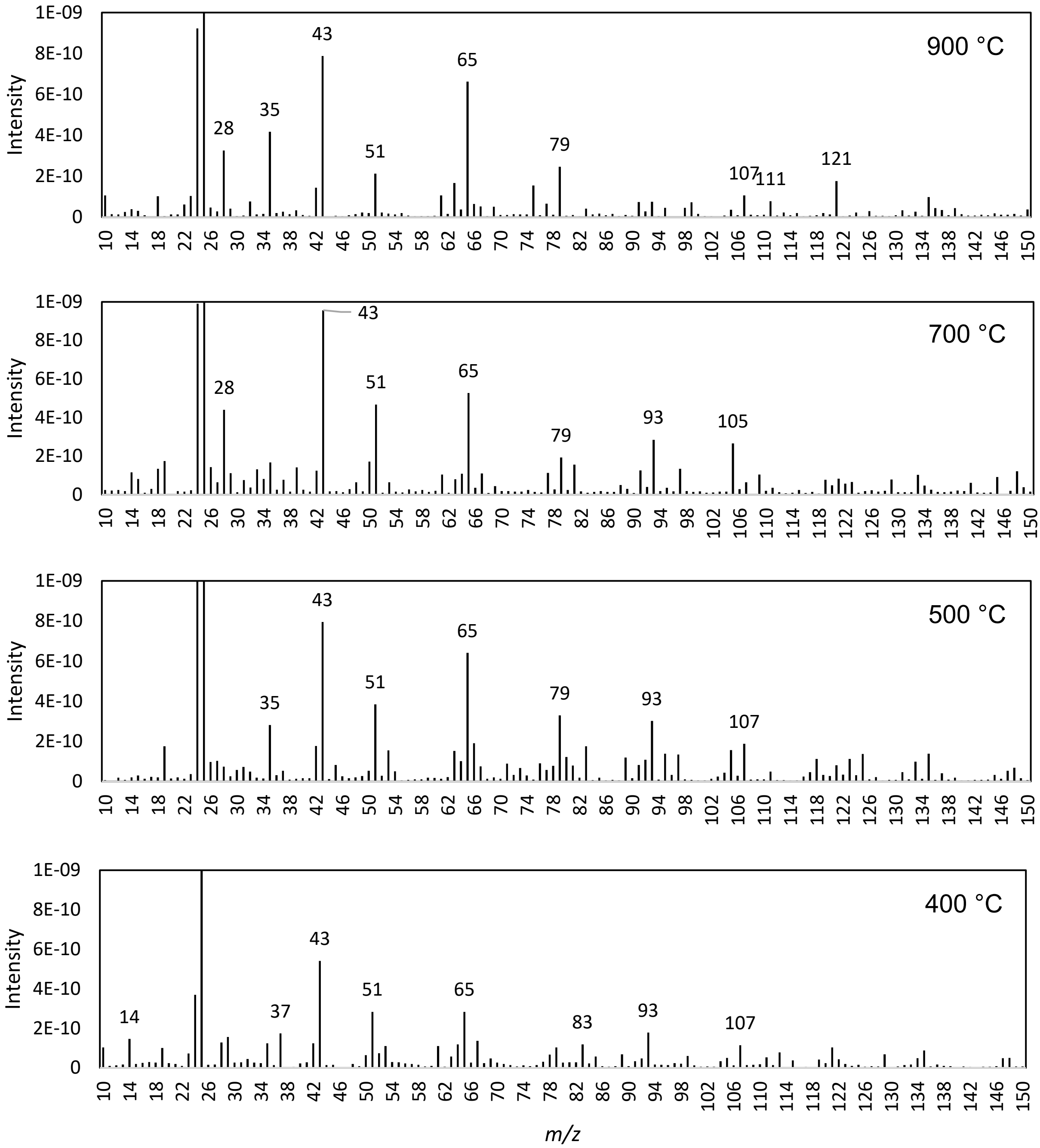


Figure 3: The mass spectra of paraffin oil obtained by Py-IA/MS using skimmer system at 139 °C $min^{-1}$.

## 4. Conclusion

The pyrolysis tests under different heating condition were performed to investigate the influence of heating rate on pyrolysis process of paraffin oil which is a main component of LT fuel. This tests used two types of IA/MS devices. One is the use of curie-point pyrolyzer and capillary interface system to obtain the pyrolysis products under fast heating condition. The other is the use of IR furnace chamber and skimmer interface system to conduct the decomposition test under slow heating condition. Under fast heating condition, the paraffin oil has unique spectra pattern that depends on pyrolysis temperature. The other hand, no remarkable change on mass pattern was detected with increased temperature in slow heating test. The comparison of these results revealed that influence of heating rate of paraffin oil is agree with that of polyethylene. The hybrid rocket tends to use the low molecular weight polymer (Mw~1000) such as a paraffin

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wax to obtain the high regression rate. The elucidation of pyrolysis step of low molecular weight sample at high heating rate would require to investigate combustion process of hybrid rocket fuel.

## References

[1] Arisawa, H., and Brill, T.B., (1996) Flash Pyrolysis of Hydroxyl-Terminated Polybutadiene (HTPB) I: Analysis and Implications of the Gaseous Products, Combustion and Flame, vol. 106(1–2), pp. 131–143. Magin, T., and G. Degrez. 2004. Transport algorithms for partially ionized and unmagnetized plasmas. *J. Comput. Phys.* 198:424–449.

[2] Chiaverini, M.J., Harting, G.C., Lu, Y.-C., Kuo, K.K., Peretz, A., Jones, H.S., Wygle, B.S., and Arves, J.P., (1999) Pyrolysis Behavior of Hybrid-Rocket Solid Fuels Under Rapid Heating Conditions, Journal of Propulsion and Power, vol. 15(6), pp. 888–895.Rini, P. 2006. Analysis of differential diffusion phenomena in high enthalpy flows, with application to thermal protection material testing in ICP facilities. PhD Thesis. Université Libre de Bruxelles, Faculté des Sciences Appliquées.

[3] Gascoin, N., Fau, G., Gillard, P., and Mangeot, A., (2013) Experimental flash pyrolysis of high density polyethylene under hybrid propulsion conditions, Journal of Analytical and Applied Pyrolysis, vol. 101, May, pp. 45–52.

[4] Tsugoshi, T., (2018) Revolution of Evolved Gas Analysis/Mass Spectrometry, Bunseki Kagaku, vol. 67(3), pp. 135–143.

[5] Arii, T., (2011) Evolved Gas Analysis-Mass Spectrometry (EGA-MS) Using Skimmer Interface System Equipped with Pressure Control Function, Journal of the Mass Spectrometry Society of Japan, vol. 53(4), pp. 211-216.

[6] Wada, Y., Jikei, M., Kato, R., Kato, N., and Hori, K., (2012) Application of Low Melting Point Thermoplastics to Hybrid Rocket Fuel, Transactions of the Japan Society for Aeronautical and Space Sciences, Aerospace Technology Japan, vol. 10, pp. 1–5.

[7] Kawabata, Y., Wada. Y., Kato, N., Hori, K., Nagase, R., (2015) Study on Improvement of Mechanical Characteristics of LT Fuels for Hybrid Rocket, Proceeding of International Conference on Flow Dynamics.

[8] Morishita, S., (1992), Conversion of Constituents of Marine Fuel Oil into Aromatization and Carbonization on Pyrolysis, Journal of the Japan Institution of Marine Engineering, vol. 27(3), pp. 231-237.