



## Experimental Study on Thermal Decomposition Characteristics of exo-THDCPD

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### Abstract

When hydrocarbon aviation fuel is heated above its critical point inside a regenerative cooling channel, the fuel is decomposed into hydrogen and various low molecular-weight hydrocarbons, which affects the performance of active regenerative cooling systems. Therefore, this study investigates the pyrolysis of exo-THDCPD ( $C_{10}H_{16}$ , exo-tetrahydrodicyclopentadiene), the major component of JP-10 aviation fuel experimentally. In order to understand the thermal decomposition characteristics of exo-THDCPD within a regenerative cooling channel, a batch reactor with a fluidized sand bath heater was used to expose the fuel under supercritical conditions (4 MPa, 540-630 K) to have the conversion rate of 3-76%. The constituents of the pyrolysis products were identified by GC-MS, GC-FID and GC-TCD systems, which have revealed that hydrogen, methane, ethylene, ethane, propylene, propane, and butane are found to be the major gaseous products. In the liquid products, on the other hand, cyclopentane, cyclopentene, cyclopentadiene, cycloheptadiene, benzene, and toluene are dominant. Furthermore, a brief analysis on the thermal decomposition mechanism was carried out based on the experimentally obtained data.

**Keywords:** *Hypersonic vehicle, Regenerative cooling, Hydrocarbon fuel, Endothermic reaction, Supersonic combustion*

### Nomenclature

Y – Gas production rate

m – weight of the liquid fuel

w – mass fractions of the exo-THDCPD

x – Fuel conversion rate

Subscripts

l – After the reaction

o – Before the reaction

### 1. Introduction

Hypersonic vehicles fly through the atmosphere at the speeds over Mach 5 by utilizing scramjet air-breathing propulsion systems, and several technical challenges must be addressed to develop and operate such hypersonic vehicles; first, there is a problem of aerothermodynamic heating due to the high-speed flight as well as high temperatures inside the scramjet combustor. Second, the complex and very fast air flow makes combustion very difficult inside the scramjet engine [1]. As a result, active regenerative cooling systems have been investigated as an effective solution to resolve these problems. Usually, hydrocarbon fuels are used as coolant in an active regenerative cooling system because they exist in liquid state at room temperatures as well as have high heat-absorbing capability. When the hydrocarbon fuel is heated to high temperatures, it decomposes into hydrogen and light hydrocarbons such as methane, ethylene, ethane, propylene, and propane through endothermic reactions [2, 3]. In addition, the resultant gaseous products of light hydrocarbons mix with air much faster than the original fuel in liquid state, which significantly enhances the efficiency of supersonic combustion. However, the hydrocarbon fuel is exposed inevitably to high temperatures and pressures in the regenerative cooling channel, and thus reaches a supercritical condition [4]. It is, therefore, essential to understand the

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thermal decomposition characteristics of supercritical hydrocarbon fuel in order for the development of an effective regenerative cooling systems.

The pyrolysis of hydrocarbon aviation fuel is a very complex phenomenon, and the distribution of pyrolysis products plays an important role in determining ignition delay and flame holding characteristics as well as chemical heat sink. In order to predict the distribution of the reaction products, therefore, pyrolysis models have been studied extensively. They are categorized typically into detailed, lumped, and global models according to their complexity. Detailed models can simulate the pyrolysis mechanism most accurately. However, they are complex and computationally expensive because hundreds of chemical species and thousands of reactions are considered therein, which makes it difficult for them to be used for engineering purposes [5]. On the other hand, lumped models are relatively simple compared to detailed ones because they simplify actual pyrolysis products into appropriate virtual components, which results in that the computational cost becomes much lower than that of detailed models [6]. But it is disadvantageous because the product distribution of the pyrolysis reaction cannot be predicted. Global reaction models, in addition, focus on the distribution of pyrolysis products by a single-step reaction. Compared to the previous two models, they are much simpler, faster and more efficient for numerical simulation, so they are used largely in practical engineering applications. Particularly, many previous studies have proposed Proportional Product Distribution (PPD) models for various types of hydrocarbon fuels as a representative global reaction model [7]. The PPD model is, however, valid only at low conversion rates, usually less than 15%. In order to overcome this limitation, several methods have been proposed by combining secondary reactions at higher conversion rates over the primary reaction. Furthermore, as the actual pyrolysis reaction is affected not only by the conversion but also by other factors such as pressure, the Differential Global Reaction (DGR) model representing the stoichiometry coefficients as a function of the pressure as well as the conversion rate has been proposed recently to improve the accuracy of the PPD models [8].

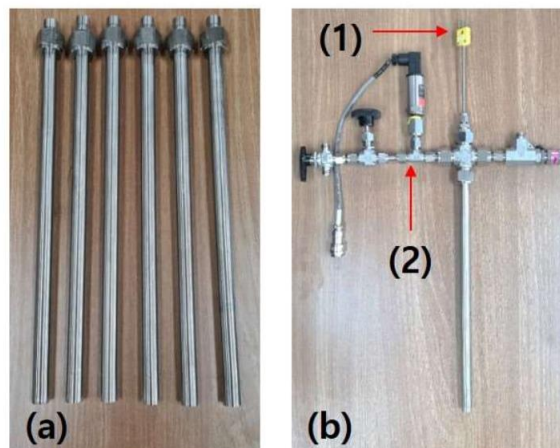
JP-10 is a single component hydrocarbon aviation fuel composed of exo-THDCPD ( $C_{10}H_{16}$ , exo-tetrahydrodicyclopentadiene), which has a polycyclic molecular structure that provides high energy storage. It also has a high heat capacity, making it suitable for use as a coolant in active regenerative cooling systems for a hypersonic vehicle. As a result, the pyrolysis of JP-10 has been studied extensively for the past decades. Davidson et al. [9] conducted thermal decomposition experiments of JP-10 using a shock tube and analyzed the products using high-temperature UV absorption spectra. The results showed that the initial major product of JP-10 was cyclopentene. Rao et al. [2] conducted pyrolysis experiments of JP-10 at the temperature range of 903 - 968 K at atmospheric pressure using an annular tubular reactor and obtained the fuel conversion range of 10.4-61.1%. The main pyrolysis products were found to be methane, ethylene, propylene, cyclopentene, cyclopentadiene, benzene, and toluene. Xing et al. [3] conducted pyrolysis experiments on JP-10 in the pressure range of 0.1-3.8 MPa covering the subcritical and supercritical states. They confirmed that the production rate of alkene decreased with increasing pressure and analyzed the pyrolysis mechanism through their product distribution. Vandewiele et al. [10] conducted experiments in the temperature range of 930-1080 K at atmospheric pressure and showed the widest fuel conversion range of 4-94%. They presented a kinetic model of JP-10 using the San Diego model and Reaction Mechanism Generator (RMG). Liu et al. [11] compared the pyrolysis characteristics of JP-10 with and without catalysts using a batch reactor. Pan et al. [12] conducted pyrolysis experiments at supercritical conditions - the temperature range of 550-735 °C and the pressure of 4.5 MPa - using an electrically heated tube. They found that coke in bulk fluid was approximately 70-170 times higher than that deposited on the wall. Wang et al. [8] also conducted pyrolysis experiments at supercritical conditions and developed a DGR model of JP-10.

Even though there have been a lot of research on the JP-10 pyrolysis, most of them have been carried out at subcritical conditions while hydrocarbon fuel in a regenerative cooling channel circulates usually in supercritical states. Furthermore, there have been few experimental results with the fuel conversion rates above 70% in microchannel pyrolysis through flow reactor configurations because coking occurs at higher conversion due to the cyclic nature of exo-THDCPD [8]. This study, therefore, aims to analyze the thermal decomposition characteristics of exo-THDCPD by using a batch reactor setup. Experiments of exo-THDCPD at various supercritical conditions were conducted to obtain thermal cracking results for a wide range of fuel conversion rates and to analyze the product distribution of the pyrolysis reaction. Based on the obtained experimental data, it is expected that the pyrolysis reaction model of JP-10 can be generated, and thus to be utilized in the design of active regenerative cooling systems.

## 2. Experimental section

### 2.1. Batch reactor

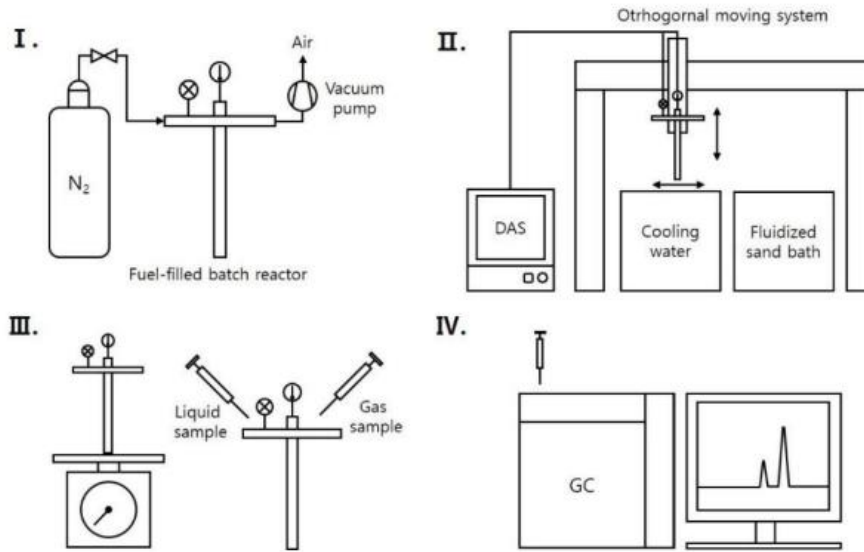
As mentioned in the introduction, most of the previous studies have performed pyrolysis experiments using flow reactors. However, in this study, pyrolysis experiments were conducted using a batch reactor to obtain a wide range of fuel conversion rates under supercritical conditions. Two materials, Inconel and SUS, were considered for the batch reactor in terms of heat resistance and corrosion resistance. Inconel has excellent heat resistance and corrosion resistance, making it suitable for experiments in high temperature and pressure environments, but it has a high nickel content that promotes the pyrolysis reaction, which may affect the results of this experiment. Therefore, in order to minimize the effect on the pyrolysis reaction, this study used a reactor made of SUS, which is less heat resistant than Inconel but has a lower nickel content. Fig. 1 shows a picture of the reactors and batch reactor assembly used in the experiment.



**Fig 1.** (a) Reactors and (b) batch reactor assembly with (1) thermocouple and (2) pressure transducer

### 2.2. Experimental procedures

The thermal decomposition experiments followed the process outlined in the following Fig. 2 ( I ) First, the fuel was put into the reactor and measured the mass, after which the remaining air inside the reactor was removed using a vacuum pump, and the reactor was pressurized to the reaction pressure using high-purity nitrogen, an inert gas. The fuel temperature was measured in the batch reactor using a type K thermocouple. (II) After the reactor was pressurized to the set pressure, mounted on an orthogonal moving system, and moved to a fluidized sand bath heater. And the reactor was heated for the set reaction temperature and time. After reaching the reaction conditions, the reactor was moved to cooling water and cooled to room temperature to stop the reaction. (III) Subsequently, the liquid and gaseous reaction products were extracted and measured the mass of reactor. (IV) And the quality and quantity of the extracted products were analyzed using gas chromatography.



**Fig 2.** Schematic of the experimental procedures [13]

### 2.3. Analysis method

Hydrogen was analyzed by iGC7200A (GC, DS Science Inc., iGC7200A) with thermal conductivity detector (TCD). The gas products were analyzed qualitatively and quantitatively by Agilent GC with VPHS-B capillary column (30m x 0.53mm x 20 $\mu$ m) and flame ionization detector (FID). The liquid products were identified using an Agilent 7890/5975 gas chromatography/mass spectrometry (GC/MS) with a HP-5 MS column (30m x 0.25mm x 0.25 $\mu$ m) and quantified using GC with DB -WAX capillary column (60m x 0.32mm x 0.50 $\mu$ m) and FID. The formulas for fuel conversion rate and gas yield are represented by Eq. 1 and Eq. 2 below.

$$x = \left(1 - \frac{w_l m_l}{w_o m_o}\right) \times 100\% \quad (1)$$

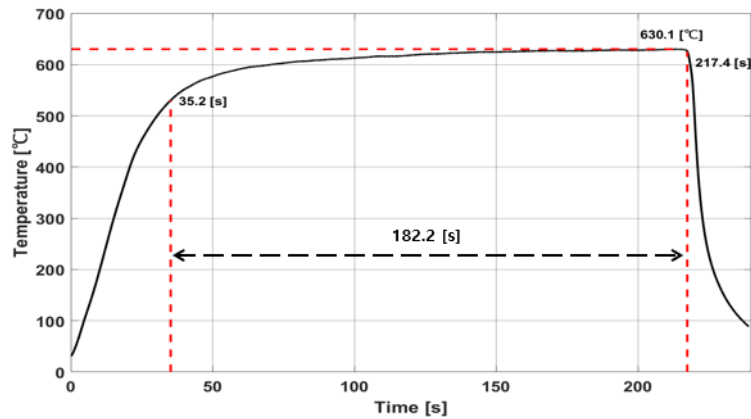
$$Y = \left(1 - \frac{m_l}{m_o}\right) \times 100\% \quad (2)$$

In the Eq. 1 and Eq. 2,  $m_o$  represents the weight of the liquid fuel before the reaction, and  $m_l$  denotes the weight of the liquid fuel after the reaction. Additionally,  $w_o$  and  $w_l$  represent the mass fractions of the exo-THDCPD before and after the reaction, respectively. The mass fraction of the exo-THDCPD was calculated using the area ratio of peak signals obtained from the GC-FID analysis of the liquid products.

## 3. Results and Discussion

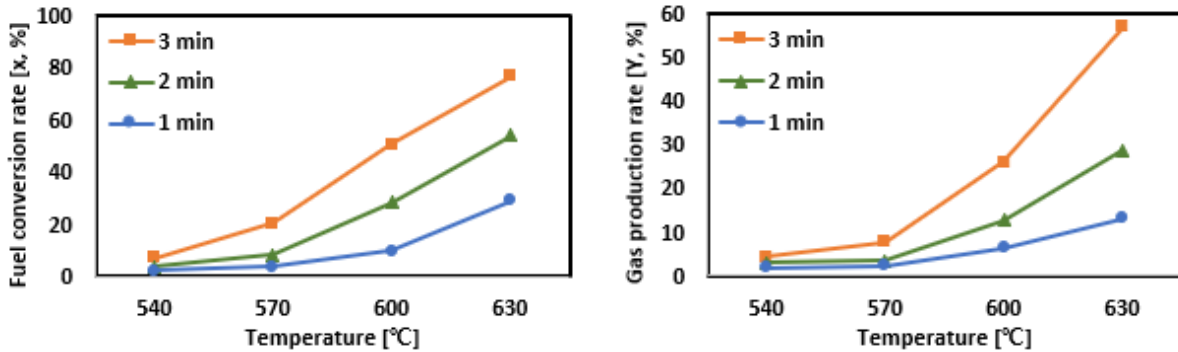
### 3.1. temperature profile and fuel conversion rate and gas production rate

It is known that the critical pressure of exo-THDCPD is about 3.7 MPa and the critical temperature is 425 °C. Therefore, in this experiment, the initial pressure was set to 4 MPa to maintain the supercritical state, and the target reaction temperature range was set to 540-630°C. In each condition, the reaction time was set to 1, 2, and 3 minutes. The temperature of the heater was set to be the same as the target reaction temperature, and the reaction start temperature was set to be 100 °C lower than the target reaction temperature. When the target reaction temperature was reached and the set reaction time passed, the reaction was finished by cooling immediately. Fig. 3 shows the temperature profile of the experiment at a starting pressure of 4 MPa, a target reaction temperature of 630 °C, and a reaction time of 3 minutes.



**Fig 3.** Temperature profile of 630 °C, 4 MPa, 3 min condition

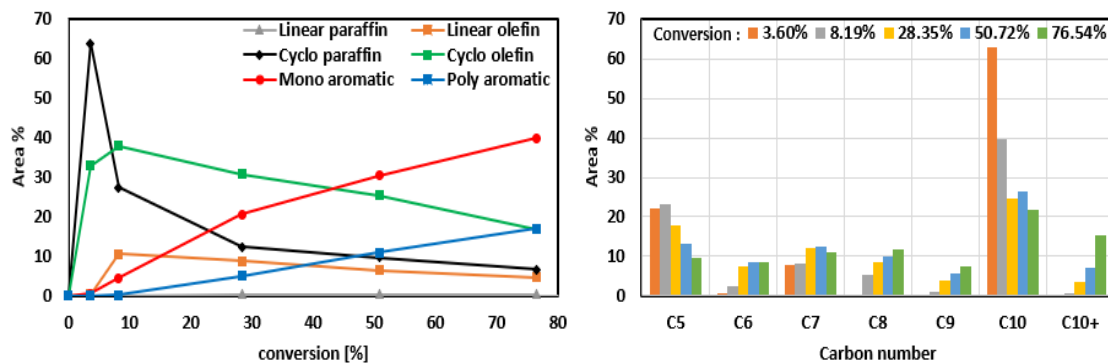
The experimental results in Fig. 4 demonstrate that the fuel conversion rate and gas production rate increased with an increase in reaction temperature. Additionally, at the same temperature, an increase in reaction time lead to an increase in both the fuel conversion rate and gas production rate. The fuel conversion rate ranged from approximately 3-76%, while the gas production rate ranged from approximately 2-56%.



**Fig 4.** Fuel conversion rate and gas production rate as a function of temperature plotted over time

### 3.2. Liquid Product Distribution

The liquid products were analyzed by GC/MS. Fig. 5 shows the distribution of the liquid product as a function of fuel conversion. The pyrolysis reaction produced mostly cyclic compounds. Cyclo paraffin and cyclo olefin increased rapidly immediately after the start of the reaction, but gradually decreased as the fuel conversion rate increased. On the other hand, aromatic compounds increased gradually as the conversion rate increased.



**Fig 5.** Distribution of liquid product composition by conversion rate and carbon number

**Table 1.** Composition and components in the liquid products for thermal cracking of exo-THDCPD at 4 MPa, 630°C, 3 min

Linear paraffin		Linear olefin		Cyclo paraffin	
Composition [%]	component	Composition [%]	component	Composition [%]	component
0.38	Pentane	4.54	1-Pentene	0.57	substituted cyclopropane
0.11	Hexane	0.14	substituted Pentene	3.79	substituted cyclopentane
				1.95	Adamantane
				0.34	substituted Cyclobutane
				1.28	Cyclopentylcyclopentane

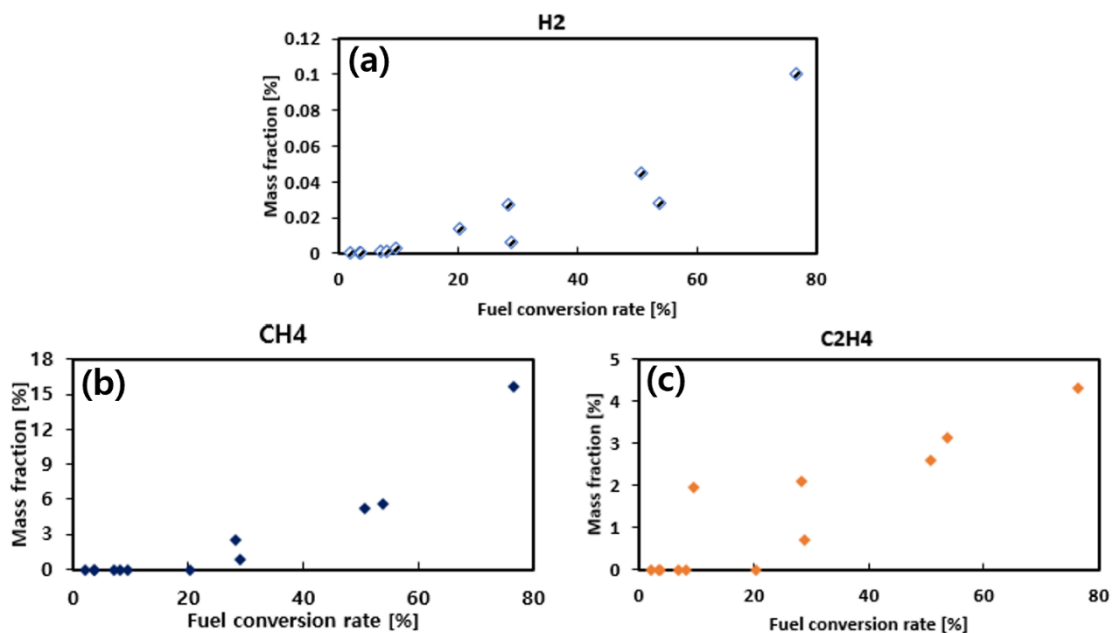
**Table 2.** Composition and components in the liquid products for thermal cracking of exo-THDCPD at 4 MPa, 630°C, 3 min

Cyclo olefin		Mono aromatic		Poly aromatic	
Composition [%]	component	Composition [%]	component	Composition [%]	component
3.45	Cyclopentene	4.51	Benzene	5.19	Azulene
5.21	substituted cyclopentene	6.04	Toluene	7.04	substituted Napthalene
0.18	Cyclohexene	4.17	Ethylbenzene	0.55	Biphenyl
0.19	substituted Cyclohexene	0.74	p-Xylene	1.18	Acenaphthene
0.7	1,3-Cyclopentadiene	1.57	o-Xylene	1.65	substituted 9H-Fluorene
0.05	substituted 1,3-Cyclopentadiene	7.89	substituted benzene	1.48	Phenanthrene
0.04	1,3-Cyclohexadiene	3.39	Indane		
0.14	1,3-Cycloheptadiene	1.38	Substituted Indane		
0.16	Bicyclo[4.1.0]hept-2-ene				
1.52	Pentalene, 1,2,3,3a,4,6a-hexahydro-				
1.76	3a,4,5,6,7,7a-Hexahydro-4,7-methanoindene				
2.11	Bicyclopentylidene				
0.36	Bicyclopentyl-1,1'-diene				

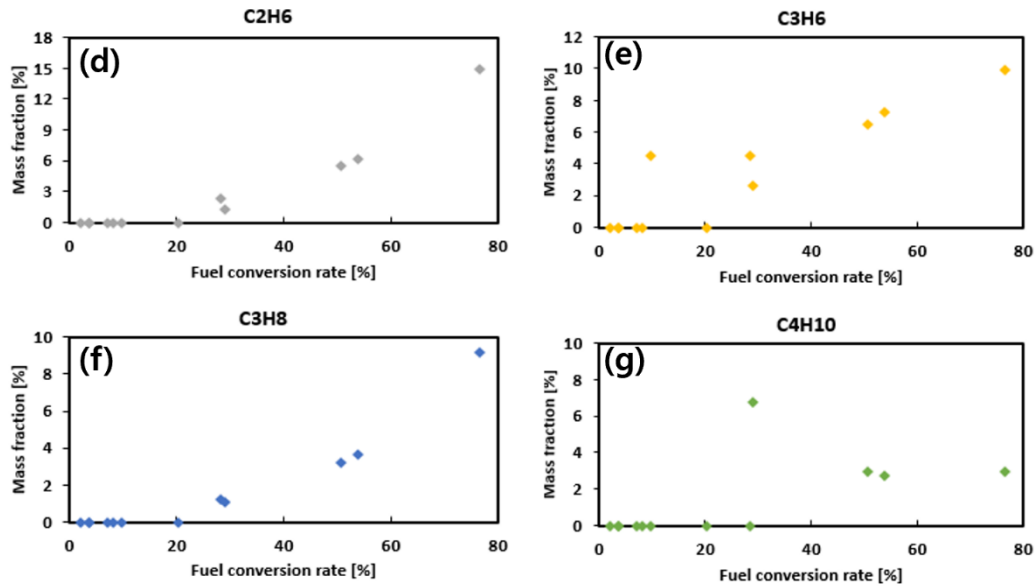
At fuel conversion rates below 5%, cyclo paraffin occupied about 65% of the liquid product. However, as the fuel conversion rate increased to near 10%, its composition decreased to below 30%. This means that in the initial pyrolysis reaction, cyclo paraffin is the main product, but as the reaction progresses, it decomposes or reacts with other products and decreases. Cyclo olefin was also produced rapidly from less than 5% fuel conversion to more than 30% of the liquid product and then decreased with increasing fuel conversion from near 10% fuel conversion. Mono aromatics were more dominated than poly aromatics, and both increased in composition with increasing fuel conversion. Above 70% fuel conversion, aromatics compounds accounted for more than 50% of the liquid product. Chain compounds decreased as the conversion rate increased, with linear olefin producing about 10% early in the reaction. Very few linear paraffins were produced. The liquid product of the 4 MPa, 630 °C, 3 min experiment, which showed the highest fuel conversion (about 76%), was about 70 components, and the detailed list is summarized in Table 1. and Table 2. Substances with methyl-, ethyl-, and other functional groups are summarized as substituted.

### 3.3. Gas Product Distribution

Hydrogen was analyzed by GC-TCD and low molecular weight hydrocarbons were analyzed by GC-FID. The main gaseous products are hydrogen, methane, ethylene, ethane, propylene, propane, and butane. Fig. 6 and Fig. 7 shows the change in mass fraction of each gas product as a function of fuel conversion. The mass fraction of all gaseous products tended to increase as the fuel conversion rate increased.



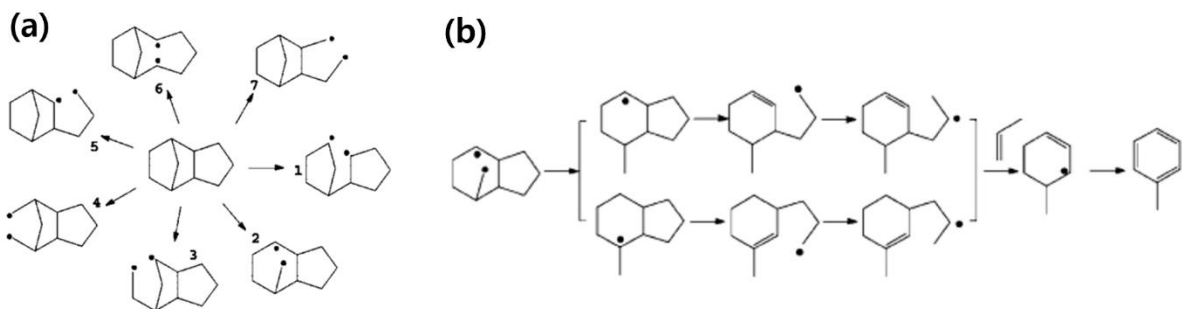
**Fig 6.** Mass fraction of gas product, hydrogen(a), methane(b), ethylene(c)



**Fig 7.** Mass fraction of gas product, ethane(d), propylene(e), propane(f), butane(g)

### 3.4. Theoretical Mechanism

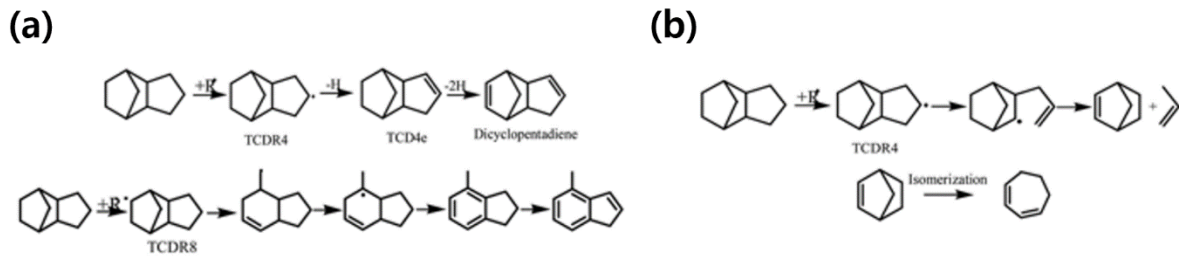
Previous studies have shown that *exo*-THDCPD, a polycyclic compound, undergoes thermal decomposition at atmospheric pressure with the breaking of C-C bonds and the formation of unstable intermediates, biradicals [3, 14]. Fig. 8 (a) shows the seven types of biradicals that can be generated from *exo*-THDCPD. The *exo*-THDCPD molecule absorbs a hydrogen atom from the biradical and transforms into a single radical. It forms a second radical with lower molecular weight substances through the  $\beta$ -scission process, and the final product is generated through successive reactions. Fig. 8 (b) shows the mechanism by which a biradical forms a second radical and the final product through  $\beta$ -scission [3]. This pyrolysis reaction finally produces ethylene, propylene, cyclopentadiene, benzene, and toluene.



**Fig 8.** Theoretical pyrolysis mechanisms: (a) Biradicals generated from *exo*-THDCPD, (b) Two pathways to generate toluene and propylene from *exo*-THDCPD biradicals [3, 14]

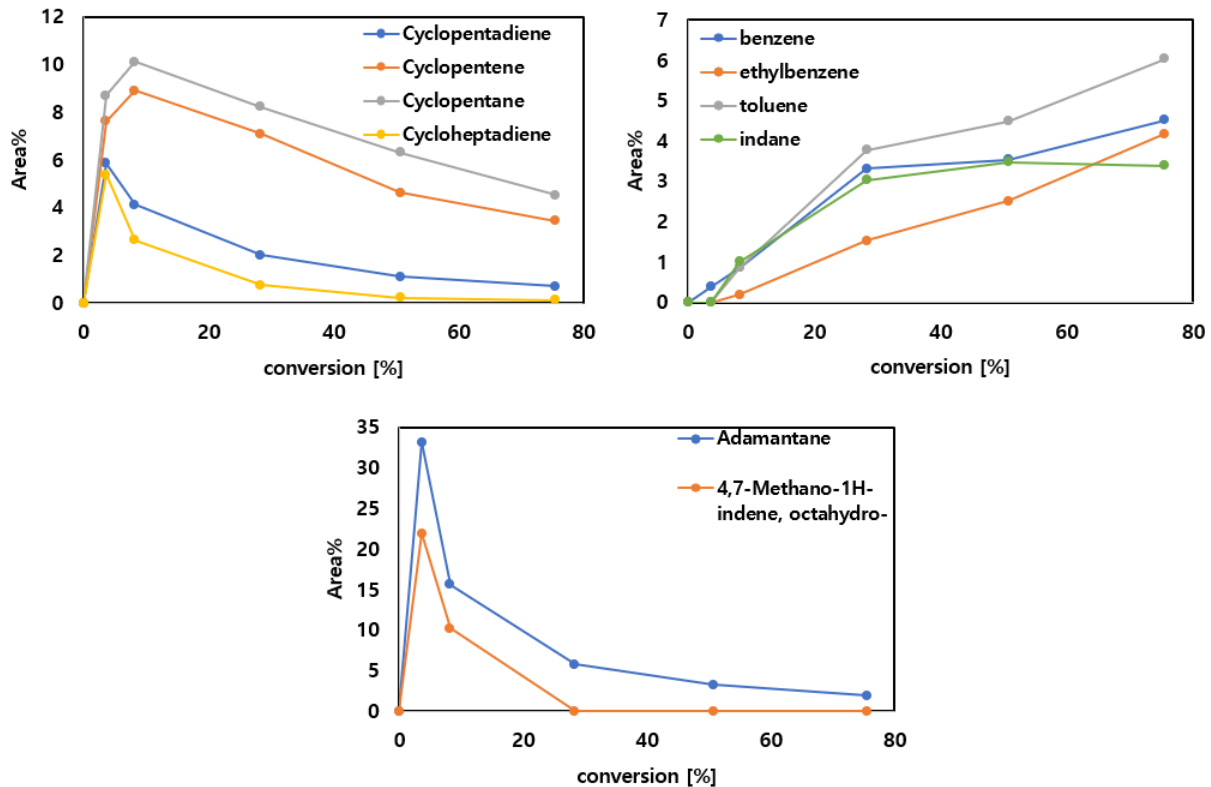
However, the results of Xing, Pan, and Wang's study showed that at supercritical condition, the formation of low molecular weight substances such as ethylene, propylene, and benzene through C-C bond cleavage and  $\beta$ -scission was inhibited, and the mass fraction of substances with a carbon number of 10 increased. Based on these results, Pan concluded that the main pyrolysis mechanism under supercritical condition is C-H bond cleavage and isomerization, not C-C bond cleavage and deep cracking to produce low molecular weight substances. Fig. 9 shows the mechanism of the pyrolysis reaction under supercritical condition [12].





**Fig 9.** (a) Formation of dicyclopentadiene and indene by C-H bond cleavage, (b) Formation of cycloheptadiene via isomerization [12]

The experimental results shown in Fig. 10 are similar to those of Xing and Pan. At supercritical conditions, cyclopentene and cyclopentane having higher proportions of the major products than cyclopentadiene. Benzene and toluene also tended to increase with increasing conversion rate, similar to Pan's results. The isomers of exo-THDCPD, adamantane and 4,7-Methano-1H-indene, octahydro-, accounted for more than 50% of the pyrolysis liquid product at low conversion rates, confirming that the isomerization process is the dominant pathway of the reaction as mentioned earlier. The previous mechanisms can explain the pyrolysis reaction of exo-THDCPD in the supercritical state, and further experiments are expected to expand the understanding of the pyrolysis reaction mechanism with more data.



**Fig 10.** Detailed liquid products by fuel conversion rate

#### 4. Conclusion and future plan

In order to develop a practical pyrolysis model of JP-10 aviation fuel that can be used in the design of microchannels of active regenerative cooling systems for a hypersonic vehicle, an experimental study has been conducted on the pyrolysis of exo-THDCPD at supercritical conditions using a batch reactor test rig. Extensive data on the thermal cracking of exo-THDCPD were obtained for a wide range of fuel conversion rates, and the distributions of the endothermic reaction products were analyzed systematically. It has been found that the main gaseous products are hydrogen, methane, ethane, ethylene, propene, propane, and butane, and the major liquid products are identified as cyclo-paraffins and cyclo-olefins at low conversion rates. Both of the gaseous and liquid products, however, decreased

while the aromatics increased as the fuel conversion rate increased. Further quantification is needed on the pyrolysis products of exo-THDCPD more specifically, and based on the identification results, it is scheduled to elucidate the pyrolysis mechanism as well as to develop an improved pyrolysis reaction model of the JP-10 fuel.

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