



The effect of temperature and pressure on n-heptane thermal cracking in regenerative cooling channel



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ABSTRACT

A thermal cracking experimental equipment of hydrocarbon fuels was built to study n-heptane pyrolysis and the effect of reaction conditions on this reaction process. The main species were measured and the change rules were analyzed on the range of temperature 873–1073 K and pressure 0.1–3.5 MPa. The total content of alkenes products was more than alkanes on this pyrolysis process. Compared to alkenes with same number carbons, the alkanes were more easy to decompose with temperature but more conducive to formation with pressure increasing. The content of ethylene is usually the most on above reaction conditions, but its descent is also the fastest with pressure increasing. A mechanism model of n-heptane pyrolysis (44 species and 166 reactions) was constructed and validated by experiments on different conditions. Compared with n-heptane oxidation detailed model of Version 3.1 from Lawrence Livermore National Laboratory (LLNL), the pyrolysis model present a better accordant with experiment results on a range of temperature and pressure. The kinetic reaction of n-heptane pyrolysis was analyzed with present pyrolysis model, and the pyrolysis reaction pathway for the main products was obtained. The formation of alkenes are mainly through C–C bond dissociation reaction, especially β -C dissociation, and small alkanes are formed mainly by radical metathetical or synthesis reaction, the former are endothermic reactions, but the latter are mostly exothermal reactions. The properties of some main reactions have a critical role for the change of product content with temperature and pressure, which is the main reason for the variety of products selectivity under different conditions. Pressure increased the pyrolysis residence time and mass density but it does not significantly affect the reaction energy, so its contribution to conversion rate of fuels thermal cracking is limited, although it changes the reaction pathway greatly. However, the temperature can increase obviously the reaction activation energy, even though the residence time and concentration is decreased, the conversion rate of n-heptane pyrolysis still increased.

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1. Introduction

To deeply investigate the pyrolysis and combustion reaction rules of liquid transportation fuels, such as diesel oils, gasoline and aviation kerosene, various reaction models have been built for optimizing the target products [1], enhancing combustion efficiency [2], and reducing pollutant emissions [3]. These chemical reaction models such as experimental model, molecular model and mechanistic models have been developed progressively [4–6], mechanistic

model mainly refers to the free radical chain reaction model, which contain chain initiation, growth, transfer and termination [7,8], but modeling all the physical and chemical properties of real fuels is challenging as the entire detailed molecular composition of these fuels is not fully known, and the mechanistic model contains many more intermediates and complex reactions, which is imperfect and in the continuous development. These liquid transportation fuel mixtures are usually composed of hundreds or thousands of hydrocarbon components. To deal with this complexity, the most prevalent solution is to develop substitute fuels [9], but the accurate kinetic models of these fuels still remain challenging due to the difficulties in experimental and theoretical investigations of most representative components.

N-heptane has been widely used as a representative in liquid transportation fuels as it has similar sixteen alkane values to

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diesel oils [10], and it is included as iso-octane and toluene in any gasoline surrogate [11]. N-heptane is also a typical endothermic jet fuels in hypersonic engine, its extra heat sink through endothermic pyrolysis reaction can meet the requirements of thermal management for hypersonic vehicle with certain flight Mach numbers. Meanwhile, the large heat load found in a hypersonic vehicle, engine temperature is expected to increase that leading in the thermal decomposition of the fuel circulating at their cooling walls before the injection in the combustion chamber. A consequence of the decomposition of the hydrocarbon fuel is the production of the small molecule alkanes and alkenes in the cooling micro-channel which can also improve the combustion efficiency in combustion chamber, and then of aromatic and poly-aromatic compounds [12]. In order to quantify the heat transfer through the walls of the engine and the composition of the fuel entering the combustion chamber on different conditions, an accurate kinetic model of the thermal decomposition for fuels is required [13].

Pant [14] and Olahová [15] both established a total molecular model for n-heptane thermal cracking including primary and secondary reactions, and then validate by catalytic pyrolysis and steam cracking experiments with different reactors, respectively, but the molecular model is deficient to explain their experimental phenomenon. Xie and Xing [16–18] studied experimentally the formation of n-heptane thermal cracking products and the heat sink under supercritical conditions. Zeng [19] and Jia [20] experimental and simulated the pyrolysis and oxidation of n-decane under low pressure and wide range of temperature, and n-decane with ten carbons has the similar cracking products with n-heptane. Aribike [21] and Yuan [22] all built a detailed mechanistic model of n-heptane, but the predict results are still disagreement with the experimental data in some certain condition. The detailed n-heptane oxidation models of Version 3.1 (654 species and 2827 reactions) from Lawrence Livermore National Laboratory (LLNL) [23], and a recently update n-heptane oxidation model (1268 species and 5336 reactions) by Zhang et al. [24] from National University of Ireland Galway (NUI-Galway), have been developed and validated by many correlative combustion experiments with a wide range of reaction conditions, such as ignition delay time and the flame propagation speed. However these combustion model of n-heptane may be more or less unsuitable for pyrolysis reaction process, because the pyrolysis reactions of fuels are not completely consistent with the oxidation reactions. Besides, with so large number of participating species and reactions, the computational costs are very huge unnecessarily in numerical simulations [25], so it is necessary to construct a simplified and precise mechanism of n-heptane. There are numerous factors that affect the pyrolysis cooling in the micro-channel, such as the diameter of the channel, reaction temperature, and pressure and residence time and so on. Some experiments [26] have measured the properties of the products with the varieties of pressure, but rarely explain the reasons from reaction kinetic on fuels pyrolysis process. The effect of reaction condition is important for the selectivity of pyrolysis products, which have a close relationship with chemical heat sink and coke formation in cooling micro-channel, even the combustion efficiency on the combustion chamber, so it is meaningful to explore the changing rule with reaction conditions and analyze the kinetic on pyrolysis process.

In this work, one n-heptane pure pyrolysis model with 44 species and 166 elemental reactions was developed and validated against the pyrolysis experiment of n-heptane on a flow reactor. As a comparison the simulation were also conducted by n-heptane oxidation model of Version 3.1 from LLNL under the same conditions. The effects of temperature and pressure on pure n-heptane pyrolysis in the flowing circular pipe was analyzed emphatically, and the change characteristics of the pyrolysis products were detected and quantified, the kinetics process of products formation

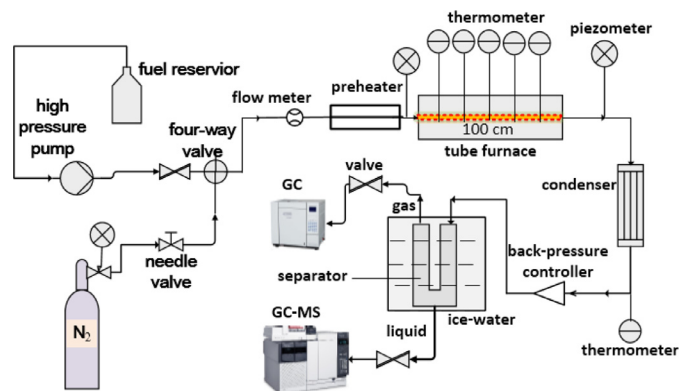


Fig. 1. Schematic diagram of the n-heptane pyrolysis experiment.

were investigated to get an in-depth understanding of the kinetics effect of temperature and pressure on pure n-heptane pyrolysis process.

2. Experiments

The n-heptane pyrolysis experiments were conducted in a micro-channel flow reactor. In order to mimic the active cooling system on the wall of supersonic ramjet combustor, the micro-circular pipe with internal diameter and length of 2.18×1000 mm was selected as the reactor in present experimental device. Short diameter also can reduce the turbulence effect and long tube can ensure a smaller change range of temperature and a fully reaction on pyrolysis process. Figure 1 shows the schematic diagram of the pyrolysis apparatus. A stainless steel tube (i.d. 2.18 mm, o.d. 3.18 mm) was heated in a tube furnace. The tube of stainless steel is oxidized with high-temperature so as to form a passive film before experiment. Liquid n-heptane (99.9% pure, MW. 100.2, bp. 371.65 K) treated with vacuum filtration to get rid of any dissolved oxygen and small particles. The reaction channel was purged with nitrogen for 20 min to exclude air in the whole reactor channel, and then the liquid fuel is loaded and regulated by a high-pressure pump that deliver the fuel into the micro-channel reactor. n-heptane liquid fuel was preheated to 573.15 K for gasification, the pressure of the whole reaction system was regulated using a back pressure valve and the maximum fluctuation is less than 0.1 MPa, the pressure drop from inlet to outlet of the reactor was also within 0.1 MPa, which could be negligible and the outlet pressure was selected for numerical calculation. The outlet products were rapidly cooled to 353 K to lessen the secondary reactions and gas-liquid species intermiscibility. These mixture products were then cooled in ice-water bath and separated. The heating temperature of the furnace was set from 873 K to 1073 K (increased according to experimental case). The actual reaction temperature on the outer wall of the reactor tube was measured by ten R-type thermocouple for a certain temperature distribution along the flow reactor as shown in Fig. 2. Each temperature profile is named with its setting temperature on every experimental case. The temperature rises rapidly at the beginning because n-heptane is endothermic during the heating process, and then the temperature nearly keeps constant and maintains about 40 cm long along the reactor on the pyrolysis process, in the end the reaction temperature decreases when the furnace temperature drops. The internal wall temperature was nearly accordant with outer wall and the uncertainty of measurement value was with ± 20 K. The flow rate was set to 1 or 2 mL/min and measured with flow meter, and the inlet Reynolds number could be ensured below 2300 with low flow rate in experimental conditions, so the turbulence effect in the tube was ignored and the experimental uncertainty could be reduced.

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