



## Full Length Article

## Effects of molecular structures on the pyrolysis and anti-coking performance of alkanes for thermal management



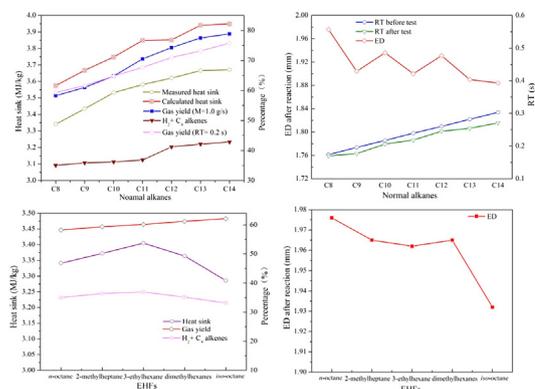
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## GRAPHICAL ABSTRACT

Pyrolysis of alkanes was carried out using a supercritical cracking experimental apparatus equipped with an electrically heated tubular reactor under supercritical conditions. Effects of molecular structures on pyrolysis and anticoking performance of alkanes were studied.



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## ABSTRACT

Pyrolysis of *normal*- and *iso*-alkanes were carried out using a supercritical cracking experimental apparatus equipped with an electrically heated tubular reactor under supercritical conditions (3.5 MPa and 700 °C). The hydraulic resistance method (HRM) was applied to quantitatively evaluate the carbon deposition. Effects of molecular structures on the pyrolysis and anti-coking performance of alkanes were studied. It was found that the gas yield and heat sink (HS) increased with the increasing carbon chain length of normal alkanes. Normal alkanes with even carbon number (NPEC) exhibited better anti-coking performance than those with adjacent odd carbon number (NPOC). Compared with normal alkanes, *iso*-alkanes could generate higher gas yields. However, lower HS and yield of hydrogen and alkenes ( $\leq C_4$ ), as well as poorer resistance to carbon deposition were observed for *iso*-alkanes with more than two methyls. There was an optimum value of the ratio of NPEC/NPOC for the balanced HS and anti-coking performance in the design of high-performance endothermic hydrocarbon fuels (EHFs).

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**Abbreviations:** HRM, hydraulic resistance method; NPEC, normal alkanes with even carbon number; NPOC, normal alkanes with adjacent odd carbon number; EHF's, endothermic hydrocarbon fuels; HS, heat sink; RT, residence time; S, signal; T, temperature; ED, effective diameter; PAHs, polycyclic aromatic hydrocarbons.

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## 1. Introduction

Aircraft operation at hypersonic flight speed causes severe heat loads generated by engines and combustors because of the atmosphere dynamic friction, leading to terrible thermal barrier [1–3]. It is generally accepted that regenerative cooling strategy using EHF is considered one of the most effective ways for thermal protection [4–6]. Before entering the combustion chamber, EHF undergo temperature rise, phase transition (physical HS) and then pyrolyze at high temperatures (chemical HS), which could serve as a cooling source for hypersonic vehicles. Meanwhile, light gaseous products such as H<sub>2</sub> and C<sub>2</sub>H<sub>4</sub> from thermal stressing of EHF are conducive to engine ignition and combustion [7,8].

Currently, alkanes are extremely important components of EHF. For instance, JP-7, a typical American military active EHF, includes abundant alkanes with a volume content of 59% [9–11]. It is well-known that HS and carbon deposition are the two most important parameters to weigh EHF. Demand for HS increases with the increasing flight speed. The differences in physical HS provided by diverse EHF under supercritical conditions are not significant [12,13]. Therefore, an improvement in chemical HS is extremely necessary in order to enhance the heat absorptivities of EHF. In other words, EHF should have preminent thermal cracking performance. However, coking is inevitable during the pyrolysis of EHF due to some secondary reactions such as condensation and polymerization. Carbon deposition can lead to failures of the feed system, deteriorative heat transfer, carburization and so on, which restrict engineering application of EHF [14,15]. Clearly, higher HS and lower carbon deposition are desired for high-performance EHF.

Effects of fuel compositions on the pyrolysis and anti-coking performance of EHF are reported in previous researches. For example, compared with cycloalkanes, alkanes crack more easily with higher alkenes ( $\leq C_4$ ) selectivities and HS [16]. However, cycloalkanes demonstrate more excellent anti-coking performance than alkanes due to the presence of hydrogen donors. Song et al. [17] found that the JP-8C saturates were much more stable than the JP-8P saturates because of the different compositions. JP-8C is rich in one- to three-ring cycloalkanes and two-ring hydroaromatics, while JP-8P is composed mainly of long-chain alkanes.

As for alkanes, a few scattered studies have been done to gain some informations on the molecular structure effects on the pyrolysis and anti-coking performance. Gong et al. [18] presented that the gas mole yield increased from 9.11 m mol/g to 16.55 m mol/g from *n*-octane to *n*-decane, which suggested that longer carbon chains promoted the cracking of *n*-alkanes. Study on supercritical thermal decompositions of *normal*- and *iso*-dodecane was conducted by Jiang et al. in a tubular reactor [19]. They found that *iso*-dodecane posed different anti-coking performance from *n*-dodecane. Besides, the *iso*/*normal* ratios had an influence on the conversion and morphology of coke. Yu et al. [20] investigated thermal decompositions of C<sub>10</sub>–C<sub>14</sub> *n*-alkanes in near-critical and supercritical regions at 425 °C. They observed that the chain length had a large effect on the products distribution, although similar conversions were obtained.

Undoubtedly, the compositions of EHF are extremely complicated including a large number of alkanes which are made up of various *normal*- and *iso*-alkanes. These alkanes exhibit different degradation behaviors because of the differences in the molecular structures. Even more importantly, some of them may be unsuitable for EHF due to the poor pyrolysis and anti-coking performance. However, to our knowledge, there has not been specialized and systematic research of the molecular structure effects on the pyrolysis and anti-coking performance of *normal*-/*iso*-alkanes with the carbon number from 8 to 14. Furthermore,

up until now all these studies have not referred to the HS which is the most important indicator of EHF. Therefore, it is fairly essential to carry out relevant research to select proper alkanes as the components of EHF.

The objective of this study is to obtain HS and quantitatively evaluate the carbon deposition of different alkanes. Effects of molecular structures on the pyrolysis and anti-coking performance of alkanes are investigated in order to illuminate the inherent relation between them. This work is expected to provide fundamental information on the design of advanced EHF.

## 2. Experimental

### 2.1. Materials

All the fuel samples used in this work were industrial grades with mass fraction higher than 98%. Normal alkanes (C<sub>8</sub>–C<sub>14</sub>) and *iso*-alkanes were supplied by Beishun Fuyuan Fine Chemicals Ltd. and Shanghai Zhixin Chemicals Ltd. (China), respectively. The dimethylhexane reagent was a mixture of various isomers due to the fairly high separation difficulty and expensive cost.

### 2.2. Apparatus and methodology

A schematic diagram of the experimental apparatus is shown in Fig. 1. Cracking experimental tests were conducted on the supercritical cracking experimental apparatus equipped with an electrically heated reactor made of GH3128 alloy steel. The reactor is 900 mm length with an inner diameter (ID) of 2.0 mm. The experimental apparatus could be divided into the following sections: fuel feed unit, electrical heating unit, cooling unit, gas-liquid separation unit and data acquisition unit.

Prior to each run, the reactor was heated to 700 °C in air for 1 h to eliminate metal-catalyzed effect. And then, the whole experimental system was purged with N<sub>2</sub> to eliminate air and impurities. A set of K-type thermocouples with diameter of 0.2 mm were welded on the outside surface of the reactor to measure the temperature distributions along this reactor with 50.0 mm space between each other. Typically, the temperature profile during the pyrolysis of *n*-dodecane under quasi steady-state condition was given in the Supporting Information. The reactor was thermal insulated by compact and heat-resistant quartz wool. The feed was pumped into the reactor without preheating at the required flow rate of 1.0 g/s using a metering pump and heated to 700 °C under 3.5 MPa. The system pressure was maintained by a back pressure valve. The cracked fuel was cooled by a condenser and then delivered to a gas-liquid separator. The gas flow rate was determined by a gas flowmeter. The products of each fuel sample were collected for 5 min to ensure enough weight of gas and liquid samples for the materials balance. Each run was repeated for three times in order to verify the reproducibilities. The error of mass balance was less than 3.0% by comparing the masses of the feed and products involving gas, liquid products, and carbon deposition.

In this paper, the law of energy conservation is adopted to calculate the HS of EHF, including the physical and chemical one. The HS can be determined by Eq. (1).

$$HS = (Q_{\text{input}} - Q_{\text{loss}})/M \quad (1)$$

where M is the mass flow rate of the fuel (g/s), Q<sub>input</sub> and Q<sub>loss</sub> are the input power and the heat loss, respectively.

The heat loss is caused by natural convection with the environment and heat radiation. It can be determined by fitting heat loss equation according to the relationship between a series of wall temperatures of the tube without fuel employed and imposed input power under thermal equilibrium. The details about the

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