Heat Management in Supersonic/Hypersonic Vehicles Using Endothermic Fuel: Perspective and Challenges

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ABSTRACT: In this study, an in-depth analysis has been performed on various technoengineering aspects of hydrocarbon cracking under supercritical conditions toward developing an endothermic fuel. The paper is segregated into several sections with specific emphasis. The major areas covered in this work include physicochemical characteristics of different endothermic fuels, supercritical pyrolysis of hydrocarbon fuels, phenomena of coking, and its suppression from an application viewpoint. The influence of various parameters (e.g., temperature, pressure, catalysts, space–time, etc.) on fuel conversion, endothermicity, and coke propensity has been emphasized in detail. The typical value of endothermic heat sink capacity for different fuels consisting of C8 to C15 hydrocarbons ranges from 500 to 1150 kJ/kg over temperature and pressure ranges of 550–750 °C and 25–55 bar, respectively. The effectiveness of various additives/initiators in improving endothermicity has been screened for wide ranges of temperature and pressure. Physicochemical properties like distillation characteristics, hydrocarbon composition, °API gravity, and sulfur content of different hydrocarbon fuels are compared in a single window. Most of the findings are abridged meticulously with relevant tables and plots. Toward the end, we have highlighted the critical issues/challenges on the experimental findings and prospective.

1. INTRODUCTION

Thermal resource management (TRM) of onboard hypersonic vehicles is an important field of research and development, and considerable attention has been received from the scientific community in the past few decades. Rockets are considered a high-speed propulsion vehicle, which is limited by its ratio of lower thrust to the mass of fuel burnt. The thrust-to-fuel burnt ratio is generally higher for a turbo engine due to its inherent design. A supersonic combustion ramjet (scramjet) is an advanced propulsion engine that usually works in high Mach number regions (>Mach 4) and provides power for hypersonic air-breathing vehicles. With the increase in Mach number, the intake air temperature becomes too high to cool the engine structure. A scramjet engine at hypersonic speed warrants stringent cooling requirements to manage its thermal load. A regenerative cooling using onboard fuel could be an effective thermal management method.1 The idea of regenerative cooling is to transfer heat from the hot engine to the cold hydrocarbon fluid. In a regenerative cooling process, the fuel temperature increases gradually, and eventually, it reaches a temperature that triggers endothermic chemical reactions.2 The concept of endothermic fuel development is not new, and many researchers are trying to develop it still today. Scientists are of the common opinion that coke formation and its accumulation in the fuel line are two of the critical constraints for regenerative cooling using hydrocarbon fuels.

The heat absorbed by the fuel is moderate at a low Mach number, and the fuel exists in a liquid state. With the increase in vehicle speed, the temperature of the aerothermal environment would increase. Consequently, the fuel temperature in the regenerative cooling channel rises, and beyond a specific temperature, the fuel can undergo a pyrolysis reaction. Usually, the sensible heat of the fuel can suffice the cooling requirements of an engine up to Mach 3, and beyond this value, the cooling of an engine can be fulfilled through endothermic reactions.3,4 In a few studies, regenerative cooling via endothermic reactions has been referred to as a chemical recuperative heat removal device.5–7 In the presence of high thermal loads, hydrocarbons tend to break or crack into smaller hydrocarbon molecules. These thermally cracked products would be injected into the combustor as a fuel to fulfill supersonic combustion requirements like lower ignition times, superior burning rate, etc.8,9

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Therefore, managing thermal loads in an advanced engine to power future aircraft/engines is challenging. In practice, when an engine approaches hypersonic speeds, the temperature of the air entering into the combustion chamber is too high. An X-51 waverider and similar flight engines are designed to operate at a high pressure (typically 250 to 300 times higher than the ambient pressure) and high fuel-to-air ratio (about 0.05 to 0.06), which significantly manifests the heat loads and worsens thermal management.\(^\text{10}\) Hence, thermal management has turned out to be a key concern in the development of scramjet engines. Therefore, to fulfill the high energy output and high heat sink capability, specific hydrocarbon fuels can be chosen to substitute conventional solid propellants or hypergolic fuels along with oxidizers. Research and development groups are of the common opinion that active and spontaneous cooling could be a better approach than providing passive cooling like thermal protection of the scramjet engine. Significant research has been carried out to understand hydrocarbon fuel cracking behavior at elevated temperatures and pressures. Most investigations have been carried out under supercritical conditions using small-diameter (<5 mm) tubular reactors. Hydrocarbon fuels such as JP-8, RP-1, RP-3, JP-7, JP-900, JP-10, n-heptane, n-decane, and n-dodecane have been chosen for experimental studies by the majority of authors.

The present paper summarizes the effects of various parameters like fuel flow rate, reactor pressure, temperature, fuel composition on cracking conversion, heat sink capacity, and coke propensity. For the benefit of the readers, the present paper has been subdivided into different sections with specific objectives and outcomes. The major technoeengineering aspects covered in the present paper are as follows: (i) physicochemical characteristics of different endothermic fuels, (ii) pyrolysis of endothermic fuels, (iii) catalytic cracking of endothermic fuels, (iv) phenomena of coking during cracking, (v) influence of additives on suppression of coking, and (vi) suitability of initiators to improve the endothermicity of hydrocarbon fuels. The critical outcomes of individual sections are briefed with necessary figures and tables. Finally, the salient features of each section are summarized along with the perspective and conclusions. The present work mainly emphasizes the engineering and application aspects of fuel cracking under supercritical or near-critical conditions and not the fundamental chemistry of hydrocarbon cracking under subcritical conditions.

2. PHYSICOCHEMICAL CHARACTERISTICS OF VARIOUS JET FUELS

Various types of jet propellants (e.g., JP-7, JP-8, RP-1, and RP-3) are commonly used for supersonic applications due to their excellent combustion quality, low coke deposition, and high energy density. However, due to high production costs and limitations for hypersonic applications, the development of an alternative/modified fuel has become an important research area across the globe. From a plethora of literature, it has been found that many research groups have studied the suitability of modified JP-7- and JP-8-equivalent fuels for hypersonic applications.

Lovestead and Bruno\(^\text{11}\) and Smith and Bruno\(^\text{12}\) have investigated the boiling characteristics and composition of different grades of jet fuels. The ASTM D86 distillation characteristics of representative JP-7 and JP-8 fuels are shown in Table 1. The initial boiling point (IBP) of JP-7 is relatively higher than that of JP-8, which indicates the better thermal stability of JP-7. The major hydrocarbon contents in JP-8 are in the range between C\(_7\) and C\(_{14}\), whereas for JP-7, the major hydrocarbons lie between C\(_6\) and C\(_{14}\).

Song et al.\(^\text{13}\) have studied the physicochemical characteristics of coal-derived JP-8C fuel. The fuel was prepared by coal gasification followed by a hydrotreating process. The density of JP-8C is relatively higher than that of a petroleum-derived JP-8 fuel, and the fuel consists of more than 75 wt % cycloalkanes and about 20 wt % aromatics. The study concluded that the JP-8C fuel was more stable (thermally) than a petroleum-derived JP-8 fuel at 450 °C. Balster et al.\(^\text{14}\) have studied the fouling characteristics of synthetic aviation kerosene fuel. The fuel was derived from coal and was almost free from aromatics, sulfur, and nitrogen compounds. The pour point, flash point, and specific gravity of the fuel were relatively higher than the fuel specifications laid down for military applications.

Li et al.\(^\text{7}\) have examined the combustion characteristics of JP-10 fuel. It is a single-component (tricyclodecane) synthetic fuel consisting of 99% cyclopentanes. The average boiling point and \(^\circ\)API gravity of the fuel are 192 °C and 19.1, respectively. The combustion energy of JP-10 is around 39 MJ/L. Balster et al.\(^\text{15}\) have studied the suitability of coal-derived JP-900 fuel for heat sink capability in a propulsion engine. The fuel was prepared by blending an equal volume of coal-derived refined chemical oil (RCO) and petroleum-derived light cycle oil (LCO), followed by a hydrotreating process. The boiling range and specific gravity of the blended fuel are 180–267 °C and 0.87, respectively. The fuel was thermally stable up to 480 °C, and it consists of more than 50 vol % decalin hydrocarbon. The polar species content in the fuel was around 22 mg/L, whereas for typical jet fuels, the corresponding value is in the range of 100 to 600 mg/L. The amount of coke deposition of JP-900 was 10 times less than a JP-8 fuel under similar test conditions. Bruno and Smith\(^\text{16}\) have studied the distillation and compositional characteristics of RP-1 fuel.

A comparison of ASTM D86 distillation characteristics of various jet fuels is shown in Figure 1, and the details are mentioned in Table 1. The data indicates that JP-7 is relatively a narrow cut fuel, and for jet fuel, the boiling range is maximum among the six fuels. The estimated values of the average boiling point of JP-7, JP-8, RP-1, RP-3, and JP-900 fuels are 219, 199, 213, 203.7, and 207.3 °C, respectively.

| Table 1. Distillation Characteristics of JP-7, JP-8, RP-3, JP-900, and Jet Fuels* |
|-----------------------------------------------|-----------------------|
| distillate (vol %) | temperature (°C) |
|-------------------|-------------------|
| JP-7\(^\text{11}\) | JP-8\(^\text{12}\) | RP-1\(^\text{16}\) | RP-3\(^\text{16}\) | JP-900\(^\text{12}\) | jet fuel\(^\text{19}\) |
| IBP 172 | 131 | 167 | 189 | |
| 5 206 | 175 | 197 | 180 | 191 | 160 |
| 10 208 | 179 | 194 | 189 | 195 | 170 |
| 20 211 | 185 | 202 | 189 | 197 | 195 |
| 30 213 | 185 | 205 | 193 | 199 | 205 |
| 40 215 | 194 | 209 | 198 | 202 | 212 |
| 50 218 | 200 | 212 | 203 | 206 | 220 |
| 60 221 | 204 | 217 | 209 | 211 | 228 |
| 70 226 | 212 | 222 | 215 | 217 | 237 |
| 80 232 | 219 | 228 | 224 | 228 | 242 |
| 90 239 | 241 | 237 | 257 | |

*Temperature data has been extracted from a distillation curve in many cases, so there may be a deviation of ±0.5 °C between actual and tabulated data.
The nature of hydrocarbon and its amount in a fuel play a vital role in offering a specific heat sink capacity. DeBlase et al.\textsuperscript{17} have examined the effects of aliphatic versus aromatic content on the composition of an endothermic fuel using in situ mass spectroscopy. The smaller aromatics and their methyl-substituted derivatives showed a higher tendency to form larger polycyclic aromatic hydrocarbons (PAHs), a precursor for coke formation at the highest temperatures. Various properties such as the hydrocarbon composition, \( ^{2} \)API gravity, sulfur content, and boiling range of different jet fuels are summarized in Table 2. The information is helpful in analyzing and correlating various thermal characteristics, e.g., thermal stability, coke propensity, and cracking conversion. The paraffin content in JP-7 is relatively higher than that in a JP-8 fuel. However, the aromatic content in JP-8 is about four times higher than that in a JP-7 fuel. The presence of cyclic and heteroatomic species is of significant concern for coke and gum propensity during a thermal cracking process.

3. THERMAL CRACKING CHARACTERISTICS OF ENDOHERMIC HYDROCARBON FUELS

The concept of endothermic hydrocarbon fuel has received significant attention from the academic community due to its higher energy density and higher heat sink capacity. Although hydrogen is considered one of the best endothermic fuels, safe handling and logistics to maintain it as a liquid are significant concerns. The logistics are even more critical for an onboard space vehicle due to space and weight constraints. Several engineering issues related to quick combustion and space vehicle due to space and weight constraints. Several researchers have proposed using hydrocarbon fuel as an active precursor for coke formation. Two dominant factors, namely, fuel cracking conversion and the distribution of cracked species patterns, are crucial to reducing the extent of thermal load. Combustion quality is related to cracked products at the cooling channel end, whereas fuel conversion and product composition are related to the heat sink capacities.

Daniau and Sicard\textsuperscript{30} have developed a global kinetic model to predict product composition from thermal cracking of long-chain saturated hydrocarbons\((C_{n}H_{2n+2})\). Norpar-12 fuel (a mixture of \( C_{9} \) to \( C_{12} \) hydrocarbons) was used to develop the kinetic model, and the model was validated with an \( n \)-dodecane \((C_{12}H_{26})\) hydrocarbon in the temperature range between 380 and 1225 °C and pressures up to 100 bar. The authors claimed that the model-predicted data matched well with the experimental data for methane, ethane, and other major alkenes except for ethylene. However, the authors have not disclosed the details of the model parameters in the article. Ning et al.\textsuperscript{31} have reported that the propagation of cracking reaction via a free radical mechanism favored the increase in paraffin-to-olefin ratio beyond the critical pressure of hydrocarbons. However, the generated olefins can undergo further reactions to form alkanes at elevated temperatures and pressures. The addition reaction is being exothermic, leading to a decrease in the overall heat sink capacity. The authors have also mentioned that beyond the critical pressure of the fuels, the rupture of five- and six-membered cyclic compounds reduced drastically and converted into cyclic isomers that act as an active precursor for coke formation.

The operating variables such as temperature, pressure, residence time, etc., play an important role in cracking. The simulation of cracking products from multicomponent fuels under a supercritical environment is a challenging task. The variation in chemical composition and the thermophysical properties of the fluid along the flow path need to be considered to obtain more realistic and accurate results. In many studies, researchers have used surrogate fuel to reduce complexity and understand the pyrolysis mechanism. Most authors have estimated the heat sink value of an endothermic fuel by measuring the fluid inlet and outlet temperatures and assuming that the fluid composition largely remains constant between the reactor inlet and the outlet. The chemical or endothermic heat sink value was obtained by subtracting the sensible heat from the total heat input. The expressions used by different authors to estimate the endothermic heat sink value of various fuels are shown below:\textsuperscript{12}

\[
Q_{\text{total heat sink}} = Q_{\text{input}} - Q_{\text{loss}}
\]  

(1)

Table 2. Various Properties of JP-7, JP-8, RP-1, RP-3, JP-900, and Norpar-12 Fuels

| property | JP-7\textsuperscript{11} | JP-8\textsuperscript{2,15} | RP-1\textsuperscript{20,21} | RP-3\textsuperscript{22,23} | JP-900\textsuperscript{12,15} | Norpar-12\textsuperscript{24} |
|---|---|---|---|---|---|---|
| paraffins (vol %) | 45.0 | 40.8 | 36.8 | 52.2 | 1.3 | 99 |
| monocylopentanes (vol %) | 35.0 | 30.3 | 37.0 | 33.8 | 32.2 |
| monocycloparaffins (vol %) | 15.0 | 11.4 | 16.0 | 6.0 | 63.1 |
| alkybenzenes (vol %) | 3.0 | 16.8 | 8.9 | 5.1 | 3.3 |
| naphthalenes (vol %) | 1.0 | 0.3 | 0.9 | 1.5 | 0.0 |
| total sulfur (wt %) | 0.1 | 0.3 | 0.05 | 0.2 | 0.0 |
| smoke point (mm) | 19.0 | 25.0 | 22.0 | 0.0 |
| \( ^{2} \)API gravity | 47.1 | 37 | 44.2 | 44.8 | 32.1 | 57.2 |
| boiling range from 5 to 90 vol % (°C) | 206–239 | 175–238 | 197–241 | 180–237 | 191–243 | 189–217 |

Figure 1. ASTM D86 distillation data of various hydrocarbon fuels.

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The thermal cracking mechanism is quite complex. Generally, three main types of thermal reaction models, namely, detailed, lumped, and global mechanisms, are mentioned in some literature. Although there are many articles on the mechanism of hydrocarbon cracking under sub- and supercritical conditions, the mechanistic chemistry is kept aside from the present study to focus more on technoeconomical aspects on endothermic fuel development. Ward et al.\(^4\) have investigated the thermal cracking of \(n\)-decane and \(-\)dodecane under high-pressure conditions using a tubular flow reactor. The reactor pressure and temperature were varied between 34 and 114 bar and between 550 and 600 °C, respectively, with a lower value (\(\approx 0.5\) mL/min) of fuel flow rate. Based on two-dimensional CFD simulation, the authors proposed the “Proportional Product Distribution” (PPD) model to describe the product pattern under mild (conversion < 20%) thermal cracking situation and validated it with experimental data. The study also demonstrates that increasing pressure was beneficial for bimolecular reactions and the overall conversion because of residence time increased. However, the effect of pressure on carbon deposition is not emphasized. Goel and Boehman\(^1\) demonstrated the use of modeling for the thermal degradation of \(n\)-dodecane and Norpar-13 using a flow reactor. A one-step global model is proposed to describe the pyrolysis of jet fuels under high-pressure conditions. The study showed that the outlet temperature and fuel degradation decreased with the increase in fuel flow rate. For high temperatures, the simulation was performed by extrapolating the batch reactor kinetics obtained at 460 °C.

The total heat sink capacity of different hydrocarbon fuels is shown in Figure 2, along with operating temperature and pressure. The value of total heat sink capacity of various fuels ranges between 2500 and 3200 kJ/kg for a temperature range of 600 to 750 °C. A summary of the total and endothermic heat sink capacities of various hydrocarbon fuels for ranges of temperature of 650−750 °C and pressure of 24−60 bar. Reprinted (adapted or reprinted in part) with permission from refs 32, 34−37 and 39. Copyright 2004 The American Society of Mechanical Engineers, 2017 Elsevier, 2001 American Institute of Aeronautics and Astronautics, Inc., 2014 American Chemical Society, and 2020 American Chemical Society.

\[ Q_{\text{input}} = V \times I \]  \hspace{1cm} (2)

\[ H(T_{\text{exit}}) - H(T_{\text{inlet}}) = \Delta H_{\text{sensible}} \]  \hspace{1cm} (3)

\[ H_{\text{endothermic}} = \left( \frac{Q_{\text{input}}}{m} \right) - \Delta H_{\text{sensible}} \]  \hspace{1cm} (4)

where \( Q \) is the energy per unit time, \( V \) is the voltage, \( I \) is the current, \( H \) is the enthalpy, and \( m \) is the mass flow rate.

NIST SUPERTRAPP software was used in many studies to estimate the physicochemical properties of fuels under elevated temperature and pressure conditions. The Peng–Robinson equation of state and extended corresponding states (EXCST) are used in the software for phase equilibrium calculations to generate thermophysical properties of various systems. The software consists of around 210 components along with their properties. Jackson et al.\(^3\) studied the thermal cracking characteristic of RP-3 fuel at different values of pressures and temperatures. The experiments were carried out in the temperature and pressure ranges of 500−750 °C and 7−60 bar, respectively. The study showed that the feed conversion and endothermic heat sink capacity increased with both pressure and temperature. The alkene selectivity decreased with pressure, thereby affecting the chemical heat sink capacities.

The thermal cracking behavior of \(n\)-octane, JP-7, and JP-8+100 fuels under elevated temperature and pressure conditions has been investigated by Huang et al.\(^3\) The experiments were performed in a test rig consisting of a combustor, heat exchanger, and liquid-vapor nozzle systems. The study was carried out in the temperature range of 700−815 °C and under 23 bar pressure. The reported values of total heat sink capacity of \(n\)-octane, JP-7, and JP-8+100 fuels are 3279, 3233, and 2954 kJ/kg, respectively, at 703 °C and 23.4 bar pressure. Heinrich et al.\(^3\) have conducted an in-depth study on endothermic cracking of Norpar-12 and \(n\)-dodecane to investigate the heat sink capacity. A tubular reactor was used to carry out the cracking experiments at a temperature range of 627 to 1027 °C and a pressure range of 25 to 35 bar. The estimated values of the total heat sink capacity of Norpar-12 and \(n\)-dodecane fuels are 2750 and 2590 kJ/kg, respectively, at 647 °C. The authors claimed that the estimated value of the heat sink is sufficient to meet the thermal management requirements for a hypersonic vehicle at Mach 5 speed.

Jiang et al.\(^3\) investigated the heat sink of kerosene range fuel (HF-1) under supercritical conditions using a flow reactor. The total heat sink capacity of the fuel is about 3045 kJ/kg at 680 °C and 50 bar. Zhu et al.\(^3\) performed the endothermic cracking of \(n\)-decane and the estimated value of the total heat sink capacity of \(n\)-decane is around 2700 kJ/kg at 667 °C and 40 bar pressure. Chakraborty and Kunzru\(^3\) have studied the thermal cracking behavior of \(n\)-heptane at a temperature range of 640−680 °C under subcritical pressure conditions. The conversion of \(n\)-heptane and alkane selectivity increased with the increase in pressure, while the selectivity of lighter olefins decreased with pressure. Pan et al.\(^3\) have studied the pyrolysis of JP-10 fuel in a nickel-coated tubular reactor at 45 bar pressure. The total heat sink capacity value is around 2600 kJ/kg of the fuel at 730 °C for 60 g/min feed flow rate. The coke deposition on the reactor surface was about 100 times lower than the coke obtained from the downstream filter.
heat sink capacities of various hydrocarbon fuels at different temperatures and pressures is shown in Table 3. The endothermic heat sink capacity of various fuels ranges between 500 and 1200 kJ/kg of fuel. Based on the reported data, it can be said that the heat sink capacity of hydrocarbon fuels depends on many parameters like fuel composition, nature of hydrocarbon, fuel flow rate, and operating temperature and pressure. The data also revealed that in most cases, the total (physical and chemical combined) heat sink value is three to four times higher than the corresponding endothermic (chemical) heat sink value.

### Table 3. Total and Endothermic Heat Sink Capacities of Various Fuels

| fuel          | temperature (°C) | pressure (bar) | total heat sink (kJ/kg) | endothermic heat sink (kJ/kg) | reference |
|---------------|------------------|----------------|------------------------|-------------------------------|-----------|
| Norpar-12     | 647              | 25             | 2750                   | 35                            |           |
| n-dodecane    | 647              | 35             | 2590                   | 35                            |           |
| JP-7          | 700              | 23.4           | 3233                   | 988                           | 35        |
| JP-7          | 815              | 23.4           | 3791                   | 1186                          | 32        |
| n-octane      | 700              | 23.4           | 3023                   | 953                           | 32        |
| JP-8+100      | 700              | 23.4           | 2954                   | 802                           | 32        |
| JP-8+100      | 770              | 23.4           | 3302                   | 1023                          | 32        |
| HF-1          | 680              | 50             | 3045                   | 1000                          | 36        |
| n-decane      | 667              | 40             | 2700                   | 550                           | 37        |
| RP-3          | 750              | 60             | 3250                   | 740                           | 34        |
| JP-10         | 730              | 45             | 2600                   | 39                            |           |

4. SUPERCRITICAL CATALYTIC CRACKING OF ENDOETHERMIC HYDROCARBON FUELS

Catalytic cracking of hydrocarbons is carried out to improve fuel quality and olefin selectivity in cracked products. Generally, a catalytic cracking process required a lower severity operation compared to the thermal cracking process for a similar extent of cracking. The catalyst selection is vital for a specific feed to obtain maximum benefits from a catalytic cracking process. Although many articles are available on the catalytic cracking of hydrocarbons, very few of them are related to the current topic, i.e., supercritical catalytic cracking of endothermic fuels.

Zhang et al. have studied the catalytic cracking of NNJ-150 (a mixture of C₈ to C₁₇ hydrocarbons) fuel in the presence of Ag- and La-impregnated silica–alumina-based USHY, HZSM, and SAPO-34 catalysts. In the presence of catalysts, the fuel conversion increased by more than 2-fold in comparison to the thermal cracking under similar operating conditions. The estimated values of feed conversion in the presence of USHY, HZSM, and SAPO-34 are 75, 76, and 53%, respectively, at 500 °C. Xian et al. studied the cracking characteristics of n-dodecane in the presence of HZSM-5. The study was performed in the temperature and pressure ranges of 400–450 °C and 16–40 bar, respectively, using a fixed-bed flow reactor. The dodecane conversion decreased with the increase in reactor pressure. The estimated values of fuel conversion at 16 and 40 bar pressures are 71 and 50%, respectively, at 450 °C with a catalyst-to-fuel ratio of 0.5 and 20 min run time. The coke yield at 450 °C and 40 bar was around 0.032 wt % with a 3 g/min feed flow rate. Huang et al. studied the pyrolysis of JP-10 with zeolite Y using a fixed-bed reactor. The product distribution pattern for the catalytic cracking was significantly different from the thermal cracking without zeolite Y. It was observed that the endothermic capacity of the fuel for catalytic cracking was slightly less than that for pyrolytic cracking for similar levels of conversion.

Huang et al. performed an exhaustive study on the endothermic cracking of JP-7, JP-10, and n-octane fuels over a zeolite-coated tubular reactor. The experiments were performed at 41 bar pressure for a duration of 15 min with a feed flow rate of 36.3 g/min. The amount of coke deposition was estimated by converting the coke into CO₂, and the endothermicity of the fuel was calculated using SUPERTRAPP software. The estimated values of the coke formation rate for JP-7, JP-10, and n-octane are 0.94, 0.88, and 0.43 mg/min, respectively. Lander and Nixon studied the thermal cracking of JP-7 fuel, and the estimated value of total heat sink capacity at 650 °C is about 2721 kJ/kg of fuel, which is insufficient to cool an engine operating above Mach 6 speeds. The team worked on single-component fuels such as JP-10 and methylcyclohexane (MCH) to improve the heat sink capacity. The heat sink was more than 4500 kJ/kg of fuel when a combined process of dehydrogenation and cracking was followed at 727 °C and 10 bar pressure in the presence of a Pt/Al₂O₃ catalyst. Although the heat sink number appears to be very attractive for the combined process, its implementation in actual hypersonic vehicles could be a significant challenge due to various reasons like the deposition of coke on the catalyst surface, coating of the catalyst layer inside the fuel line, maintaining of supercritical condition, etc.

Gao et al. have studied the suitability of the Ni-doped Al₂O₃ catalyst for the suppression of coke during the cracking of RP-3 fuel. The experiments were performed at 680 °C and 30 bar pressure using a rectangular flow reactor in the presence of steam. The study claims that the catalytic steam reforming improved the chemical heat sink capacity by around 750 kJ/kg of RP-3 fuel. It is also highlighted that the presence of the catalyst and steam together reduced the coke deposition rate from 148 μg/(cm²-min) to 22.5 μg/(cm²-min). However, the individual effect of steam and the catalyst on heat sink capacity and coke deposition is not reported.

Yeh et al. have studied the endothermic reforming of n-hexane on a Ga-promoted H-ZSM-5 catalyst under elevated pressures using a fixed-bed flow reactor. The experiment was carried out at 550 °C and 137 bar pressure with a feed flow rate of 0.3 mL/min. The catalyst was used in the form of a pallet. It is reported that the addition of Ga on H-ZSM-5 significantly increased the heat of reaction by increasing the selectivity of small aromatics. The reported value of n-hexane conversion is 9.5% at 550 °C and 137 bar. The study also reports that lighter olefin production decreased significantly at elevated pressures. Tian et al. studied the effect of JP-10 cracking over HZSM-5 zeolites. The cracking performance on nanosheet zeolite was relatively better compared to bulk zeolite for the similar value of the Si/Al ratio due to the better accessibility of acid sites and reduced diffusion paths. The enhanced diffusion of JP-10 increased the olefin yields. Yeh et al. have investigated the cracking of n-hexane at 500 °C and 60 bar pressure on a surface of HZSM-5 and Zn-HZSM-5 catalysts. The study reports that the reaction is mildly endothermic at low conversions of n-hexane (<120 kJ/kg) on HZSM-5, and at conversions above 50%, the reaction is exothermic. However, the Zn-HZSM-5 catalyst showed better endothermicity for a similar range of n-hexane conversion.
A summary of the endothermic heat sink capacity of various fuels in the presence of different catalysts is shown in Table 4. It has been observed that the operating temperatures in catalytic cracking studies are relatively higher than the thermal cracking temperatures. Also, this was possible due to a lesser amount of coke formation in the presence of a catalyst. Lower coke yield offered an extra cushion to increase the operating temperature and improve the endothermicity of fuels. Although catalysts can enhance the heat sink capacity of fuel, their demonstration in a hypersonic engine can be a significant challenge to engine designers and fabricators.

5. PHENOMENA OF COKING DURING THE THERMAL DEGRADATION OF HYDROCARBON FUELS

Coke and gum formation is a common phenomenon that occurs during the degradation and cracking of fuels. The coke deposition in a fuel flow line can create potential failure by blocking the fuel injection line. Coking is a primary concern for hydrocarbons for their effective utilization in scramjet engines. Generally, unsaturated and cyclic hydrocarbon compounds (e.g., C\textsubscript{4}H\textsubscript{6}, C\textsubscript{5}H\textsubscript{12}, and C\textsubscript{6}H\textsubscript{14}) are prone to agglomeration and can act as a coke precursor. The amount of coke formation depends on several factors like operating temperature, pressure, hydrocarbon composition, dissolved oxygen level, and the metallurgy of the fuel transfer line. Generally, for straight-chain alkanes, gum formation starts at relatively lower temperatures compared to branched-chain hydrocarbons. Once the gum formation starts, it increases exponentially via the reactions with alkenes and aromatics. The carbonaceous solid deposit consists of both amorphous films and uniformly sized spheroids. An investigation shows that the reduction of the sulfur content in the jet fuel from 0.10 wt % to 0.01 wt % reduced the formation of amorphous films significantly but not the amount of fluid-phase deposits.

Jin et al. studied the effect of pressure on the pyrolysis of RP-3 fuel at temperature and pressure ranges of 500–750 °C and 7–60 bar, respectively, in an electrically heated tubular reactor. The fuel conversion increased by 3.3 times when the pressure increased from 7 bar to 60 bar at 650 °C. The selectivity of alkanes increased, and the selectivity of lighter olefins decreased with pressure. The coke yield increased by 4.5 times when the pressure increased from 7 bar to 35 bar. The study inferred that at lower values of pressure (<15 bar), filamentous coking was profound due to metal-catalyzed reactions. But for higher values of pressure (>35 bar), amorphous coking was the dominating phenomenon. Zhu et al. have studied the phenomena of coking during the process of pyrolysis of RP-3 fuel under supercritical conditions. The experiments were carried out using a tubular reactor with a feed flow rate of 0.8 g/min. The cracking of the fuel started at around 470 °C under 50 bar pressure, and the estimated value of the coking rate is about 0.34 mg/(cm\textsuperscript{2}-min), and more than 85% of the coke deposits are carried away by the fluid. Furthermore, a GC-MS analysis confirmed the increase in aromatic components in the liquid product by more than 2-fold.

The chemical composition of a typical jet fuel consists of nearly 80 vol % alkanes, 10–20 vol % alkylated aromatics, and traces of heteroatomic species like oxygenates, sulfur, and nitrogenous compounds. Development of coke deposits at a miniature level could be routed via two major methods: (i) oxidative coking and (ii) pyrolytic cracking. “Cracking coke” is another category of coke that forms during cracking reactions at high temperatures. The amount of cracking coke mainly depends on the degree of cracking.

5.1. Formation of Oxidative Coke and Its Suppression Techniques. The presence of dissolved oxygen or oxygenate species in the fuel can enhance the unwanted oxidative coking in the presence of metallic species. The fuel temperature nearer to the entrance zone is relatively low, and in that zone, the dissolved oxygen reacts with hydrocarbon to form alkyl peroxide, which ultimately converts into oxidative coke deposits. The phenomena of oxidative coking are prominent when the fuel temperature ranges between 200 and 425 °C. The probable scheme of oxidative coking as depicted by Edwards is

\[
\text{R}^* + \text{O}_2 \rightarrow \text{RO}_2 \rightarrow \text{RO}_2\text{H} \rightarrow \text{precursors} \rightarrow \text{oxidative coke deposits}
\]  

Oxidative coke formation starts via an initiation process with the formation of the hydrocarbon radical R*, which reacts with dissolved oxygen to generate the \( \text{RO}_2* \) radical. The \( \text{RO}_2* \) radical extracts a hydrogen atom from the parent hydrocarbon (RH), regenerate the \( \text{R}^* \) radical, and propagate oxidative coke formation. Hydroperoxides that are formed through an oxidation process are prone to thermal decomposition. The presence of metallic species like Cu, Fe, Mn, etc., can enhance oxidative coke by accelerating peroxide radical formation. Hydroperoxides can decompose thermally in the presence of sulfur species. A general scheme of oxidative coking via the free radical mechanism is shown in Figure 3.

Therefore, reducing the oxygen concentration in fuel could be another option to suppress oxidative coking, which can be partially achieved by purging the fuel with inert nitrogen gas. The elimination of direct contact between the fuel and the metal surface could be another option to minimize the formation of oxidative coke, as reported by a few authors.

Yang et al. studied the suitability of alumina to suppress the metal-catalyzed oxidative coking of China RP-3 fuel. The
Initiation reaction: \( RH \rightarrow R^* + H^* \)

Propagation reaction: \( R^* + O_2 \rightarrow RO_2^* \rightarrow RO_2^* \rightarrow RO_2 + R^* \)

Acceleration reaction: \( RO_2 H \rightarrow RO^* + OH^* \)

Gum formation reaction: \( RO^* + RH \rightarrow ROH \rightarrow RO^* + O_2 \rightarrow acid \rightarrow gums \)

Termination reaction: \( 2RO_2^*(AO_2^*) \rightarrow \text{products} \)

**Figure 3.** Probable scheme of oxidative coking.

Chemical vapor deposition (CVD) technique was used to coat the alumina on the metallic (SS321) surface. The thickness of the alumina coating was varied in the range of 318 to 1280 nm. The cracking experiment was carried out at 650 °C and 50 bar for a duration of 30 min. It was reported that the coke formation reduced by about 35% in the presence of a 318 nm-thick alumina coating, and it further suppressed to around 50% when the coating thickness increased to 1280 nm. Tang et al.\(^56\) have investigated the aptness of TiO\(_2\) coating on the coking propensity of \(n\)-hexane. The inner surface of the SS304 tube was coated with TiO\(_2\) using a CVD technique. The pyrolysis was carried out at 600 °C and 33 bar pressure. Scanning electron microscopy (SEM) analyses were performed to understand the coke morphology. A myriad of granular structures with a sharp tip of 0.2 to 1 \(\mu\)m in size was observed on the uncoated tube, and the filamentous coke gets interlocked and turns into particles. The study revealed that the coke formation reduced by around 65 wt % in the case of the 6 \(\mu\)m-thick TiO\(_2\) coating.

Gong et al.\(^57\) examined the coking propensity of an in-house-developed MCRI-1 (mainly consisting of C\(_{12}\) to C\(_{16}\) hydrocarbons) fuel using a tubular reactor. To understand the metal-catalyzed coking, the surface of the stainless steel tube was coated with Al\(_2\)O\(_3\) layers of different thicknesses ranging between 55 and 220 nm by an atomic layer deposition technique. The degradation study was carried out at 800 °C and 40 bar pressure at a feed flow rate of 60 g/min. It is reported that the run time of the reactor increased 3-fold in the presence of a 165 nm-thick coating compared to a bare tube. SEM analysis was performed to ensure the metal-catalyzed filamentous coking. In the case of alumina-coated tubes, the population of spherical coke particles (characteristics of amorphous coking) dominated the coke deposits. Gascoin et al.\(^58\) performed the pyrolysis of \(n\)-decane at 850 °C using a titanium mixed stainless steel alloy reactor under a pressure range between 10 and 60 bar. The variation of different types of coke formations with operating temperature, pressure, and reactor metallurgy is emphasized in the work.

**5.2. Formation of Pyrolytic Coke and Its Suppression Techniques.** For a thermal cracking process, the phenomena of dehydrogenation and condensation reactions are common above 475 °C. Heterogeneous species like sulfur, nitrogen, etc., can enhance the coke deposition rate.\(^59,60\) At higher temperatures (>425 °C), condensation reactions lead to pyrolytic coke deposits. The probable scheme\(^57\) of pyrolytic coking is

\[
R \rightarrow R^* \rightarrow \text{polycyclic aromatics (precursors)} \rightarrow \text{pyrolytic coke deposits}
\]

A plethora of literature mentioned that the Diels−Alder reaction is a major pathway for pyrolytic coke deposits. The formation of diene groups during a cracking process is inevitable. Therefore, identifying a suitable additive, which can reduce diene formation, could be an effective route to suppress the coke deposition. Various research groups have examined the suitability of different additives to suppress the coke formation in a thermal degradation process of hydrocarbon fuels.

Wickham et al.\(^61\) have examined the aptness of diphenyl selenide as an additive to reduce coke propensity during the thermal cracking of \(n\)-heptane. The experiment was performed at 655 °C and 37 bar pressure with a feed flow rate of 2.9 mL/min. It is reported that the coke formation reduced significantly (more than 13 times) in the presence of 300 ppm of diphenyl selenide in the fuel and for a test duration of 12 h. Sobkowiak et al.\(^62\) have investigated the influence of

| fuel name   | additive name                         | additive loading (ppm) | temp (°C) | pressure (bar) | coke amount (mg/cm\(^2\)) | references |
|------------|---------------------------------------|------------------------|-----------|----------------|----------------------------|------------|
| \(n\)-heptane | no additive                           |                        | 655       | 37             | 2.630                      | 61         |
| \(n\)-heptane | diphenyl selenide                      | 300                    | 655       | 37             | 0.200                      | 61         |
| JP-8       | no additive                           |                        | 675       | 38             | 0.500                      | 62         |
| JP-8       | tetralin and tetralone                 | 20,000                 | 675       | 38             | 0.300                      | 62         |
| JP-8       | no additive                           |                        | 280       | 26             | 0.032                      | 63         |
| JP-8       | DTMBP                                 | 16                     | 267       | 30             | 0.015                      | 63         |
| JP-8       | 2-methoxyethanol                      | 480                    | 267       | 26             | 0.030                      | 63         |
| JP-8       | DSPDA                                 | 5.7                    | 267       | 26             | 0.001                      | 63         |
| JP-8       | no additive                           |                        | 363       | 38             | 0.017                      | 64         |
| JP-8       | proprietary material                  | 256                    | 363       | 38             | 0.007                      | 64         |
| JP-8       | no additive                           |                        | 675       | 38             | 0.023                      | 65         |
| JP-8       | DCP                                   | 100                    | 675       | 38             | 0.003                      | 65         |
| JP-8       | DCP                                   | 200                    | 675       | 38             | 0.009                      | 65         |
| \(n\)-heptane | no additive                           |                        | 560       | 37             | 0.058                      | 66         |
| \(n\)-heptane | proprietary material                  | 8600                   | 560       | 37             | 0.025                      | 66         |
| JP-8+100   | no additive                           |                        | 600       | 51             | 0.006                      | 66         |
| JP-8+100   | decalin                               | 10,000                 | 600       | 51             | 0.004                      | 66         |
| JP-8+100   | tetrahydroquinoline                   | 10,000                 | 600       | 51             | 0.011                      | 66         |

\(^{57}\)DTBMP: 2,6-di-tert-butyl-4-methylphenol; DSPDA: N,N-disalicyldiene-1,2-propane diamine; DCP: dicyclohexyl phenyl-phosphine.
tetralin and tetralone mixture as an additive on the coke propensity of JP-8 fuel under supercritical conditions. The study was carried out in a silica-coated tubular reactor at 675 °C and 38 bar pressure with a feed flow rate of 2.2 mL/min. In the presence of 2 wt % additive mixtures, the coke formation reduced by 40 wt % in comparison to an additive-free case. Purvis 63 has compared the coke deposition rates of JP-8 fuel in the presence of different additives such as 2,6-di-tertiary-butyl-4-methylphenol, 2-methoxystyrenol, and N,N-disalicyliediene-1,2-propane diamine. The study was carried out in a flow reactor with a feed flow rate of 300 mL/min for a duration of 60 min. The experiments were performed at lower temperatures (below 280 °C) under 26 bar pressure. A gravimetric technique was used to estimate the coke deposits. Among the additives, N,N-disalicyliediene-1,2-propane diamine showed better performance in suppressing the coke deposition.

DeWitt and Zabernick 64 performed a comparative study on the oxidative coke deposition of JP-7 and JP-8 fuels in the presence of triphenylphosphine and butylated hydroxyl toluene as antioxidant additives. The study was performed at 347 °C and 38 bar pressure. It is reported that 200 ppm of triphenylphosphine was more effective in suppressing oxidative coking than butylated hydroxyl toluene. Beaver et al. 65 studied the suitability of dicyclohexylphosphenphosphate (DCP) on the coking performance of JP-8 fuel. The experiment was performed at 675 °C and 38 bar pressure using a flow reactor. The addition of 100 ppm of DCP in JP-8 fuel reduced the coke amount by 3 times. Maurice et al. 66 have examined the coking characteristics of n-heptane and JP-8+100 fuel in the presence of different additives, namely, TDA (preparatory material), decalin, and tetrahydroquinoline. Among the studied additives, decalin was found to be the most effective in decreasing coke propensity. It is also reported that 1 wt % decalin loading reduced 33% of amorphous coke at 577 °C and 45 bar pressure. But in the presence of 1 wt % tetrahydroquinoline, filamentous deposition increased more than five times.

The influence of different additives and their concentrations on coke susceptibility for various fuels under different operating conditions is summarized in Table 5. Some of the additives show a significant reduction in coke formation. The positive effect of butylated hydroxyl toluene and triphenylphosphine in reducing oxidative coking has also been highlighted in a few studies. Based on the available data, it can be said that the extent of coke suppression depends on parameters like the type of additive and its concentration, operating temperature and pressure, and the nature of fuels.

6. SUITABILITY OF INITIATORS TO ENHANCE THE ENDOThERMICITY OF HYDROCARBON FUElS

The cracking of hydrocarbons increases with the increase in temperature, and the consequence of more cracking is the deposition of more coke. Coke deposition reduces the heat sink capacity of fuel, and finally, it may lead to choking of the fuel line. To mitigate this limitation, the suitability of initiators to improve the endothermicity of fuels has been examined by several authors. 59,67,71

The suitability of tributylamine (TBA) to improve the heat sink capacity of n-heptane has been investigated by Wang et al. 69 In the presence of 10 wt % TBA, the n-heptane conversion increased more than 250% at 550 °C and under atmospheric pressure. However, at 650 °C, the enhancement was only about 12%. In the presence of amine, the energy consumption increased by about three times at 650 °C. Although the effect of the initiator on feed conversion and energy consumption is reported explicitly, no details about the variation in coke yield and selectivity of products are reported. Also, the heat sink terminology used in work is the amount of energy supplied to maintain the desired temperature. The details of heat loss and physical and chemical (endothermic) heat sink capacities are not reported in the article. The same group of scientists also studied the suitability of triethylamine on heptane cracking performance under supercritical conditions. 70 At 600 °C and 35 bar pressure, the heptane conversion increased by about 1.7 times (from 7.5 to 12.5%) in the presence of 5.5 wt % triethylamine. Wickham et al. 72,73 have examined the effect of diphenyl selenide (DPS) on the endothermic heat sink capacity of various fuels, namely, n-heptane, JP-7, n-decane, and Norpar-12. The addition of 4 wt % DPS enhanced the total heat sink capacity of n-heptane to a tune of around 17.5% and feed conversion from 5.4% to 32% at 570 °C and 38 bar pressure. The heat sink capacity of n-decane and JP-7 fuel increased by around 10 and 3%, respectively. Under similar conditions, the cracking conversion of n-decane and JP-7 increased by around 1.7 and 1.2 times, respectively.

Liu et al. 68 have studied the suitability of nitropropane (NP), triethylamine (TEA), and 2,2,6,6-tetramethylperidine-1-yl)-oxidanyl (TEMPO) as initiators for the cracking of n-dodecane. Experiments were performed in a small batch reactor with 10 mL of feed. The temperature and pressure of the reactor were varied in the ranges of 420–450 °C and 32–44 bar, respectively. Among the additives, NP showed the best performance in enhancing the cracking conversion of n-dodecane. In the presence of 2 wt % NP, the n-dodecane conversion increased to 40% at 440 °C and 38 bar, whereas for TEA, the corresponding conversion was 20%. In the presence of the initiator, the alkane-to-alkene ratio increased in the liquid product, which may be due to increased hydrogen-donating bimolecular reactions.

He et al. 4,74,75 have studied the aptness of palmitoyl-modified hyperbranched polyglycerol (PHPG) macroinitiators to enhance the heat sink capacity of n-tridecane. The experiments were performed in an electrically heated flow reactor under supercritical conditions at a temperature range of 600–720 °C under 35 bar pressure. In the presence of 0.06 wt % PHPG, the heat sink capacity enhanced by about 7.5% at 720 °C, and the estimated value of total heat sink capacity is 3660 kJ/kg of fuel. Chakraborty and Kunzru 67 have studied the effect of triethylamine (TEA) on the thermal cracking behavior of n-heptane at a temperature range of 500–540 °C under 30 bar pressure. The heptane conversion increased by around 20% in the presence of 3 wt % TEA at 540 °C. Although the authors mentioned the benefits of initiators on the feed conversion and selectivity of a few lighter olefins (e.g., ethylene, butene, etc.), no information about the variation in coke yield and heat sink capacity is furnished.

From the 2000 millennium onset, focus on endothermic fuel development has been shifted from a multicomponent fuel toward single- or two-component fuels like JP-10. Tricyclodecane, commercially known as JP-10, is a single component of synthetic fuel. Li et al. 69 have examined the combustion energy of JP-10 fuel, and the estimated value of the combustion energy is 39 MJ/L, and it is sufficient to maintain the required thrust for a supersonic vehicle. Jia et al. 76 have studied the influence of nitropropane on the cracking performance of n-decane in a tubular reactor (1 m in length and 1 mm in diameter). The work was carried out in the temperature range
of 450–680 °C and under 32 bar with a 60 mL/min feed flow rate. The study demonstrated that the initiator enhanced propane yield through H-abstraction of propyl radicals. The selectivity of alkenes (C₃−C₉) increased by 10% in the presence of nitropropane. The initiator loading increased from 1 wt % to 4 wt %, the conversion of n-decane increased by 5%, and the chemical heat sink capacity improved from 330 kJ/kg to 410 kJ/kg at 614 °C.

A summary of the consequence of different initiators on the cracking characteristics of hydrocarbon fuels is tabulated in Table 6. The effect of initiators on feed conversion at various temperatures and pressures is shown in Figure 4. Although most of the initiators perform well in enhancing the conversion and endothermicity, the extent of improvement depends on the type of initiator, the concentration of the initiators, and operating conditions.

### Table 6. Influence of Initiators on Feed Conversion and Heat Sink Capacities of Various Fuels

| fuel name | temp (°C) | pressure (bar) | initiator name | initiator conc. (wt %) | total heat sink (kJ/kg) | conversion (%) | references |
|-----------|-----------|----------------|----------------|------------------------|------------------------|---------------|------------|
| n-heptane | 540       | 30             | TEA            | 3                      | 38                     | 67            |            |
| n-heptane | 540       | 30             | NP             | 2                      | 48                     | 67            |            |
| n-dodecane| 440       | 38             | TEMPO          | 2                      | 12                     | 68            |            |
| n-dodecane| 440       | 38             | TEA            | 2                      | 29                     | 68            |            |
| n-heptane | 600       | 1              | TBA            | 5.5                    | 28                     | 70            |            |
| n-heptane | 600       | 35             | TEA            | 5.5                    | 38.5                   | 70            |            |
| JP-7      | 600       | 38             | 2170           |                        | 36.2                   | 73            |            |
| NP        | 600       | 38             | 2230           | 4                      | 44.0                   | 73            |            |
| Norpar-12 | 575       | 38             | 1880           |                        | 5.4                    | 73            |            |
| n-heptane | 575       | 38             | 2209           | 8                      | 32.0                   | 72            |            |
| n-decane  | 600       | 38             | 2212           |                        | 28.3                   | 72            |            |
| n-dodecane| 600       | 38             | 2440           |                        | 49.7                   | 72            |            |
| n-tridecane| 720      | 35             | 3400           |                        | 85                     | 72            |            |
| n-tridecane| 720      | 35             | 3510           | 0.03                   | 90                     | 73            |            |
| n-tridecane| 720      | 35             | 3660           | 0.06                   | 94                     | 74            |            |
| n-tridecane| 720      | 35             | 3450           | 0.12                   | 88                     | 74            |            |
| n-decane  | 615       | 32             | NP             | 1                      | 2100                   | 10            | 74          |
| n-decane  | 615       | 32             | 2300           |                        | 21                     | 77            |            |
| n-decane  | 615       | 32             | 2350           | 4                      | 27                     | 77            |            |
| of 450–680 °C and under 32 bar with a 60 mL/min feed flow rate. The study demonstrated that the initiator enhanced propane yield through H-abstraction of propyl radicals. The selectivity of alkenes (C₃−C₉) increased by 10% in the presence of nitropropane. The initiator loading increased from 1 wt % to 4 wt %, and the chemical heat sink capacity improved from 330 kJ/kg to 410 kJ/kg at 614 °C.

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### 7. INFLUENCES OF SPACE VELOCITY AND PRESSURE ON FUEL CRACKING BEHAVIOR

This section highlights the influences of fuel space velocity, temperature, and pressure on cracking characteristics of liquid fuel under subcritical and supercritical conditions. Generally, the operating pressure for rocket fuel is much higher compared to a supersonic ramjet engine. The fuel exists in a single-phase liquid state in rockets due to high pressure. On the contrary, the fuel exists as a supercritical state in the supersonic ramjet. The multiphase and complex behavior of fuel gives rise to unprecedented changes in its thermophysical properties.

Xu and Meng have studied the effect of fuel flow rate on the thermal decomposition of RP-3 fuel using an electrically heated tubular reactor (500 mm in length and 1 mm in diameter). The fuel conversion decreased from 80% to 13% as the fuel velocity increased from 0.5 m/s to 4 m/s. The increase in fuel velocity reduces the fuel residence time and consequently reduces the fuel conversion and heat sink capacity. Hua et al. have studied the variation of fluid temperature along a reactor length for different values of n-heptane flow. The bulk fluid and wall temperatures decreased with the increase in fuel flow for a constant heat flux value. Li et al. have investigated the feasibility of power generation for hypersonic vehicles driven by hydrocarbon fuels. An analytical model was developed to predict the expansion characteristics of the cracked hydrocarbon. It is concluded that the minimum temperature required to obtain output work could be around 26749

![Figure 4. Comparison of various initiators on feed conversion at different temperatures and pressures (the number on the right side of the letters indicates the corresponding conversion).](https://doi.org/10.1021/acsomega.1c04218)
$525\, ^\circ\mathrm{C}$, and the work output from the cracked hydrocarbons is larger than the uncracked fuel. Although the temperature is considered to be a dominant factor for cracking reactions under subcritical states, pressure also has some effect on the cracking characteristics of hydrocarbon fuels. Edwards and Andersen and Bruno have reported that hydrocarbon cracking characteristics at lower pressures differ significantly from supercritical cracking. Xing et al. studied the thermal cracking phenomena of JP-10 fuel under subcritical and supercritical conditions. The experiment was performed in a flow reactor at temperature and pressure ranges of $550\textendash 630\, ^\circ\mathrm{C}$ and $1\textendash 38\, \text{bar}$, respectively. The cracking of JP-10 started above $550\, ^\circ\mathrm{C}$. The fuel conversion increased with pressure up to 20 bar (near critical pressure), and no significant change in conversion was observed above the critical pressure of the fuel. The yield of C$_3$H$_8$ and C$_4$H$_{10}$ in the cracked products decreased, but the number of alkanes like CH$_4$ and C$_3$H$_8$ increased with pressure. The study also shows that the sensitivity of temperature on the extent of fuel pyrolysis is higher than the sensitivity of pressure.

Researchers have simulated the fluid flow behavior and heat transfer patterns of different fluids under subcritical and supercritical conditions. Various databases like NIST SUPERTRAPP and NIST REFPROP 83 as well as Peng–Robinson and Redlich–Kwong equations of state were used to estimate the thermodynamic and transport properties. Wang et al. have used the Benedict–Webb–Rubin (BWR) and Soave–Redlich–Kwong (SRK) equations of state to estimate the density and specific heat of methane and n-heptane at supercritical states. Hoawei et al. studied the thermodynamic characteristics of hydrocarbon fuels under elevated temperature and pressure conditions. Li et al. have studied the heat transfer characteristics of China RP-3 fuel. It is reported that the heat transfer rate from the wall to the bulk fluid gradually decreased when the wall temperature exceeded the critical temperature of the working fluid. Zhou et al. have observed similar heat transfer characteristics for n-pentane hydrocarbon cracking. Li et al. have compared the thermal cracking behavior of HF-1 fuel (properties of HF-1 are shown in Table 7) among rectangular, square, and circular geometric channels with the same cross-sectional area under 35 bar pressure. The study was performed at $700\, ^\circ\mathrm{C}$ with a feed flow rate of 60 g/min. Both rectangular and square channels offered better conversions of HF-1 than the circular ones. The carbon deposits were also more in rectangular and square channels. The amount of carbon deposits was in the range of 1.5–2.3 mg/(cm$^2$-min) depending on channel geometry.

Wu et al. have examined the effect of temperature and pressure on n-heptane cracking using a regenerative cooling channel. The study was performed in the ranges of temperature of $600\textendash 800\, ^\circ\mathrm{C}$ and pressure of 1–35 bar. The feed conversion increased with temperature, even though the residence time was decreased (Figure 5a). However, pressure increased the pyrolysis residence time and decreased the average molecular weight of the cracked product (Figure 5b). It is reported that the olefin selectivity decreased with the increase in pressure.

Therefore, based on the aforementioned studies, it can be said that the fuel flow rate has a profound impact on fuel residence time, conversion, and fuel endothermicity. The fuel conversion improved with pressure when the operating pressure is less than the critical pressure of fuel, and above critical pressure, the influence is relatively low.

### A. COMPARISON OF LABORATORY TEST SETUP ADOPTED FOR ENDOThERMIC CRACKING EXPERIMENTS

The concept of endothermic fuel cracking is to absorb the heat of combustion to safeguard the internal parts of scramjet engines from a high-temperature environment. When a cold fuel passes through the fuel transfer line (as shown in Figure 6), it is expected to absorb the heat and undergo a pyrolysis reaction beyond $500\, ^\circ\mathrm{C}$ before entering the combustion chamber. It is also reported that the cracked product helps improve the quality of combustion by lowering the ignition delay time. Ignition of a scramjet engine is generally initiated using ethylene as an igniter, and then the hydrocarbon fuel is circulated in cylindrical tubes placed in the outer wall of the combustion chamber. Hydrocarbons are preferred due to their high energy density and ease of storing and handling compared with gaseous fuels like H$_2$.

To simulate the actual scenario in a laboratory, different approaches were adopted by various researchers in designing the test rig for the experimental investigation. Some groups of scientists have used direct heating DC power systems (as

![Figure 5. Effect of temperature and pressure on (a) feed conversion and (b) molecular weight of the product samples. Reprinted (adapted or reprinted in part) with permission from ref 85. Copyright 2018 Elsevier.](https://doi.org/10.1021/acsomega.1c04218)
shown in Figure 7a) to heat the reactor to the desired temperature.34,36,39 The other groups29,62,65 have used furnace heating systems as shown in Figure 7b. We believe that the furnace heating approach is justifiable if the objective is to estimate the fuel conversion and coking rate. In comparison, the direct electric heating approach is more meaningful for estimating the endothermicity of a fuel. Further, in some cases, a preheater was used upstream of the reactor to heat the fuel around 300−350 °C. The details of mode of heating, reactor dimension, and feed flow rate are shown in Table 8. Also, in a few investigations, rectangular and square tubes were used to understand the heat transfer and coking characteristics of hydrocarbon fuels.46,84

9. SUMMARY AND PERSPECTIVE OF THE STUDY

On the subject of “endothermic fuel”, many research and development groups investigated the cracking behavior of varieties of fuels, namely, JP-7, JP-8+100, RP-3, HF-1, JP-10, n-octane, n-decane, n-dodecane, etc., over wide ranges of temperature of 400−800 °C and pressure of 1−60 bar pressure. It is clear from the evidence that the heat sink capacity of fuels depends on several factors like composition of fuel, operating temperature and pressure, feed flow rate, feed residence time, etc. The reported value of the total heat sink capacity of various fuels containing C8 to C15 hydrocarbons is around 2500−3500 kJ/kg of fuel for a temperature range of 550−750 °C and pressure of 25 to 60 bar pressure. However, the endothermic (chemical) heat sink value lies in the range of 500 to 1100 kJ/kg for most fuels. A diversity in reactor setups and methodologies adopted by different researchers to estimate the heat sink capacity of fuels is noted. A few groups have used furnace heating systems, whereas others used a direct electric heating system to raise the reactor temperature. A preheater is also employed in some studies to heat the fuel before entering the actual cracking reactor. The use of furnace heating systems and preheaters may not be a realistic approach to estimate the endothermicity of fuels for a supersonic/hypersonic vehicle application.

Researchers have used different terminologies such as total heat sink, total heat absorption, physical heat sink, etc., to report the heat sink capacity of hydrocarbon fuels. However, they appear to be similar in some sense, if not precisely the same. Another gray area is the estimation of heat loss quantities in experimental studies. Different groups of scientists have used a different amount of heat loss quantity to estimate the physical and chemical heat sink capacity, even though the operating temperature and pressure are nearly the same. Almost in all studies, it is reported that the chemical heat sink capacity increased with the increase in temperature. However, the calculation of endothermicity is not explicitly mentioned in most of the articles. For multicomponent fuels, the challenges
are multifold to estimate the enthalpy of the exit stream under supercritical conditions. NIST SUPERTRAPP software has been used by many scientists to estimate the fluid property under supercritical conditions, but the SUPERTRAPP data is limited up to around 725 °C in temperature. It is also observed that in many findings, the fuel residence time is more than 60 s. However, for actual hypersonic engine applications, the fuel residence time is supposed to be much less and could be around 2 to 10 s.

The occurrences of coking are unavoidable in a cracking process. The amount and nature of coke formation depend on various parameters like the type and composition of the fuel, the severity of cracking operation, the presence of impurities in the fuel, the metallurgy of the reactor, etc. Based on the literature analysis, it can be said that coke propensity increases with the increase in operating temperature, the concentration of dissolved oxygen, and the concentration of sulfur, nitrogen, and metallic impurities in the fuel. Two notable routes (namely, oxidative and pyrolytic) of coke deposition are agreed upon and confirmed by several authors. Coke susceptibility can be suppressed by various ways such as sparging of nitrogen gas into the fuel, coating of the reactor tube with a catalyst layer, the addition of additives with fuel, and reduction of sulfur and nitrogen content in the fuel. Various chemicals such as diphenyl selenide, decalin, tetralin, phosphine, and triethylamine have been examined by scientists in suppressing the coke deposition rate. Although few of them showed a positive effect, the loading of additives could be a crucial parameter. Scientists have examined the suitability of catalysts to enhance the endothermic heat sink capacity under supercritical environments. The cracking performance of n-heptane, JP-7, JP-8, n-octane, and Norpar-12 were tested in the presence of different catalysts such as Pt−Al2O3, HZSM-5, SAPO-34, and zeolites. Although the catalysts showed some positive effects on heat sink capacities, the housing/coating of catalysts inside the narrow (typically 1 to 3 mm in internal diameter) tube could be a significant challenge in actual scenarios. The other issues could be the disengagement of catalyst particles/fines from the coating surface and choking of the fuel nozzle by the carry-over particles.

The effectiveness of various initiators (e.g., diphenyl selenide, nitropropane, tributylamine, triethylamine, etc.) in enhancing endothermicity has been examined by many scientists. Although most amine-based initiators are beneficial in enhancing the endothermicity and cracking conversion, the extent of improvement heavily depends on the type and concentration of the initiator and operating temperature and pressure. It is also found that most of the initiator studies are performed with single-component hydrocarbon fuels. Various physicochemical properties such as the distillation characteristics, composition of hydrocarbon groups, °API gravity, sulfur content, etc., of jet propellants have been compiled in a single place. The effect of pressure on endothermicity is almost insignificant if the operating pressure is greater than 1.5 times the critical pressure of the fluid. A summary of various aspects of experimental investigations on endothermic cracking is shown in Table 9. It has been observed that when some groups of scientists focused primarily on the heat sink and coking aspects, the others highlighted the conversion and kinetic aspects of hydrocarbon pyrolysis. To the best of our knowledge, none of the articles (except a few modeling studies) on endothermic fuel development have mentioned the complete mass balance information for a flow system.

### Table 9. Summary on Various Aspects of Experimental Studies on Endothermic Fuel Cracking above 400 °C and 25 bar

| fuel name | total heat sink reported (yes/no) | chemical heat sink reported (yes/no) | coke analysis reported (yes/no) | gas & liquid analysis reported (yes/no) | feed conv. reported (yes/no) | mass balance reported (yes/no) | references |
|-----------|---------------------------------|-------------------------------------|---------------------------------|----------------------------------------|-----------------------------|--------------------------------|------------|
| JP-10     | no                              | no                                  | no                              | yes                                    | yes                         | no                             | 29         |
| RP-3      | yes                             | yes                                 | yes                             | yes                                    | yes                         | no                             | 34         |
| JP-7 & JP-8 | yes                             | yes                                 | yes                             | yes                                    | yes                         | no                             | 32         |
| dodecane  | yes                             | no                                  | no                              | no                                     | yes                         | no                             | 35         |
| HF-1      | yes                             | yes                                 | yes                             | yes                                    | yes                         | no                             | 36         |
| n-decane  | yes                             | no                                  | no                              | yes                                    | yes                         | no                             | 37         |
| JP-10     | yes                             | no                                  | yes                             | yes                                    | no                          | 39                             |            |
| decane    | yes                             | no                                  | yes                             | yes                                    | yes                         | no                             | 40         |
| NNJ-150   | no                              | no                                  | yes                             | yes                                    | no                          | 43                             |            |
| RP-3      | no                              | no                                  | yes                             | no                                     | yes                         | no                             | 46         |
| hexane    | yes                             | yes                                 | yes                             | yes                                    | no                          | 49                             |            |
| JP-900    | no                              | no                                  | yes                             | no                                     | no                          | 62                             |            |
| JP-8      | no                              | no                                  | yes                             | yes                                    | yes                         | 2                              |            |
| JP-8      | no                              | no                                  | yes                             | no                                     | no                          | 65                             |            |
| heptane   | no                              | no                                  | yes                             | no                                     | yes                         | 38                             |            |
| JP-7      | yes                             | yes                                 | no                              | yes                                    | no                          | 71                             |            |
| dodecane  | no                              | no                                  | yes                             | no                                     | yes                         | 68                             |            |
| tri-decane| yes                             | no                                  | yes                             | yes                                    | no                          | 74                             |            |
| decane    | yes                             | yes                                 | yes                             | yes                                    | no                          | 77                             |            |

In the present paper, an in-depth review has been performed on various technoengineering aspects of endothermic fuel development for supersonic and hypersonic speed applications. The paper has been segregated into several sections with specific emphasis. The topic covered in the present paper broadly includes the thermal cracking behavior of endothermic fuels, the influence of catalysts on endothermicity, coking and application of additives in suppressing coke formation, and the suitability of initiators to improve fuel endothermicity. The limitations like the use of preheaters in laboratory experiments vis-à-vis the absence of preheaters in actual applications,
estimation of heat loss quantity, estimation of enthalpy and other properties of reactor exit stream under supercritical conditions and chemical heat sink capacity, finding the phase behavior of multicomponent hydrocarbons under supercritical conditions, and lack of complete mass balance information are some of the critical concerns in this area. The relationship between endothermicity and fuel conversion is not reported explicitly in most of the studies. The information would be useful to analyze and correlate various properties like thermal stability, coke propensity, cracking conversion, and endothermicity of different hydrocarbon fuels and be helpful to scientists working or who tend to work in the field of endothermic fuels.

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