

Thermal cracking of aviation kerosene for scramjet applications

ZHONG FengQuan, FAN XueJun[†], YU Gong & LI JianGuo

Key Laboratory of High Temperature Gas Dynamics (LHD), Institute of Mechanics, Chinese Academy of Sciences, Beijing 100190, China

Thermal cracking of China No.3 aviation kerosene was studied experimentally and analytically under supercritical conditions relevant to regenerative cooling system for Mach-6 scramjet applications. A two-stage heated tube system with cracked products collection/analysis was used and it can achieve a fuel temperature range of 700–1100 K, a pressure range of 3.5–4.5 MPa and a residence time of approximately 0.5–1.3 s. Compositions of the cracked gaseous products and mass flow rate of the kerosene flow at varied temperatures and pressures were obtained experimentally. A one-step lumped model was developed with the cracked mixtures grouped into three categories: unreacted kerosene, gaseous products and residuals including liquid products and carbon deposits. Based on the model, fuel conversion on the mass basis, the reaction rate and the residence time were estimated as functions of temperature. Meanwhile, a sonic nozzle was used for the control of the mass flow rate of the cracked kerosene, and correlation of the mass flow rate gives a good agreement with the measurements.

thermal cracking, aviation kerosene, lumped model, scramjet applications

1 Introduction

Hydrocarbon fuels have been considered as the primary coolant in regenerative cooling system for hypersonic applications^[1,2]. For high Mach number (≥ 5) flights, by absorbing heat from the combustor wall, the fuel is easily heated to a temperature at which significant thermal cracking occurs. In thermal cracking, the bonds of large molecules are broken and thousands of decomposition processes take place. Thermal cracking is usually an endothermic reaction^[2,3], which can provide extra heat sink for the cooling. To study the cracking process, various chemical models have been developed, which can be divided into two categories in general: detailed model and lumped model. The detailed model may include hundreds to thousands of elementary reactions, and is complicated and not practical for engineering applications. So far, most of the detailed models have been developed for only pure hydrocarbons such as *n*-decane and *n*-dodecane^[4–6]. Compared to the detailed model, a

lumped model groups cracked products into several kinetic lumps and regards them as pseudo-products^[7]. The cracking process is then simplified to a few reactions associated with the pseudo-products. Despite of lack in the cracking details, the lumped model reduces the complexity of reactions and has been widely used for engineering problems. Sheu et al.^[8] developed a three-step lumped model for Norpar-13 cracking based on the experimental data of a heated tube system. They incorporated it into a 2-dimensional computation and the calculated wall temperatures were in good agreements with the measurements. Ward et al.^[7] proposed a concept of “proportional product distribution (PPD)”, which describes that for mild cracking, a product forms at constant proportion with respect to the other products. With

Received August 28, 2008; accepted November 22, 2008

doi: 10.1007/s11431-009-0090-8

[†]Corresponding author (email: xfan@imech.ac.cn)

Supported by the National Natural Science Foundation of China (Grant Nos. 10672169 and 10742003)

the PPD assumption, a one-step model was developed for mild cracked n-decane and n-dodecane. Tran and Chen^[9] proposed a one-step lumped model for Norpar-12 under supercritical conditions and the model parameters such as activation energy were extracted from the experimental data. To our knowledge, no study of thermal cracking of aviation kerosene under supercritical conditions has so far been reported. Hence, one objective of this work is to investigate thermal cracking of aviation kerosene under supercritical conditions relevant to a regenerative cooling system for Mach-6 scramjet application.

Another objective of this work is to develop a method for prediction and control of mass flow rate of thermal cracked kerosene. It is known that with light-molecule species produced, the fuel density decreases significantly and its compositions change as functions of fuel pressure and temperature. An effective fuel heating and injection system needs to account for these factors to achieve a reliable control of the mass flow rate. In our early study, a sonic nozzle was used for the control of mass flow rate of supercritical kerosene^[10,11]. It is known that the heated fuel flow is choked at the nozzle throat and its mass flow rate is then fixed. With the temperature and pressure upstream of the nozzle known, the fuel mass flow rate can be determined analytically^[12]. Our early studies^[10,11] have proved that the analytical method can provide good predictions of the mass flow rate at fuel temperatures from 650 to 800 K and at pressures from 3 to 5 MPa. For cracked kerosene, however, the above method is no longer valid since the fuel composition and thermodynamic properties are changed dramatically. To predict the mass flow rate of the cracked fuel accurately, the analytical method needs to be modified with a cracking model.

In this paper, thermal cracking of China No.3 aviation kerosene was investigated in a heated tube system. The heating system has been used for our previous studies^[10,11,13,14]. For the present study, the fuel pressure was in the range of 3.5–4.5 MPa, higher than the critical pressure (~2.4 MPa) of the kerosene and the fuel temperature varied from 700 to 1050 K. The fuel residence time was estimated as approximately 0.5–1.3 s, depending on operation conditions. The mass flow rate of the kerosene, the fuel conversion and components of the gaseous products were determined experimentally. Based on the experimental data, a one-step lumped model was proposed, which divided the cracked kero-

sene into three groups: unreacted kerosene, gaseous products, and a residual including liquid products and carbon deposits. Compared with the measurements, the modified analytical method gave good predictions of mass flow rate of cracked kerosene. Many of the cracking properties, such as reaction rate, the residence time, etc. were determined based on the experimental results and the lumped model.

2 Experimental set-up

2.1 The kerosene heating system

To minimize the fuel coking at high temperatures^[15], a two-stage heating system was designed and is shown in Figure 1. The first stage was a storage type heater that could heat kerosene of 2 kg up to a temperature of 570 K within half an hour with negligible coking deposits. The second stage was a flow reactor type heater, which could rapidly heat the kerosene to a temperature of up to 1100 K. The residence time of kerosene in the second heater was relatively short, less than a few seconds.

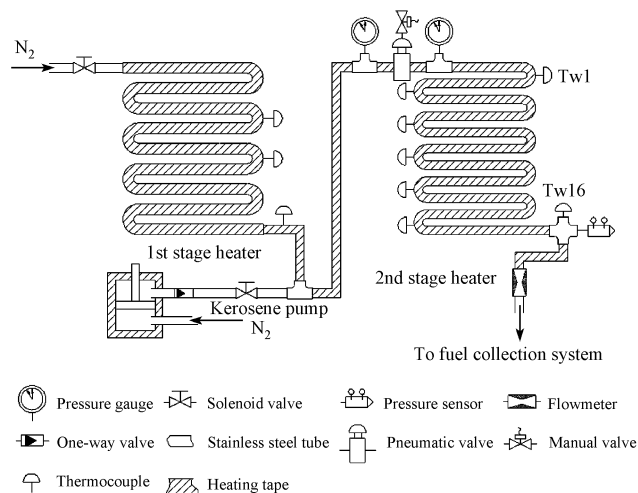


Figure 1 Schematic diagram of the two-stage heating system.

The first-stage heater consisted of a 20 m long stainless steel tube with 20 mm outer diameter and 2 mm wall thickness. The tube was wrapped with five 960 W heating tapes, which could be controlled independently in order to achieve a uniform temperature distribution along the tube. The second stage heater was made of stainless steel tube with 16 mm outer diameter, 2 mm wall thickness and a total length of 22 m. In order to rapidly raise the fuel temperature, the tube system was heated electrically by passing a current through the tube at 80–100 DC voltages from a pulsed AC/DC welder

power supply of 30 kW.

As shown in Figure 1, pneumatic valves were employed to turn on/off the two heaters. Type-K thermocouples were spot-welded to the outer wall of the heater tubes to monitor and achieve a feedback control of the wall temperature distribution. At the same locations with respect to the wall thermocouples, type-K sheath thermocouples with a sheath diameter of 0.5 mm, were mounted through the tube wall and positioned at approximately the tube centerline for the measurement of fuel temperatures. After each run, nitrogen and air were used to purge the residual kerosene and to eliminate the carbon deposits in the tube system.

2.2 The kerosene collection and analysis system

A schematic diagram of the kerosene collection and analysis system is shown in Figure 2. The mass flow rate of the cracked kerosene was controlled using a sonic nozzle with a throat diameter of 2.55 mm installed at the exit of the second heater. After the sonic nozzle, the cracked fuel mixture was cooled to the room temperature using a water condenser. The liquid products and carbon deposits were then collected and weighed, while the gaseous products were collected using a container immersed in a water pool and its volume was measured by the volume of water displaced. Compositions of the gaseous product were analyzed using gas chromatography. The mass flow rate of the kerosene was directly measured by the total mass of the liquid (including carbon deposits) and gaseous products collected per second. Table 1 presents summary of the test conditions.

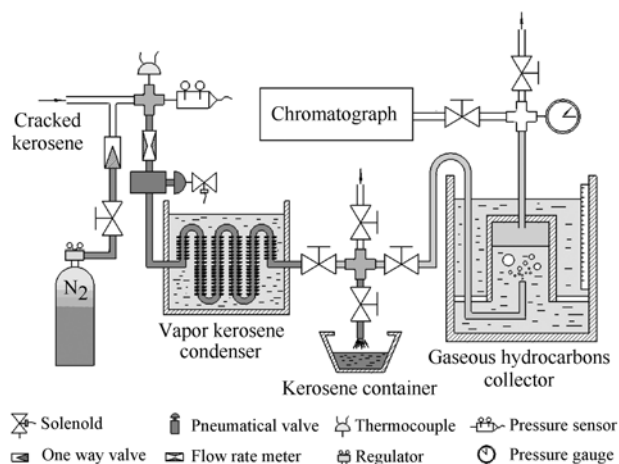


Figure 2 Sketch of the kerosene collection system.

Table 1 Summary of test conditions

Pressure (MPa)	Temperature (K)	Mass flow rate (g/s)	Residence time (s)
3.5–4.5	700–1050	25–60	0.5–1.3

3 Experimental results

3.1 Compositions of kerosene and its cracked products

On the volume basis, China No.3 kerosene is composed of approximately of 53% Alkanes, 39% Cycloalkanes, 5% Benzenes and 3% Naphthalenes. Figure 3 gives the compound mass fractions by carbon numbers and an overall chemical formula is found to be approximately $C_{11}H_{21.5}$. As introduced in our previous study^[10], a 3-species surrogate that consisted of 63% *n*-dodecane, 30% 1,3,5-trimethylcyclohexane and 7% *n*-propylbenzene (molar fractions) was proposed, and with *Nist Supertrapp*^[16], the model can calculate thermodynamic properties of the uncracked kerosene when fuel temperature is lower than 800 K.

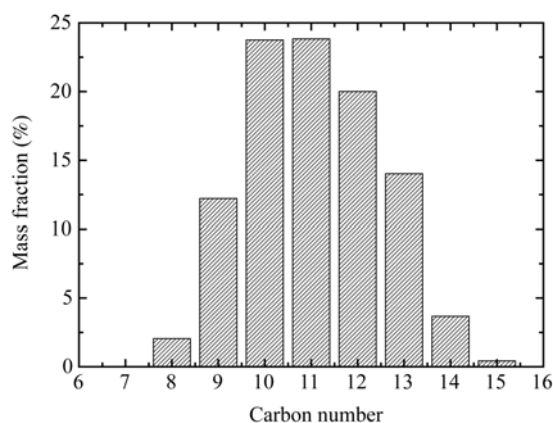


Figure 3 Mass fraction of carbon number for China No.3 kerosene.

When cooled down to ambient condition, the cracked products mainly include liquid and gaseous components. The collected liquid products also contain carbon deposits from coking and some tar-like materials. Compositions of the liquid products are very complex and difficult to be analyzed accurately. In this study, the liquid products including the carbon deposits and tar-like materials were approximated by a pseudo-product in the form of C_xH_y and the values of x , y could be determined according to the experimental results.

The primary gaseous products were low molecular number (C1–C5) alkanes and alkenes. Figure 4 shows the chromatography result of hydrocarbon compositions of the gaseous products collected at different temperatures and at a pressure of approximately 4 MPa. Hydrogen was also detected and a molar fraction of approximately 7% was found for all the fuel conditions. From Figure 4, it is found that the mass fraction for each

product does not change significantly with temperature except methane at the lowest temperature of 820 K. Thus, for the first approximation, composition of the gaseous products is considered to be independent of temperature and it can be determined based on the averaged values at varied temperatures. Table 2 gives the surrogates for the unreacted kerosene and for the gaseous products from the cracking. The chemical formula of the gaseous product including hydrogen can be approximated as $C_{1.8}H_5$ and the molecular weight is 26.6.

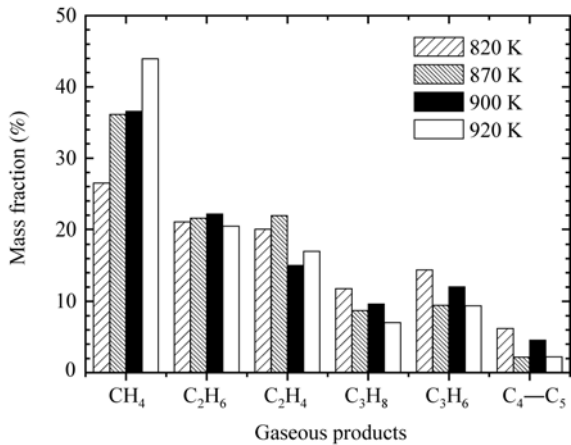


Figure 4 Hydrocarbon compositions of gaseous products at different temperatures.

Table 2 Surrogate compositions (mole fraction) for China No.3 kerosene and its gaseous products by thermal cracking

Surrogate for China No.3 kerosene		Surrogate for gaseous products	
n-Dodecane	0.63	CH ₄	0.33
1,3,5-trimethylcyclohexane	0.30	C ₂ H ₆	0.19
n-propylbenzene	0.07	C ₃ H ₈	0.13
		C ₂ H ₄	0.14
		C ₃ H ₆	0.14
		H ₂	0.07
Average molecular weight	153.3		26.6
Average chemical formula	C ₁₁ H _{21.3}		C _{1.8} H ₅

3.2 The kerosene conversion

Since kerosene is a mixture consisting of hundreds of hydrocarbons, it is very difficult to define the actual percentage of cracked kerosene. Edwards and Anderson^[17] defined a conversion of fuel to the gaseous products based on the change in the volume. In this study, the total mass of the liquid mixture m_L (including the unreacted kerosene, liquid products and carbon deposits) and the total mass of the gaseous products m_g were measured. So, a conversion of fuel to the gaseous products can be defined based on the mole fraction of the gaseous prod-

ucts.

$$\chi_g = \frac{N_g}{N_g + N_L} = \frac{m_g / \mu_g}{m_g / \mu_g + m_L / \mu_L}. \quad (1)$$

The collected liquid mixture can be further divided into two groups: unreacted kerosene with a total mole number of N_k and residuals (including liquid products and carbon deposits) with a total mole number of N_{res} . Hence, the average molecular weight of the liquid mixture μ_L can be calculated as

$$\mu_L = \frac{\mu_{res} / \mu_k + N_k / N_{res}}{1 + N_k / N_{res}} \mu_k. \quad (2)$$

If the average molecular weight of the liquid mixtures μ_L is approximated as the molecular weight of the unreacted kerosene for the first approximation, then the fuel conversion becomes

$$\chi'_g = \frac{m_g / \mu_g}{m_g / \mu_g + m_L / \mu_k}, \quad (3)$$

i.e.,

$$\chi'_g = \frac{1}{1 + (N_k + N_{res}) \mu_L / (N_g \mu_k)}. \quad (4)$$

All the variables in eq. (3) can be measured experimentally. Hence, the fuel conversion χ'_g can be determined and the result is shown in Figure 5 as a function of temperature. It is found that at temperatures lower than 800 K, χ'_g is nearly zero, indicating no significant thermal cracking occurs. When the temperature exceeds 800 K, χ'_g starts to increase rapidly and at a temperature of approximately 1000 K, χ'_g reaches a value of 0.9. Beyond this temperature (1000 K), no further increase in χ'_g is found, which implies at a temperature of 1000 K, kerosene is almost completely cracked. The maximum χ'_g is approximately 0.9, less than 1.0, which reflects molar fraction of the liquid products from the cracking. For the current study with a pressure range of 3.5 to 4.5 MPa, the results appear to be independent of the fuel pressure. From the figure, results of χ'_g can be represented by the following formula:

$$\chi'_g = \frac{1}{1 + a + e^{-\alpha(T-T_f)}}, \quad (5)$$

where $a=0.11$, $\alpha=0.0455$ and $T_f=897$. Eq. (5) is plotted in Figure 5 for comparison.

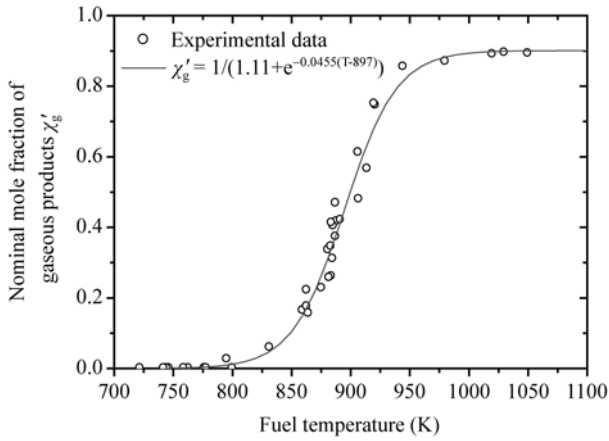


Figure 5 Nominal mole fraction of gaseous products χ'_g as function of temperature.

According to eq. (4), we have

$$a = \lim_{T \rightarrow \infty} \frac{N_{\text{res}} \mu_{\text{res}}}{N_{\text{g}} \mu_{\text{k}}} \quad (6)$$

Since the total mass is conserved during the cracking and if the total number of kerosene fed is N_0 , then

$$N_0 \mu_{\text{k}} = N_{\text{k}} \mu_{\text{k}} + N_{\text{g}} \mu_{\text{g}} + N_{\text{res}} \mu_{\text{res}} \quad (7)$$

The exact fuel conversion based on molar fraction is defined as eq. (1). It can be written as

$$\chi_{\text{g}} = \frac{1}{1 + \frac{N_{\text{k}} + N_{\text{res}}}{N_{\text{g}}}} \quad (8)$$

Combing eqs. (4) and (5), we find

$$\frac{(N_{\text{k}} + N_{\text{res}}) \mu_{\text{L}}}{N_{\text{g}} \mu_{\text{k}}} = a + e^{-\alpha(T-T_{\text{f}})} \quad (9)$$

Substituting eq. (9) into eq. (8), we have

$$\chi_{\text{g}} = \frac{1}{1 + \frac{\mu_{\text{k}}}{\mu_{\text{L}}} (a + e^{-\alpha(T-T_{\text{f}})})} \quad (10)$$

In the above equation, μ_{L} is the only unknown variable and its distribution with temperature can be determined by a lumped cracking model as described in the next section.

If χ_{g} and μ_{L} are known, the overall averaged molecular weight $\bar{\mu}$ can be calculated as

$$\bar{\mu} = \chi_{\text{g}} \mu_{\text{g}} + (1 - \chi_{\text{g}}) \mu_{\text{L}} = \frac{\mu_{\text{g}} + \mu_{\text{k}} (a + e^{-\alpha(T-T_{\text{f}})})}{1 + \frac{\mu_{\text{k}}}{\mu_{\text{L}}} (a + e^{-\alpha(T-T_{\text{f}})})} \quad (11)$$

It is also easily seen that from eqs. (4), (5) and (7), we have the following relation:

$$\frac{N_{\text{g}}}{N_0} = \frac{1}{\frac{\mu_{\text{g}}}{\mu_{\text{k}}} + a + e^{-\alpha(T-T_{\text{f}})}} \quad (12)$$

3.3 The mass flow rate

The measured mass flow rate divided by cross area of the nozzle throat $\left(\frac{q}{A^*}\right)$ at various temperatures and pressures are shown in Figure 6. For the fuel pressure other than 3.5 MPa, the measured value of $\frac{q}{A^*}$ is con-

verted to that at 3.5 MPa by $\left(\frac{q}{A^*}\right) \frac{35}{P_{\text{f}}}$. It is found that

the mass flow rate decreases significantly at a temperature from approximately 800 to 970 K, which indicates the change in the composition of the fuel mixture as a result of the cracking process.

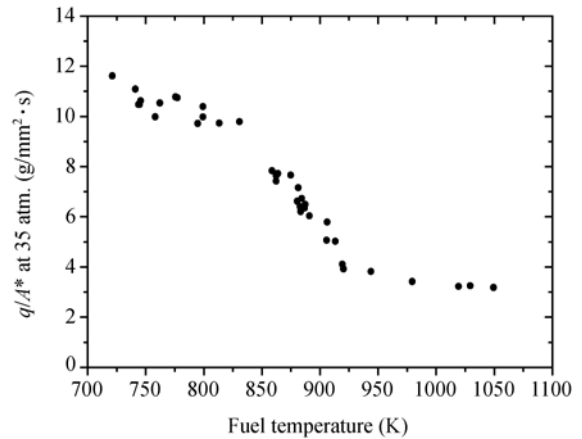


Figure 6 Distribution of the mass flow rate per unit area (at pressures converted to 3.5 MPa) as function of temperature.

Since the flow of cracked mixtures is choked at the nozzle throat and its mass flow rate q can be calculated by refs. [10, 11]

$$q = \frac{p A^*}{\sqrt{\hat{R} T / \bar{\mu}}} c f(\gamma) \quad (13)$$

where $f(\gamma) = \sqrt{\gamma \left(\frac{2}{1+\gamma}\right)^{\frac{(\gamma+1)}{(\gamma-1)}}$ and γ is approximately 1.2

because the degrees of freedom of the unreacted kerosene and mixture of the cracked products are very large. Coefficient c is a discharge coefficient and the value is set as 0.91 accounting for the pressure loss through the sonic nozzle.

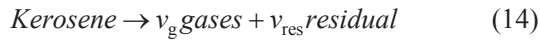
Once the average molecular weight of the cracked

fuel mixture $\bar{\mu}(T)$ is determined, using eq. (13), the mass flow rate can be determined by the pressure and temperature upstream of the nozzle.

4 A one-step lumped model

4.1 Development of the lumped model

The cracking process can be approximated as a global reaction as described as follows:



where v_g and v_{res} are the stoichiometric coefficients and will be determined later.

The reaction rate of eq. (14) is assumed to be first order, Arrhenius form, i.e.,

$$\frac{dN_k}{dt} = -kN_k. \quad (15)$$

Thus, we have

$$N_k = N_0 e^{-kt}, \quad (16)$$

where the cracking rate constant k is generally a function of fuel temperature. From eqs. (15) and (16), the mole numbers of gaseous products and residuals are

$$N_g = v_g N_0 (1 - e^{-kt}), \quad (17)$$

$$N_{\text{res}} = v_{\text{res}} N_0 (1 - e^{-kt}). \quad (18)$$

If μ_{res} , the overall molecular weight of the residuals, is approximated as a constant, substituting eqs. (17), (18) into (6) gives

$$\frac{v_{\text{res}} \mu_{\text{res}}}{v_g \mu_k} = a. \quad (19)$$

The reaction formula, eq. (14), leads to

$$\mu_k = v_g \mu_g + v_{\text{res}} \mu_{\text{res}}. \quad (20)$$

Determination of the overall chemical formula of the residual is described as follows. It is known that

$$a = \frac{1}{\beta} \frac{\mu_{\text{res}}}{\mu_k}, \quad (21)$$

where $\beta = \frac{v_g}{v_{\text{res}}}$.

Taking the high temperature limit of eq. (11), we can get

$$\bar{\mu}_{T \rightarrow \infty} = \frac{\mu_g + \frac{1}{\beta} \mu_{\text{res}}}{1 + \frac{1}{\beta}}. \quad (22)$$

The averaged molecular weight of the cracked mixture at infinite temperature $\bar{\mu}_{T \rightarrow \infty}$ can be approximated as the value at high temperatures (≥ 1000 K), at which the kerosene is completely cracked. The mass flow rate (per unit area) at a fuel temperature of 1050 K was measured to be 3.15 g/mm²; using eq. (13) inversely, the overall averaged molecular weight $\bar{\mu}$ at 1050 K (an approximate value for $\bar{\mu}_{T \rightarrow \infty}$) was calculated to be 20.

The small value of $\bar{\mu}_{T \rightarrow \infty}$ indicates that at high temperatures, there is a large amount of low molecular weight species in the cracked mixture. The low molecular weight species could be a mixture of free radicals and molecule fragments, such as CH, CH₃, etc. They can exist at high temperature but would be absorbed into the liquid products in the form of carbon deposits after cooled down to the ambient temperature.

With a and $\bar{\mu}_{T \rightarrow \infty}$ known, β and μ_{res} can be determined by solving eqs. (21) and (22). Assuming the averaged chemical formula of the residual is C_xH_y, we have

$$12x + y = \mu_{\text{res}}. \quad (23)$$

By using C₁₁H_{21.3} for the kerosene and C_{1.8}H₅ for the gaseous products, from eq. (20), we have two equations with respect to C and H elements:

$$v_{\text{res}}(1.8\beta + x) = 11, \quad (24)$$

$$v_{\text{res}}(5\beta + y) = 21.3. \quad (25)$$

Solving eqs. (23)–(25), x , y and v_{res} can be obtained and the result is summarized in Table 3.

Table 3 Parameters for the lumped model

a	$\bar{\mu}_{T \rightarrow \infty}$	β	μ_{res}	v_g	v_{res}	x	y
0.11	20	0.85	14.4	3.53	4.15	1.12	1.02

4.2 The reaction rate

The overall averaged molecular weight $\bar{\mu}$ can be written as

$$\bar{\mu} = \frac{N_0 \mu_k}{N_k + N_g + N_{\text{res}}} = \frac{\mu_k}{v_g + v_{\text{res}} + (1 - v_g - v_{\text{res}})e^{-kt}}. \quad (26)$$

The mass flow rate in the heated tube is

$$q = \rho u A = \frac{P u A \bar{\mu}}{\hat{R} T}. \quad (27)$$

And the fuel velocity can be calculated by

$$u = \frac{q\hat{R}T}{PA\bar{\mu}} \quad (28)$$

It is anticipated that the fuel flow is going to accelerate as kerosene cracks into small molecules and the density of the mixture decreases. If the length of the tube section with significant thermal cracking is L (approximately one-third of the total tube length for the present study) and the pressure and temperature through this section are nearly constant, then

$$L = \int_0^\tau u dt = \frac{q\hat{R}T}{PA} \int_0^\tau \frac{dt}{\bar{\mu}} \quad (29)$$

Substituting eq. (26) into eq. (29), we get

$$\begin{aligned} & (v_g + v_{res})\tau k + (1 - v_g - v_{res})(1 - e^{-k\tau}) \\ &= \frac{LPA\mu_k}{q\hat{R}T} k = \tau_0 k, \end{aligned} \quad (30)$$

where $\tau_0 = \frac{PAL}{qR_k T}$ and it represents a characteristic time.

With eq. (13), we have

$$\tau_0 = \frac{AL}{A^*} \frac{1}{c} \frac{1}{f(\gamma)} \frac{\sqrt{R_{\bar{\mu}}}}{R_k \sqrt{T}} \quad (31)$$

It is known from eq. (12) that

$$\frac{N_g}{N_0} = \frac{1}{\frac{\mu_g}{\mu_k} + a + e^{-\alpha(T-T_f)}} = v_g (1 - e^{-k\tau}) \quad (32)$$

Thus, by using eq. (32) and substituting $k\tau$ into eq. (30), we have the reaction rate constant k as

$$\begin{aligned} k = \frac{1}{\tau_0} & \left\{ \frac{1 - v_g - v_{res}}{v_g} \frac{1}{\frac{\mu_g}{\mu_k} + a + e^{-\alpha(T-T_f)}} \right. \\ & \left. - (v_g + v_{res}) \ln \left[1 - \frac{1}{v_g} \frac{1}{\frac{\mu_g}{\mu_k} + a + e^{-\alpha(T-T_f)}} \right] \right\}. \end{aligned} \quad (33)$$

Figure 7 gives the calculated k as a function of temperature. It is found that the change of k can be approximated by an exponential formula given as follows:

$$k = Ae^{-\frac{E_a}{RT}}, \quad (34)$$

where $A = 7.2 \times 10^{10}/s$ and E_a , the activation energy, is approximately 67.5 kcal/mol.

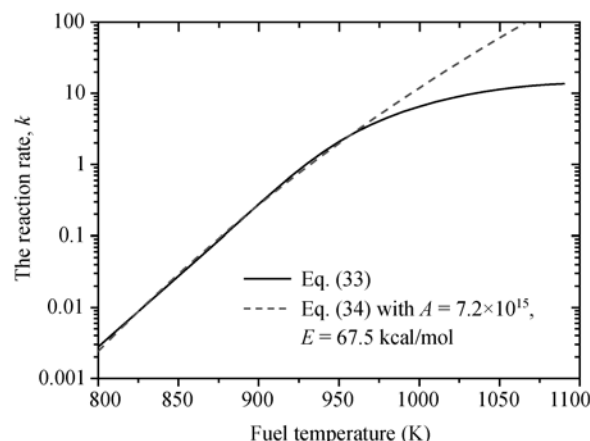


Figure 7 Reaction rate as function of temperature for the lumped model.

The exponential curve eq. (34) is also plotted in Figure 7. A good agreement between k and eq. (34) is found in the temperature range of approximately 800–960 K. Table 4 presents results of coefficient A and activation energy E_a for the current study and for the thermal cracked decane and dodecane (the two main components for common aviation kerosene) reported by refs. [5] and [8]. It is found that the parameters obtained by kerosene thermal cracking are close to those by decane or dodecane cracking even though kerosene consists of hundreds of hydrocarbon components. To our knowledge, no reports on reaction rate of thermal cracked kerosene have so far been found. The present result provides a reference of reaction parameters for analytical study and numerical simulation of kerosene thermal cracking at supercritical conditions.

Table 4 Reaction rates for China No.3 kerosene and n-alkanes

	China No.3 kerosene	Decane ^[8]	Dodecane ^[8]	Decane ^[5]
E (kcal/mol)	67.5	63	65	64
A (s ⁻¹)	7.2×10^{15}	2.1×10^{15}	1×10^{16}	$1 \times 10^{15.9}$

4.3 The fuel conversion

The fuel conversion on the mass basis can be defined as the mass fraction of the cracked kerosene as follows:

$$\chi_m = \frac{m_g + m_{res}}{m_0}, \quad \text{i.e.,} \quad \frac{N_g \mu_g + N_{res} \mu_{res}}{N_0 \mu_k} \quad (35)$$

Considering $\frac{N_g}{N_{res}} = \frac{v_g}{v_{res}} = \beta$ and substituting eq. (12)

into eq. (35), we have

$$\chi_m = \frac{N_g}{N_0} \left(\frac{\mu_g}{\mu_k} + \frac{1}{\beta} \frac{\mu_{res}}{\mu_k} \right)$$

$$= \frac{1}{\frac{\mu_g}{\mu_k} + a + e^{-\alpha(T-T_r)} \left(\frac{\mu_g}{\mu_k} + \frac{1}{\beta} \frac{\mu_{res}}{\mu_k} \right)}. \quad (36)$$

Distribution of χ_m with temperature is shown in Figure 8. It is found that the change of χ_m with temperature gives a similar trend of χ'_g , but smaller values at temperatures from 800 to 970 K. The gaseous products have larger fraction on molar basis due to the small value of the molecular weight, which causes a relatively large value of χ'_g . When temperature is higher than 1000 K, χ_m approaches 1, indicating the completeness of the thermal cracking.

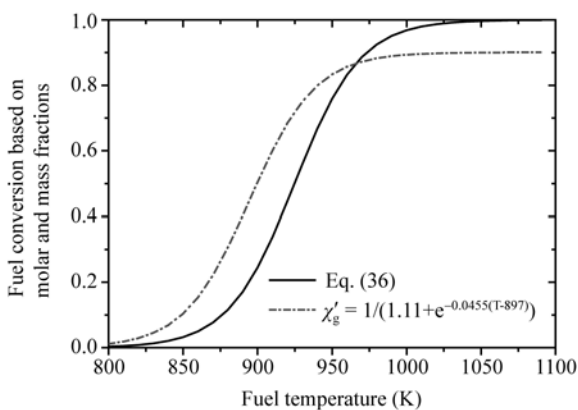


Figure 8 The fuel conversion define by mass fraction of cracked kerosene.

4.4 Correlation of mass flow rate

The average molecular weight of cracked mixture $\bar{\mu}$ can be determined by eq. (11). With eq. (13), the calculated mass flow rate per unit area at a pressure of 3.5 MPa is shown in Figure 9. From the figure, a good agreement between the calculation and the measured

mass flow rate is found, illustrating the validity of the analytical method and the one-step lumped model. For comparison, the fuel mass flow rate predicted with the 3-species surrogate proposed in our previous study^[10] for uncracked supercritical kerosene is plotted in the figure. At relatively low temperatures of $700 \text{ K} \leq T \leq 820 \text{ K}$, where thermal cracking is negligible, predictions of the mass flow rate by the 3-species surrogate agree well with the experimental results. It, however, gives much larger values than experimental results at temperatures higher than 800 K. It is shown that compositions of the cracked mixtures change due to thermal cracking at temperatures higher than 800 K and the 3-species surrogate model is no longer valid.

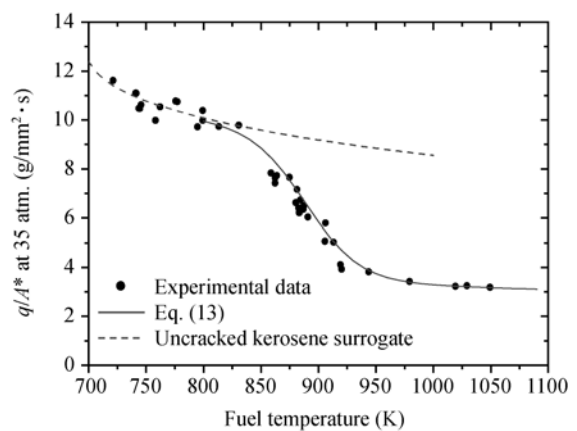


Figure 9 Correlation of the mass flow rate (per unit area) by the cracking model.

4.5 The residence time

With eqs. (30) and (33), the residence time of the kerosene flow τ can be solved and the result is shown in Figure 10(a). The residence time decreases from approximately 1.3 s for $T \sim 800 \text{ K}$ to 0.5 for $T \sim 1100 \text{ K}$. The

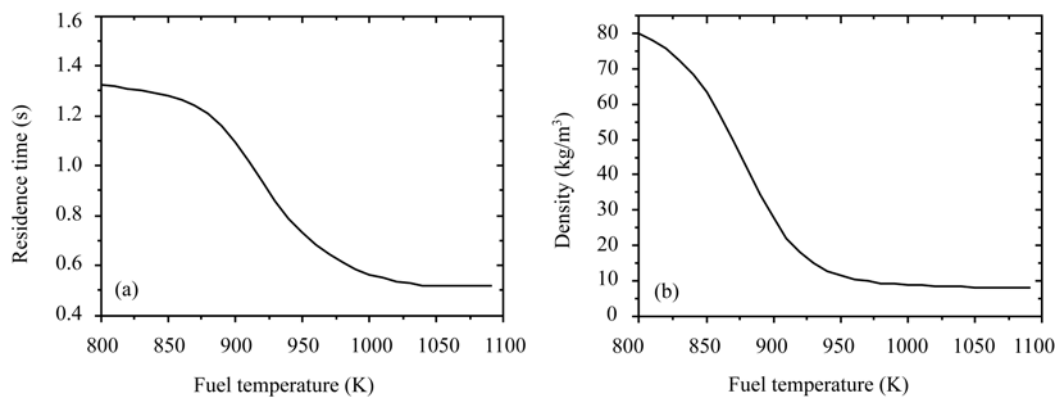


Figure 10 Distribution of the residence time (a) and density of the cracked mixture (b).

decrease in the residence time with temperature is attributed to the decrease in the density of the cracked mixture and the increase in the fuel velocity as temperature increases. Figure 10(b) gives the density as a function of temperature (pressure is 3.5 MPa), which confirms the above explanation.

5 Conclusions

Thermal cracking of China No.3 kerosene was investigated via a two-stage heating system at supercritical conditions relevant to Mach-6 scramjet applications. For the current study, the kerosene flow varied at temperatures of 700–1050 K, at pressures of 3.5–4.5 MPa and the residence time between approximately 0.5–1.3 s. It is found that thermal cracking begins at the temperature of approximately 800 K and almost completes at the temperature of 1000 K. Compositions of the gaseous products were found to be comprised mainly of low molecular number (C1–C5) alkanes, alkenes and hydrogen, and slightly to vary with temperature. Based on the experimental results, a one-step lumped model was proposed with the cracked mixtures grouped into three categories: unreacted kerosene, gaseous products

and residuals. With the lumped model, fuel conversion (defined by the mass fraction of cracked kerosene), reaction rate, residence time can be estimated as functions of temperature. The activation energy and the A-factor obtained by the present study are close to other reports about thermal cracking of decane and dodecane at relatively similar flow conditions. The correlation of mass flow rate at temperatures from 800 to 1050 K shows good agreements with the experimental data.

The analytical procedure and the correlation of kerosene mass flow rate described in this paper can be virtually applied to the study of thermal cracking of any other hydrocarbons.

The current one-step model, however, can only globally represent the cracking process. Thus, one improvement of the current model is to develop a multiple-step model, which is able to describe the cracking process more in details. Another possible improvement is to study the effect of residence time on thermal cracking and to include this factor into the model. Both of them are currently underway to upgrade the present model.

The author would like to thank Professor ZHANG XiangWen for his experimental efforts on the gas chromatograph.

- 1 Wagner W R, Shoji J M. Advanced regenerative cooling techniques for future space transportation systems. AIAA-1975-1247, 1975
- 2 Lander H, Nixon A C. Endothermic fuels for hypersonic vehicles. J Aircraft, 1971, 8(4): 200–207
- 3 Huang H, Spadaccini L J, Sobel D R. Fuel-cooled thermal management for advanced aero-engines. ASME J Eng Gas Turb Power, 2004, 126(2): 284–293
- 4 Zhou P, Crynes B. Thermolytic reactions of dodecane. J I&EC, 1986, 25(2): 508–514
- 5 Stewart J, Brezinsky K, Glassman I. Supercritical pyrolysis of decalin, tetralin and n-decane at 700–800 K product distribution and reaction mechanism. Combust Sci Tech, 1998, 136(1-6): 373–390
- 6 Dahm K, Virk P, Bounaceur R, et al. Experimental and modeling investigation of the thermal decomposition of n-dodecane. J Anal Appl Pyrolysis, 2004, 71(2): 865–881
- 7 Ward T, Ervin J, Striebich R, et al. Simulation of flowing mildly-cracked normal alkanes incorporating proportional product distributions. J Propul Power, 2004, 20(3): 394–402
- 8 Sheu J C, Zhou N, Krishnan A, et al. Thermal cracking of norpar-13 under near-critical and supercritical conditions. AIAA-1998-3758, 1998
- 9 Tran L, Chen L. Heat transfer calculation of an endothermic fuel at supercritical conditions. AIAA-1998-3762, 1998
- 10 Fan X J, Yu G, Li J G, et al. Investigation of vaporized kerosene injection and combustion in a supersonic model combustor. J Propul Power, 2006, 22(1): 103–110
- 11 Fan X J, Yu G, Li J G, et al. Combustion and ignition of thermal cracked kerosene in supersonic model combustors. J Propul Power, 2007, 23(2): 317–324
- 12 Shapiro A H. The Dynamics and Thermodynamics of Compressible Fluid Flow. New York: John Wiley & Sons, 1953
- 13 Fan X J, Yu G, Li J G, et al. Effects of entry conditions on cracked kerosene-fueled supersonic combustor performance. Combust Sci Tech, 2007, 179(10): 2199–2217
- 14 Zhong F Q, Fan X J, Yu G, et al. Heat transfer of aviation kerosene at supercritical conditions, AIAA-2008-4615, 2008
- 15 Edwards T. Liquid fuel and propellant for aerospace propulsion: 1903-2003. J Propul Power, 2003, 19(6): 1089–1107
- 16 Ely J F, Huber M L. NIST standard reference database 4-NIST thermophysical properties of hydrocarbon mixtures. Nat Inst Stand Tech, 1990
- 17 Edwards T, Anderson S. Results of high temperature JP-7 cracking assessment. AIAA-1993-0806, 1993