Article

Single-Pulse Shock Tube Experimental and Kinetic Modeling Study on Pyrolysis of a Direct Coal Liquefaction-Derived Jet Fuel and Its Blends with the Traditional RP-3 Jet Fuel

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ABSTRACT: A basic understanding of the high-temperature pyrolysis process of jet fuels is not only valuable for the development of combustion kinetic models but also critical to the design of advanced aeroengines. The development and utilization of alternative jet fuels are of crucial importance in both military and civil aviation. A direct coal liquefaction (DCL) derived liquid fuel is an important alternative jet fuel, yet fundamental pyrolysis studies on this category of jet fuels are lacking. In the present work, high-temperature pyrolysis studies on a DCL-derived jet fuel and its blend with the traditional RP-3 jet fuel are carried out by using a single-pulse shock tube (SPST) facility. The SPST experiments are performed at averaged pressures of 5.0 and 10.0 bar in the temperature range around 900−1800 K for 0.05% fuel diluted by argon. Major intermediates are obtained and quantified using gas chromatography analysis. A flame-ionization detector and a thermal conductivity detector are used for species identification and quantification. Ethylene is the most abundant product for the two fuels in the pyrolysis process. Other important intermediates such as methane, ethane, propyne, acetylene, and 1,3-butadiene are also identified and quantified. The pyrolysis product distributions of the pure RP-3 jet fuel are also performed. Kinetic modeling is performed by using a modern detailed mechanism for the DCL-derived jet fuel and its blends with the RP-3 jet fuel. Rate-of-production analysis and sensitivity analysis are conducted to compare the differences of the chemical kinetics of the pyrolysis process of the two jet fuels. The present work is not only valuable for the validation and development of detailed combustion mechanisms for alternative jet fuels but also improves our understanding of the pyrolysis characteristics of alternative jet fuels.
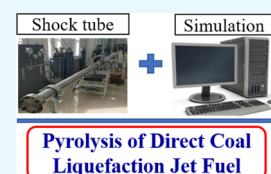
1. INTRODUCTION

Alternative jet fuels are of significant importance to meet the needs from both military and civil aviation energy goals. A series of alternative jet fuels including the Fischer−Tropsch (FT) synthetic paraffinic kerosene,[1] hydroprocessed renewable jet fuels derived from camelina and tallow,[2] alcohol-to-jet fuels,[3] hydrorefined algal oil,[4] and gas-to-liquid FT synthetic kerosene[5] are being considered. One of the essential properties for alternative jet fuels is the requirement of high energy density to ensure the range and payload of volume-limited air crafts.[6] For this purpose, highly strained multi-cyclic hydrocarbons with high energy density have been developed and studied, such as the RP-2 and JP-10 jet fuels employed in rocket and military aeroengines.[7] To achieve higher energy density alternative kerosene, many researchers have made great efforts to synthesize energy-dense jet fuels containing polycyclic hydrocarbons using different methods from different feedstocks.[6,8] For example, high energy density fuels such as 1,1,3-trimethylcyclohexane, dimers of isophorone, substituted cyclohexanes, and polycyclic alkanes were produced from isophorone, which was a promising feedstock.[8−11] The synthesized polycyclic alkanes usually exhibit higher energy density compared with the traditional jet fuels and are being considered for usage in aeroengines.

Besides the traditional synthesis method for the development of alternative high energy density jet fuels consisting of multi-cyclic hydrocarbons, the direct coal liquefaction (DCL) process for the production of liquid fuels reveals natural advantages due to the large number of aromatic hydrocarbons in coal molecules, which can be directly converted to multi-cyclic hydrocarbons from the high-pressure hydrogenation in the DCL process.[12] However, unlike the FT synthetic process that has been commercialized for a long time and employed in a wide number of countries to produce liquid jet fuels,[13] the large-scale commercial production of jet fuels from the DCL process via high-pressure hydrogenation is very resource-consuming and technologically difficult.[12] Even though, the million-ton DCL production plant for liquid jet fuels has been constructed with the progress in high-efficiency catalysts and process optimization in recent years for both strategic and environmental reasons.[12,14,15]

The usage of the DCL-derived jet fuel for aviation applications requires a basic understanding of their corresponding physical properties and combustion properties including ignition, extinction, pyrolysis, heat release, and pollution formation.[16] As demonstrated previously, the major components in DCL fuels are cycloalkanes with two or three rings due to the special molecular structure characteristics of coal.[12] There have been extensive experimental and kinetic modeling studies on pyrolysis and combustion properties of monocyclic alkanes such as cyclohexane,[17−19] methylcyclohexane,[20,21] ethyl cyclohexane,[22] n-propyl cyclohexane,[23] and *n*-butyl cyclohexane[24] due to their large amount of existence in traditional gasoline and jet fuels. However, very few studies have been reported on the real DCL-derived jet fuels besides some studies on representative polycyclic alkanes including decalin,[25−27] tetralin,[28,29] and JP-10.[30−32] In addition, the current aviation fuel testing, approval, and airworthiness certification processes limit the usage of the DCL-derived jet fuel as the single fuel in current aeroengines, and the DCL-derived jet fuel should also be used by blending with traditional jet fuels.[33,34] Hence, experimental and kinetic modeling studies on the DCL-derived jet fuel and its blends with the traditional jet fuel are one of the key procedures toward practical application of the DCL-derived jet fuel. Previously, Yang et al. studied the high-temperature ignition properties of the DCL-derived jet fuel and its blend with the traditional RP-3 jet fuel.[35] The experimental and modeling study results indicate that the species profiles of small hydrocarbon compounds during the oxidation of the DCL-derived jet fuel and RP-3 show very different phenomena, even though the high-temperature ignition properties between the two different fuels are similar.[35] Thus, pyrolysis studies of DCL-derived jet fuel are necessary to obtain a better understanding of its combustion properties and to develop more predictable combustion kinetic mechanisms, that is, within the HyChem framework.[31,36,37]

Besides the use of the DCL-derived jet fuel for civil aviation, pyrolysis of alternative jet fuels with high energy density is of crucial importance in the development of advanced hypersonic aircrafts because the jet fuel can be used to relieve the great heat load via the endothermic pyrolysis process.[38−41] Thus, extensive experimental and modeling studies have been performed to investigate the pyrolysis of traditional jet fuels including RP-3, JP-10, and Jet-A.[31,42−44] A jet-stirred reactor and a flow reactor are widely used experimental facilities for the study of fuel pyrolysis process under low-temperature conditions.[20,45,46] However, most of the interested pyrolysis kinetics and product distributions are under high-temperature conditions, which requires the design of novel experimental facilities. One of the efficient approaches is the use of shock tube apparatus in combination with advanced laser absorption to measure the pyrolysis speciation.[31,47,48] However, such analytical instruments are usually species dependent and expensive. In contrast, the single-pulse shock tube (SPST) has been implemented by several groups in recent years for fuel pyrolysis studies due to the simplicity in post-shock sampling and analysis.[3,42,49,50] A series of fuels from small hydrocarbons to complex real fuels were investigated via the SPST experimental method.[42,44,49] However, there is still a significant lack of understanding of pyrolysis characteristics of polycyclic alkanes and DCL-derived jet fuels.

Based on the above considerations, fundamental pyrolysis studies of DCL-derived jet fuels together with their blend with

traditional jet fuels are required to develop predictable detailed combustion kinetic models and to promote the fuel approval and airworthiness certification processes. Toward this end, the major aim of this work is to provide such fundamental data, evaluate modern detailed combustion kinetics mechanisms, and identify reaction pathways to improve our understanding of jet fuel combustion chemistry. To do so, the pyrolysis characteristics of the DCL-derived jet fuel and its 50/50 blend with the RP-3 jet fuel in volume are studied by using the SPST experimental facility and kinetic modeling. The paper is organized as follows. First, the experimental conditions investigated and the experimental setups used are presented. The experimental results are then described in detail and compared with modern detailed kinetic mechanisms from the literature. The pyrolysis characteristics of the DCL-derived jet fuel are also compared with pure traditional jet fuels. Finally, kinetic model analysis including reaction pathway analysis and sensitivity analysis is performed using detailed combustion kinetic mechanisms, and implications for future studies are recommended.

2. EXPERIMENTAL METHODS

2.1. NUC-SPST Facility. Pyrolysis experiments are performed using the SPST at the North University of China (NUC), which is composed of a 1.5 m driver section and a 3.05 m driven section with an inner diameter of 44 mm. The details of the experimental facility and procedures have been described previously.[44] Briefly, the driver and driven sections are separated via a polycarbonate diaphragm. A pressure vessel named a dump tank in SPST is used to consume the reflected shock waves and to ensure the reaction mixture solely under heated condition. The incident shock velocity is measured using four PCB 113B21 piezoelectric pressure transducers mounted on the sidewall of the driven section. The pressure—time profiles are measured by a Kistler 603CBA piezoelectric pressure transducer located at the end of the driven section. All pressure traces are recorded via two digital TiePie Handyscope HS4 oscilloscopes. The reflected shock wave pressure (P_5) and temperature (T_5) are determined using the one-dimensional normal shock relations employed by the program Gaseq[51] from the initial temperature/pressure, the measured incident shock velocity, and the thermodynamic properties of the reaction mixtures. The pyrolysis time is defined as the time interval between the arrival of the reflected shock wave and the 80% of the pressure signal recorded by the Kistler pressure sensor. The shock-heated products are sampled from the end wall using a solenoid valve protruding 10 mm into the SPST and are analyzed using an Agilent 7820A gas chromatograph. A flame-ionization detector and a thermal conductivity detector are used for reaction products.

The reaction mixture is prepared in stainless steel mixture tanks according to Dalton's law of partial pressure and is maintained for at least 12 h before experiments to ensure complete vaporization and homogeneity. A heating system with seven thermocouples placed along the mixing tank, a shock tube, and a sampling tube is used to maintain the experimental system with a temperature of 398 K to avoid adsorption of the liquid jet fuel. The jet fuel is provided by the Aviation Fuel and Chemical Airworthiness Certification Centre of CAAC, and the purity is larger than 99.9%. The purities of Ar and Kr are 99.99%. Helium is used as a driver gas in the SPST, and the purity is also 99.99%. Kr is used as an internal standard gas, and the system is calibrated using a 16 gas GC

Table 1. Pyrolysis Experimental Conditions in This Work

fuel	X_{Fuel} (mol %)	X_{Ar} (mol %)	X_{Kr} (mol %)	Avg. $P5$ (bar)	T_S range (K)	Avg. reaction time (ms)
DCL-derived jet fuel	0.05	99.45	0.5	4.8	1000−1700	1.65
	0.05	99.45	0.5	10.2	1060−1600	1.73
50/50 blend of DCL-derived and RP-3 jet fuels	0.05	99.45	0.5	5.1	1200−1750	1.73
	0.05	99.45	0.5	10.0	1080−1600	1.72
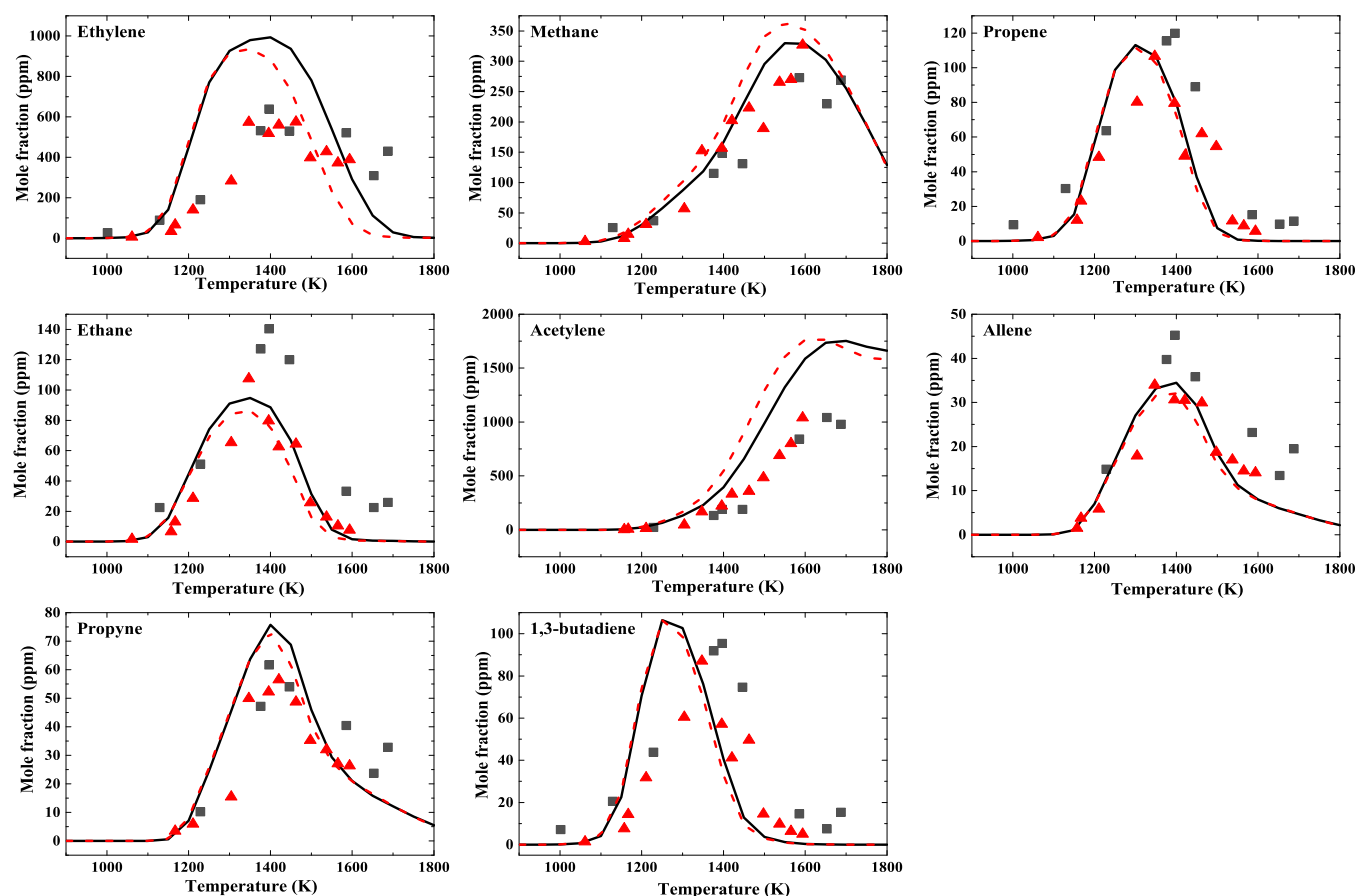
Figure 1. Species profiles as a function of temperature for 0.05% DCL jet fuel pyrolysis experiment at 5 and 10 bar together with kinetic modeling results. The black square symbols and the red triangle symbols represent the experimental results, while the solid and dashed lines represent the kinetic modeling results at 5 and 10 bar, respectively.

standard obtained from Beijing Haipubeifen gas Ltd China. The calibrated standard is used to calculate the concentration of the pyrolytic products, while the effective carbon number method is used to estimate the concentrations of species with no calibration standard. Table 1 lists the detailed experimental conditions, and the pyrolysis of 0.05% fuel diluted by Ar at about 5 and 10 bar is investigated. The high-diluted experimental condition is adopted to equalize the temperature because the jet fuel pyrolysis process is endothermic.

2.2. Experimental Uncertainty. The uncertainty in reflected temperatures is mainly induced by the uncertainty in the shock attenuation and non-ideal shock reflection from the interactions between the shock wave and the boundary layer. Using a standard error analysis procedure, the experimental temperature uncertainty is approximately ±2% based on the analysis by Petersen et al.[52] For the uncertainty of reaction time, several test experiments under different temperature conditions during the SPST debugging period are performed, and each experiment is repeated three times to measure the averaged reaction time as described previously.[44]

The results show that the uncertainty is less than 5% for all the experiments. Thus, the uncertainty in the reaction time is ±5%. For the measured species concentrations, the uncertainty in the calibrated species concentration using repetitive sampling of the standard gas is approximately ±10%, and the uncertainty in the estimated species concentration using the effective carbon number method is approximately ±20%.[53,54] It has been previously confirmed that the carbon balance mainly relies on the absorption in the mixture tank, shock tube, sampling tube, and the GC analysis method.[44,49] Previous studies using the current facilities reveal that the experimental system is accurate to describe the carbon balance within 15% uncertainty.[44,49] Therefore, the uncertainty of the measured properties in this work are generally consistent with the other related facilities and fuel pyrolysis studies.[49,53]

3. KINETIC MODELING

Kinetic modeling is performed by using Cantera software[55] assuming a closed homogeneous batch reactor at a constant volume. The residence/reaction time approach is adopted to
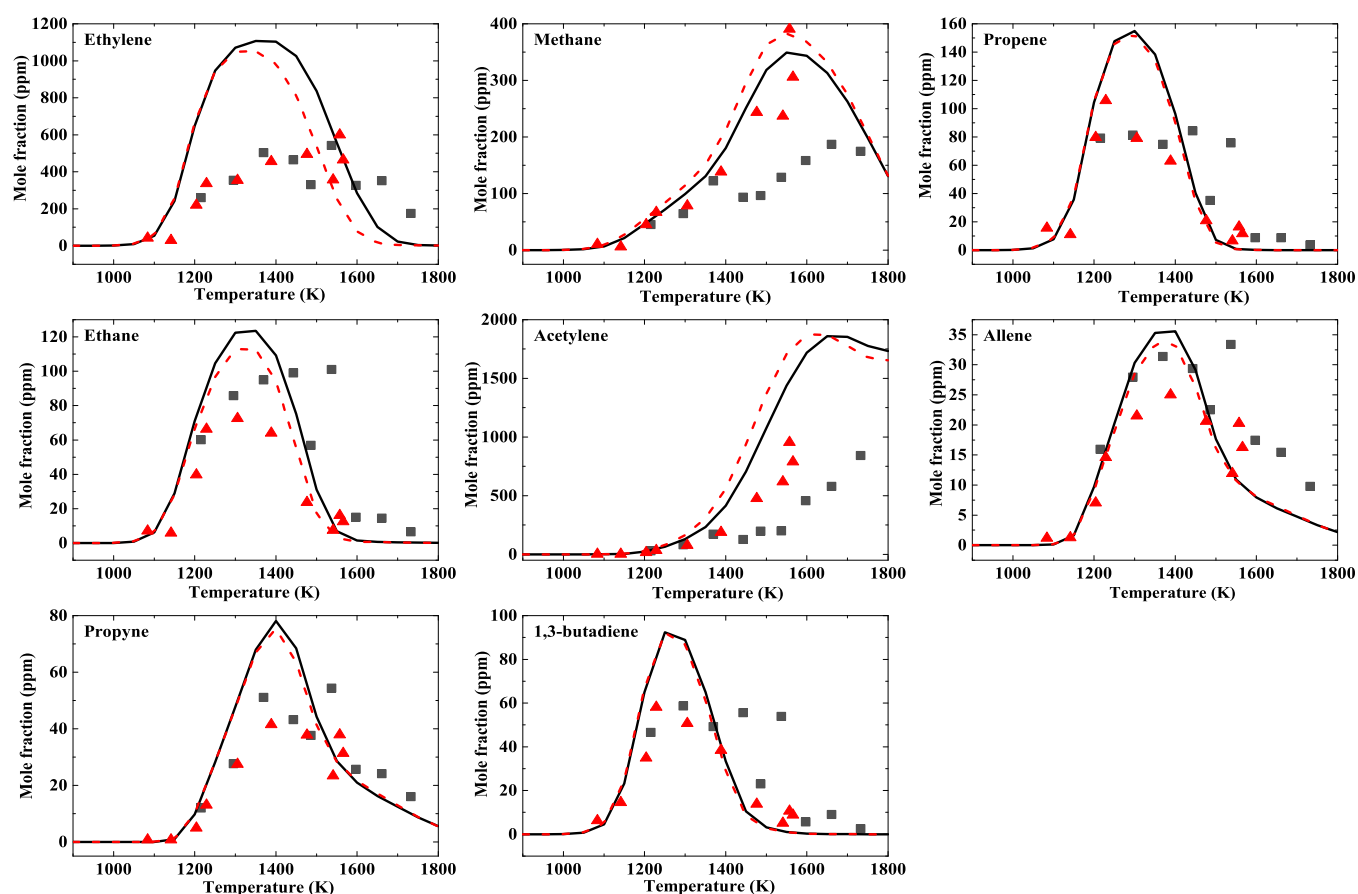
Figure 2. Species profiles as a function of temperature for 0.05% 50/50 blend jet fuel pyrolysis experiment at 5 and 10 bar together with kinetic modeling results. The black square symbols and the red triangle symbols represent the experimental results, while the solid and dashed lines represent the kinetic modeling results at 5 and 10 bar, respectively.

simulate the SPST results because it is simple, and the modeling results show no significant differences compared with the method based on the recorded pressure profiles.[56] The three-component surrogate model composed of 9% *n*-dodecane, 35% decalin, and 56% *n*-pentylcyclohexane in mole fraction is used to mimic the DCL-derived jet fuel, while the four-component surrogate model composed of 25.6% *n*-dodecane, 21.4% decalin, 49% *n*-pentylcyclohexane, and 4% *n*-propylbenzene is used for the 50/50 blend jet fuel.[35] The used surrogate models are based on previous detailed analysis on the measured physical properties, that is, density, H/C ratio, lower heating values, and molecular compositions of the real jet fuels.[35]

4. RESULTS AND DISCUSSION

4.1. Experimental and Modeling Results of the DCL Jet Fuel. Figure 1 shows the major species profiles as a function of temperature for 0.05% DCL-derived jet fuel pyrolysis experiment at pressures of 5 and 10 bar together with the kinetic modeling results. It can be seen that the kinetic modeling results using the detailed combustion mechanism can well capture most of the product distributions along the temperature profiles except that large deviations exist for ethylene. A similar reactivity trend was also found for the RP-3 jet fuel.[44] One of the major reasons may be due to the overemphasized importance of ethylene in the high pyrolysis process of large hydrocarbons from the successive *β*-scission reactions.[37] In addition, the current detailed mechanism taking

no account of the formation of large polycyclic aromatic hydrocarbons probably may further aggravate the production yield of ethylene since the formation of ethylene is the most important reaction path. The pressure change does not affect the variation tendencies of all the detected products; however, the absolute yields of the products are influenced. From Figure 1, the pressure mainly affects the yields for methane (CH_4) and ethane (C_2H_6), while the effect on propene (C_3H_6) and 1,3-butadiene are small because the formation of these alkene products is mainly through *β*-scission reactions, which is more affected by temperature. The product yields of CH_4 and C_2H_6 exhibit an opposite trend with pressure probably induced by the competition relationship between the two pressure-dependent reactions, that is, $CH_3 + H(+M) = CH_4(+M)$ and $CH_3 + CH_3(+M) = C_2H_6(+M)$ that controls the transformation between CH_4 and C_2H_6. Under high-temperature conditions, both the experimental and kinetic modeling results indicate that the pressure can also affect the product yields of ethylene, acetylene. One of the major reasons for this phenomenon can be attributed to the mutual transformation among ethane, ethylene, acetylene, and the other small molecules through high-temperature pressure-dependent pyrolysis reactions as revealed by Zeng et al. via rate-of-production (ROP) analysis.[44] To further check the pressure effect on the pyrolysis process, we perform additional kinetic modeling studies for the DCL-derived jet fuel at the same conditions with a pressure of 20 bar, and the results compared
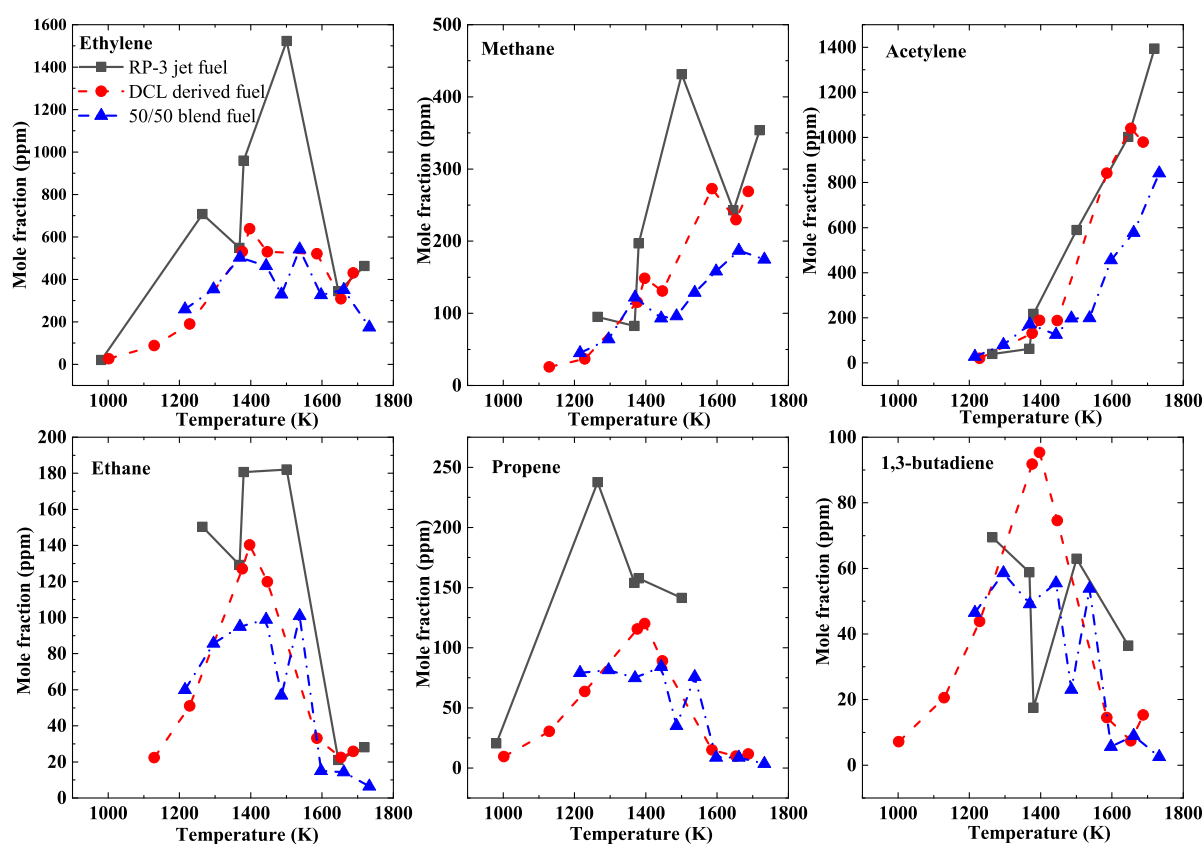
Figure 3. Comparisons of major species profiles for RP-3, DCL-derived jet fuel, and their 50/50 blend fuel with a concentration of 0.05% fuel diluted by Ar at 5 bar.

with 5 and 10 bar are provided as the Supporting Information. Similar reactivity can be observed as shown in Figure 1.

From the formation of major products, the pyrolysis process of the DCL-derived jet fuel under the studied conditions starts above 1100 K. C_2H_4 is the most abundant product for the studied two experimental conditions, which is the same as previously studied other jet fuels.[31,42,44,46,48] It is worth noting that the quantity of acetylene (C_2H_2) increases significantly as the temperature increases mainly due to the high-temperature cracking process of C_2H_4, 1,3-butadiene (C_4H_6), and so on.[44,57,58] CH_4 is another major product, and its yield gradually increases as the temperature increases. The yield of CH_4 reaches a maximum value around 1600 K for both the studied experimental conditions. However, the consumption of CH_4 is not detected under the studied temperatures due to the stable structure of CH_4. The variation tendencies as a function of temperature for C_3H_6, C_2H_6, allene (a-C_3H_4), propyne (p-C_3H_4), and C_4H_6 are similar, and the yields of these products first increase to maximum values as the temperature increases approximately from 1100 K to values around 1300−1400 K and then decrease significantly as the temperature continues to increase, indicating that these products are unstable at higher temperatures.

4.2. Experimental and Modeling Results of the 50/50 Blend Jet Fuel. The experimental and kinetic modeling results for pyrolysis of the 50/50 blend of DCL-derived and RP-3 jet fuels with a concentration of 0.05% diluted by Ar at 5 and 10 bar are explicitly shown in Figure 2. It can be seen that the variation tendencies of the pyrolysis products as a function of temperature are very similar compared with that of the DCL-derived jet fuel. The pressure effect on the pyrolysis

product distributions is also similar. For the 50/50 blend jet fuel, the yield of C_2H_4 is slightly lower than that of the DCL-derived jet fuel, which could correspond with a lower yield of C_2H_2. The pyrolysis product yields of C_3H_6 and C_2H_6 are close to that of the DCL-derived jet fuel, and small differences for a-C_3H_4 and (p-C_3H_4) are observed between the DCL-derived and blend jet fuels. It should be noted that the yield of C_4H_6 from the DCL-derived jet fuel is larger than that from the 50/50 blend fuel. The experimental observations are in accordance with previous ROP analysis during the ignition studies on RP-3 and DCL-derived jet fuels.[35]

4.3. Comparison with RP-3 Jet Fuel Pyrolysis. Figure 3 shows comparison of the major species profiles as a function of temperature for RP-3 fuel, DCL-derived jet fuel, and their 50/50 blend fuel with a concentration of 0.05% fuel diluted by Ar at 5 bar. However, it is worth noting that the absolute production yield is also affected by the real molecular formula, which is still unknown accurately. Hence, the major purpose of Figure 3 is to demonstrate the product distribution tendencies and the major product differences among the three jet fuels. It can be seen that the product yields of ethylene, methane, ethane, and propene from RP-3 pyrolysis are generally larger than that from the DCL-derived jet fuel and the 50/50 blend fuel. The product distributions of the blend fuel are much prone to exhibit similar tendencies as the DCL-derived jet fuel. Another notable difference is that the acetylene yield from the blend fuel is lower than the other two jet fuels, indicating that the blend jet fuel may have a low soot tendency because acetylene is the key precursor toward soot formation. Figure 3 also explicitly shows that the formation of 1,3-butadiene is larger than the other two fuels, probably due to the large
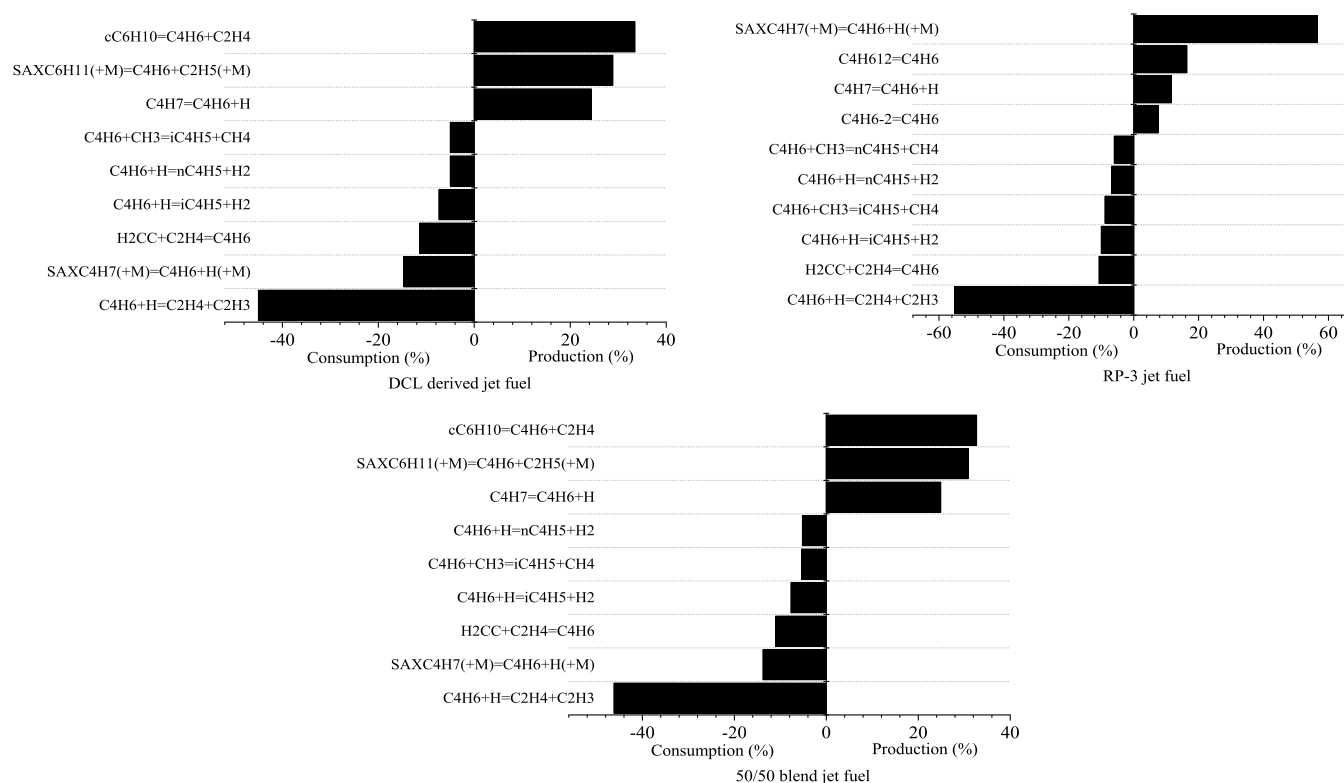
Figure 4. Relative contributions to the formation and consumption of 1,3-butadiene of the three jet fuels. The species cC6H10, SAXC6H11, and SAXC4H7 denotes cyclohexene, 1-hexen-3-yl, and 1-butene-3-yl, respectively. Other small molecules can be found in the detailed mechanism.

existence of two- and three-ring cycloalkane compounds since the decompositions of these compound tend to form larger alkene molecules.[28,29,59]

4.4. ROP and Sensitivity Analysis. ROP analysis has been conducted for 0.05% fuel concentration diluted by Ar at T = 1400 K and 10 bar with the reaction time at 1.70 ms for the three jet fuels, respectively. At the defined time, the jet fuels are in fact completely consumed, and the ROP analysis reveals the major reactions toward the formation of these pyrolysis products. The ROP analysis results for the three fuels reveal that the dominant reactions controlling the consumption and formation of the measured ethylene, methane, ethane, acetylene, and C_3 species including allene, propyne, and propene are directly related to the mutual transformation reactions involving C_0–C_3 species, which is the same as discussed in previous studies.[44] The major difference lies in the formation and consumption reactions of 1,3-butadiene, which is explicitly shown in Figure 4. The most important consumption reaction of 1,3-butadiene formed from the three jet fuels is the same, that is, C_4H_6 + H = C_2H_4 + C_2H_3. However, the dominant reactions related to the formation of 1,3-butadiene are different between RP-3 and DCL-derived jet fuels. The decomposition reaction of cyclohexene (cC_6H_{10}) that can be formed easily due to the large number of cycloalkanes in the DCL-derived jet fuel is the most important reaction for the formation of 1,3-butadiene. For RP-3, the consumption and formation reactions of 1,3-butadiene are mostly directly related to the C_2–C_4 species.

To further identify the differences of the chemical kinetics between RP-3 and DCL-derived jet fuels, sensitivity analysis is performed to identify important reactions that affect the yields of major products including ethylene, methane, acetylene, and 1,3-butadiene. The results are shown in Figure 5. It is shown

that the most sensitive reactions for methane are identical for the two fuels. However, slight differences are found for ethylene and acetylene. Specifically, the reaction C_4H_6 + H = C_2H_4 + C_2H_3 exhibits large sensitivity factors of acetylene and ethylene for the DCL-derived jet fuel due to the large production yield of C_4H_6. From Figure 5, it is obvious that the cycloalkane compounds existing in the DCL-derived jet fuel show significant effect on the formation of 1,3-butadiene. The abstraction from decalin and the decomposition reaction of the $C2H3cC6H11$ radical show large positive effect on the formation of 1,3-butadiene. The sensitivity analysis results are in good accordance with that from ROP analysis, and the results indicate that future work on the development of accurate surrogate models of DCL-derived jet fuel and the optimization of combustion mechanism of 1,3-butadiene[60,61] are critical in the study of combustion properties of the DCL-derived jet fuel.

5. CONCLUSIONS

The practical use and airworthiness certification process of the alternative jet fuel requires a basic understanding of its combustion properties. The pyrolysis of the alternative jet fuel is not only crucial in the development of their combustion kinetic models but also plays an important role in the development of advanced hypersonic aircrafts. For this purpose, this work reports the first experimental and kinetic modeling study on the pyrolysis of an alternative jet fuel from the DCL process and its 50/50 blend with the traditional RP-3 jet fuel. The SPST facility is employed to perform the pyrolysis experiments for 0.05% fuel concentration diluted in Ar at averaged pressures of 5.0 and 10.0 bar in the temperature range around 900−1800 K with the reaction time around 1.70 ms. The major products including ethylene, methane, acetylene,
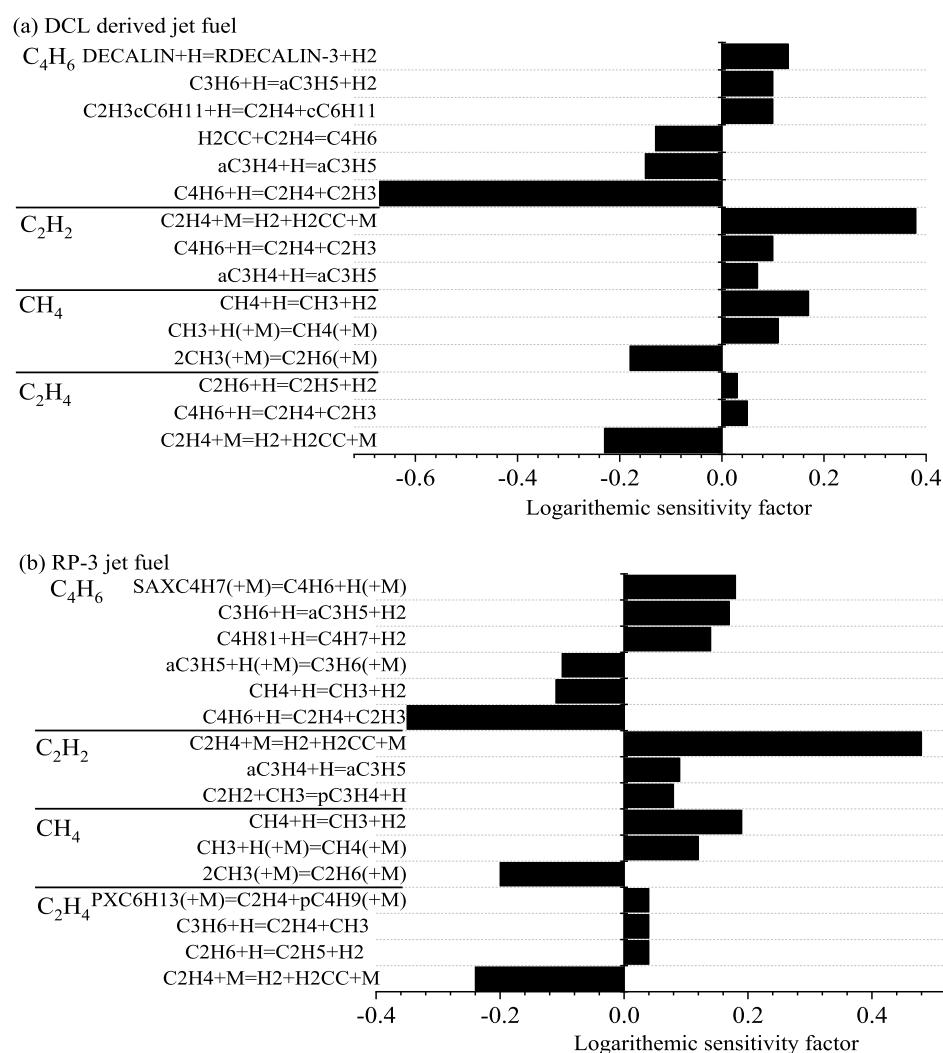
Figure 5. Important sensitive reactions for the major products including ethylene, methane, acetylene, and 1,3-butadiene from pyrolysis of DCL-derived jet fuel (a) and RP-3 jet fuels (b). Sensitivity analysis is performed for 0.05% fuel concentration at $T = 1400$ K and 10 bar with a reaction time of 1.70 ms. RDECALIN-3 and PXC6H13 denote 3-decalyl and 1-hexyl radicals, respectively.

propene, allene, propyne, and 1,3-butadiene are detected and quantified. Ethylene is the most abundant product, and acetylene significantly increases as the temperature increases. The pyrolysis characteristics of the DCL-derived jet fuel are systematically compared with that of the traditional RP-3 jet fuel. ROP analysis and sensitivity analysis are conducted to identify the important reactions related to the pyrolysis process of the three jet fuels. It is shown that the formation of 1,3-butadiene is the major difference between RP-3 and the DCL-derived jet fuel. Future work on the development of an accurate surrogate model to mimic the real molecular compositions of the DCL-derived jet fuel and optimization of the immature 1,3-butadiene combustion mechanism should be valuable for the study of DCL-derived jet fuels.

ASSOCIATED CONTENT

Ⓢ Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acsomega.1c02530.

Experimental results of jet fuel pyrolysis (PDF)

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Notes

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