Modelling research on oxidation of CH4 & C7H16 from small to large scale of temperature at high pressures

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Abstract. The change of CH4 oxidation cause by adding C7H16 from small to large scale of temperature at high pressures were precisely examined under laboratory condition with the temperatures span from 400K to 1200K and the pressures are regulated at 1atm and 10atm at a reaction container with the equivalence ratio of 0.5. The C7H16 proportion in the CH4/C7H16 mixed substances was varies from zero to one hundred percent. The molar ratios for CH4, C7H16, O2, CO, CO2, formaldehyde, ethene were investigated during several trial runs, and the mechanism is selected to establish the research results over the identical terms with the ideally stirred reaction simulation. It is revealed by the resultant that initial T for the oxidation of CH4 becomes smaller as the C7H16 proportion from the mixed substances increases, and a minor portion of C7H16 leads to a significant shift of the oxidation of CH4 from high to low temperature. The result also reflects that under the higher pressure, the CH4 oxidation is significantly promoted, and the oxidation of CH4 appears to have two reaction intervals which have different speed of reaction. According to the reaction pathway analysis at 100 atm, in lower temperature, the CH4 oxidation is enhanced by adding C7H16.

1. Introduction
Natural gas and oxygenated hydrocarbon fuels derived from biomass have become the efficient substituted fuels, because of the high performance on the price and environmental impact contrast to traditional fuel [1-20]. Due to the high proportion of H to C, Natural Gas is supposed to dramatically decrease the CO2 emissions. Moreover, Natural Gas possesses a larger #octane than conventional fuel, and this indicates it is easy to achieve a bigger compression ratio and more efficient thermal reaction inside the engine [3-6]. Regrettably, because of the unpromising reaction rate of CH4 in smaller T, it is challenging to activate natural gas by compressing it in the machines. In order to conquer this trouble, the Natural Gas–Diesel Dual-Fuel engines are established [7, 10-11]. In this model, Natural Gas is activated by a minor portion of diesel and the activation and combusting procedures will be influenced by the Diesel, and this leads to an effect on the activation performance and emissions behaviours of the machines. As a result, it is significant to do research on how the reactions of Natural Gas is influenced by adding more Diesel into the reaction, and this will help us to design and optimize better and more efficient Dual-Fuel engine.

Both of Diesel and Natural Gas are complicated mixtures consist of various substances, causing it challenging to operate the scientific researches for the combustion fuels. Therefore, it is applicable to use surrogate fuel simulation to study the chemical reaction for the complicated mixtures [20-22]. While the majority of natural gas is CH4, C7H16 is regarded as surrogate of diesel due to the likewise low-temperature activation behaviour and cetane numbers. Consequently, in the researches, the CH4/C7H16...
mixture is chosen to be the surrogate simulation of natural gas–diesel dual-fuel to interpret the combination of diesel and natural gas from low to high temperature.

As a stable substance, CH4 is formed because of the large C-H bonds energy in molecular formation, yet C7H16 displays larger reaction rate at lower T by the low-temperature-chemistry [23-27]. The variant reaction behaviour among CH4 and C7H16 and the significant non-linearity of the reaction procedure conduct into bigger challenge at related research, and consequently, just a small amount of information about the impact of adding C7H16 to CH4 is provided in the available resources. Aggarwal Et Al. [28] mathematically researched the activation features for the CH4/C7H16 mixed substances, and figured out that the delayed activation of the CH4/C7H16 mixed substances could be significantly lowered by C7H16, indicating that the activation behaviour of the substance was basically influenced by the oxidation reaction of C7H16. Li Et Al. [29] conducted a scientific experiment on Laminar Burning Speed and Markstein Lengths of premixed CH4/C7H16 mixed substances inside a combusting container, whose outcome revealed that flame instabilities and Laminar Burning Speed of the mixed substances are sensitive to the C7H16 portion less than twenty five percent. Furthermore, Liang Et Al. [30] from the crew recorded the activation delay of CH4/C7H16 mixed substances at various CH4 portion and different starting temperatures through a Shock Tube setting, and the contrast among the experimental and mathematical units of activation delay of the mixed substances are finished, by applying the reacting theories in the modelling of the 0-dimensional Consistent-Volume adiabatic activation procedures of the mixtures was activated. Nevertheless, the substances information of CH4 oxidating reaction with adding up C7H16 are barely covered, and the kinetic impact of C7H16 on the oxidating reaction of CH4 is not researched detailly either.

As a result, the purpose of the presented research is discovering the oxidation behaviour of CH4/C7H16 mixture from small to large scale of temperatures and from small to large scale of pressures. Throughout this experiment, the oxidation of CH4/C7H16 is set at 0.5 equivalent ratio, in the Atmospheric Jet-Stirred Reactor, and is recorded among the temperatures from 400 to 1200K. The pressure is regulated on 1atm and 10atm. The C7H16 portion from the CH4/C7H16 substances varies from zero to one hundred percent. The molar proportion of methane, n-heptane, oxygen, carbon monoxide, carbon dioxide, formaldehyde, and Ethene are detected in the presented research. Moreover, the reaction pathway interpretation of the CH4/ C7H16 mixed substances as well as the sensitivity interpretation of the molar proportion of CH4 are displayed in the experimental environment in order to study the reinforcement of CH4 oxidation by adding C7H16 content.

2. Simulation
A specific scientific mechanism of C7H16 suggested by Zhang Et Al. [31] is used for the simulation, and that is early mentioned in the paper. Every experiment was established inside the ideally stirred reaction container with “chemkin-pro” program applying a transitional solver [32], and the outcomes were contrasted at the following simulation conditions as shown in the table.

| Mixture | Methane (%) | n-Heptane (%) | Oxygen (%) | Argon (%) | Nitrogen (%) | Flow speed (mL/min) | Temperature (K) |
|---------|-------------|---------------|------------|-----------|--------------|---------------------|-----------------|
| M0      | 1.0         | 0.0           | 4.0        | 2.0       | 93.0         | 1800                | 400-1200        |
| M10     | 0.9         | 0.1           | 5.8        | 2.0       | 91.2         | 1800                | 400-1200        |
| M50     | 0.5         | 0.5           | 13.0       | 2.0       | 84.0         | 1800                | 400-1200        |
| M100    | 0.0         | 0.5           | 11.0       | 2.0       | 86.5         | 1800                | 400-1200        |
3. Experiment Outcome and Interpretation

3.1. Substances temperature variation
The molar proportion of CH4, nC7H16, CO, CO2, O2, C2H4 and CH2O throughout the oxidation of CH4, C7H16, and CH4/C7H16 were detected by employing the experiment devices introduced above, and the outcomes of the contrast between different experiment conditions were shown in Figure 1. As shown in Figure 1, this model is able to estimate the molar proportion of essential substances in the oxidation at various C7H16 content proportion efficiently.
In contrast, under the high pressure (10atm), the onset temperature of CH4 oxidation at M10 (720K) is lower than at 1atm M10 (900K), indicating the CH4 oxidation is promoted. In addition, the C7H16 addition does not have a significant impact on the promotion of CH4 oxidation compared to the 1atm condition, because the onset temperatures of reaction are 800K, 790K, 770K respectively when the amount of C7H16 from the reactant increases. Observed from the graph, the oxidation of CH4 has two reaction intervals at 10atm condition, as the molar proportion of CH4 slowly lowers down at the beginning, its reduction becomes faster in the following interval. Regarding C7H16, the efficiency of low-temperature-chemistry and high-temperature-chemistry is significantly promoted, and the difference between them is reduced. For CO and CO₂, the appearance of high temperature chemistry moves towards the direction of lower temperature. In addition, it is observed that CO and CO₂ are
produced in the interval of 500-700K under M10 condition, whereas no CO and CO$_2$ is produced under M0 condition. Since CH$_4$ does not have low temperature oxidation, the production of CO and CO$_2$ during 500-700K is mainly due to the low-temperature-oxidation of C$_7$H$_{16}$. Under low pressure, the difference among low-temperature-chemistry and high-temperature-chemistry was significant for CH$_3$O and C$_2$H$_4$. Nevertheless, there is no apparent distinguish among low-temperature-chemistry and high-temperature-chemistry under high pressure, and only one peak occurs on the graph. Observation from the graph of O$_2$ under 10atm indicates that onset temperature is slightly reduced in M0 and M10 condition compared to 1atm condition.

3.2. Reaction pathway interpretation
To better explain the process for oxidation of CH$_4$ with adding C$_7$H$_{16}$, the reaction pathway analysis for the mixed substances at the C$_7$H$_{16}$ content of 10 percent were conducted under the experiment environment, as displayed in Figure 2.
Figure 2. (a-c) Reaction pathway analysis for CH4 in the reaction with adding ten percent C7H16 at 800 K, 10atm and 0.5 equivalence ratio, and C7H16 in the mixed substances with 10% C7H16 addition at 550K and 750K, 10atm and 0.5 equivalence ratio.

The reaction path analysis for CH4 at the C7H16 content of 10% are conducted under the experiment environment of 10atm at the temperatures of 800K, and the reaction path way interpretation for C7H16 at the C7H16 content of 10 percent are also simulated under the experiment environment of 10atm at the temperatures of 550K, 750K, respectively, as shown in Figure 2.

With regard to the CH4/C7H16 mixture at C7H16 proportion of 10% at 800K, CH4 was mostly transferred to CH3 radicals by the H-abstractions at the start of the reactions, and the CH4 reactions with OH through the reaction CH4 + OH ⇌ CH3 + H2O made the most significant impact to the CH4 consume, accounting for 90.10%. Three channels for the conversion of CH3 were detected. The majority of CH3 reacts with O2 to form CH3O2, and is transferred into CH3O2 later, and 14.00% of CH3 was oxidized by oxygen to compose CH3O straightforward. Then, the formed CH3O are oxidized by O2 to form CH2O, which completely experience the H abstraction with Hydrogen, Oxygen, and Hydroxide radicals, and results in HCO which then is transferred into Carbon Monoxide and Carbon Dioxide as the final production from methane oxidation. The remaining CH3 mostly reacts with HO2 and HOCHO to compose CH4.

Under the temperature of 550K, the C7H16 oxidation starts with the fuel particles completely proceeding the hydrogen abstractions and yielding C7H15 in 4 kinds of isomer, mainly through the radicals of hydroxide in the process C7H15 + H2O ⇌ nC7H16 + OH. After that, the substances react with O2 to form RO2 (e.g. C7H15 + 4O2, C7H15 + 4O2), The products RO2 experience the isomerization to form QOOH (e.g. C7H154O2 + 2nC7H14OOH4-2). Due to the low temperature, the products then experience two types of reactions. The chain branching reaction with the addition of O2 produces O2QOOH (e.g. C7H14OOH4-2O2), which finally ends up with OQ'O + OH + OH. In addition, the remaining QOOH is transferred into QO + OH through chain propagating reaction.

Under the pressure of 10atm, 750K is already in the high temperature chemistry temperature range, which is because the low temperature chemistry has shifted to the left and happens at lower temperature
due to the pressure. As the temperature is modified to 750K, the reaction pathway for C7H16 is slightly different from that at 500K. Similarly, C7H16 is resolved into isomers of C7H15. Moreover, transferred from C7H14OOH2-5, C7H14O2-5 does not transfer to any substance but is decomposed into C3H6.

3.3. Sensitivity interpretation

The interpretation of the sensitivity of the molar proportion of CH4 at different C7H16 ratio is conducted at 800 K along with the sensitivity of C7H16 at various C7H16 proportion at 550K and 750K, under the pressure of 10atm and the 0.5 equivalence ratio to discover the most significant procedure impacting CH4 oxidation and C7H16, as displayed in Figure 3. The sensitivity ratio is determined to be

\[ S = \frac{\partial \ln c_j}{\partial \ln k_i} \]

where \( c_j \) is the molar proportion, and \( k_i \) is the specific rate ratio. A sensitivity ratio number that is bigger than zero demonstrates that the reaction prohibits reaction rate and vice versa.

(a) C7H16 sensitivity at 550K.

(b) C7H16 sensitivity at 750K.

(c) CH4 sensitivity at 800K.
Figure 3. Sensitivity interpretation of the molar proportion of C7H16 at 550K and 750K and CH4 at 800 K, 10atm and at 0.5 equivalence ratio.

It is seen from the graphs (a) and (b) that due to the CH4 addition, the reaction of CH4 with OH (CH4 + OH $\leftrightarrow$ CH3 + H2O) is important at both 500K and 750K. In addition, the RO2 decomposition reaction (C5H13+2O2 $\leftrightarrow$ C5H12+2 + HO2) is also significant at graph (b), even though 750K is the intermediate temperature. Compared to the lower pressure condition, the concentration of HO2 is relatively high, so the sensitivity of the reaction HO2 + HO2 $\leftrightarrow$ H2O2 + O2 becomes more significant at high pressure.

According to graph (c), because of the influence of C7H16, the reaction system has produced a large amount of CH2O and HO2, and those intermediates products impacts the oxidation of CH4 through reactions such as CH2O + OH $\leftrightarrow$ HCO + H2O and H2O2 + OH $\leftrightarrow$ H2O + HO2. Therefore, the extra production of CH2O, H2O and H2O2 leads to the CH4 oxidation at a lower temperature.

4. Conclusions
The impact of adding C7H16 on the CH4 and C7H16 mutual oxidation at 400-1200 K, 10atm and at 0.5 equivalence ratio was mathematically and experimentally tested with the C7H16 increment from 0 to 100%. The conclusion of the presented research is summarized below:

1. When the proportion of C7H16 in the CH4/C7H16 mixed substances becomes bigger, the beginning temperature for the CH4 oxidation decreases and it is observed that there is a nonlinear relationship between the C7H16 portion and the beginning temperature. The observation is that a minor content of C7H16 makes a dramatic promotion on CH4 oxidation, while adding more C7H16 makes minor kinetic reinforcement effect. Under the high pressure, the beginning temperature of the oxidation of CH4 becomes lower, indicating that CH4 oxidation is promoted. Regarding C7H16, the efficiency of low-temperature-chemistry and high-temperature-chemistry is significantly promoted under high pressure.

2. The reaction pathway interpretation of the CH4/C7H16 substances demonstrates that the addition of C7H16 has a vital impact on oxidizing CH4. By increasing the C7H16 content, the H-abstraction of CH4 by hydroxide and CH4 oxidation by HO2 are promoted. After that, the beginning kinetic reinforcement reactions of CH4 oxidation by adding C7H16 content were identified, and the rates of reactions appeared to become faster at low temperature.

3. Based on the outcomes results of the sensitivity explanation and the net rates of reaction of the most vital reactions, it is seen that due to the CH4 addition, the RO2 decomposition reaction is significant at intermediate temperature (750K). Compared to the lower pressure condition, the sensitivity of the reaction HO2 + HO2 $\leftrightarrow$ H2O2 + O2 becomes more significant at high pressure. Moreover, because of the influence of C7H16, the reaction system has produced a large amount of intermediate products, which impact the oxidation of CH4 to appear at a lower temperature.

Therefore, the presented research demonstrates the ability of C7H16 addition promoted CH4 combustion in diesel and marine engines.

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