Study of low and high temperature oxidation of n-pentane at supercritical conditions in a jet stirred reactor

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Abstract. The intermediate/low and high temperature oxidation of n-pentane from atmospheric pressure to supercritical pressures (1-100 atm) was studied by using Chemkin, a commercial software. A recently developed n-pentane model was used to predict the temperature evolutions of major and intermediate species, like n-pentane, O₂, CO, CO₂, CH₂O, C₂H₄, CH₃CHO at varied pressure and temperature conditions. It is found that as the environmental pressure increases, the difference between high temperature oxidation and low temperature oxidation becomes less obvious because the negative temperature coefficient (NTC) is decreasing (at 10 atm and 100 atm, high temperature oxidation occurs right after low temperature oxidation). At supercritical pressures, the high temperature oxidation is governed by the branching reactions of RO₂, and the addition reaction of QOOH with oxygen dominates the reaction paths at both low and high temperature oxidations because the addition reaction between QOOH and oxygen is still more important than the decomposition reaction of QOOH at high temperature and 100 atm. According to the pathway analysis and sensitivity analysis, the branching reactions of RO₂ are dominating at both low and intermediate to high temperatures.

1. Introduction
Recently, research field on chemical kinetics modeling of hydrocarbon oxidation has been moved toward the fuel with larger molecules such as n-pentane, butane, n-octane and isooctane [1-22]. Internal combustion engines have been widely in service as both industrial and infrastructural purposes. However, the efficiency of this kind of engines has been a problem troubling the engineers for a long time. The complicated internal combustion engines which are using complex fuels, such as gas turbines and pistons, could run into a problem named engine knock. The main cause of this problem is the low temperature property of the fuel. During the reaction, the activity will drop back down when it reaches a certain temperature [21].

Kinetics reaction mechanisms are complex and require a large amount of calculations. They also do not occur within only one reaction path, instead, a lot of branches are going through in the reactions. Calculations are supposed to be extremely complicated. As a solution for further understanding of the oxidation properties of these fuels mentioned above, computer programs can simulate the process of the reaction with an unapproachable speed by humans. And, the results would be purely theoretical without any unpredictable factors influencing the results.

As one of the smallest alkanes which have rich low temperature reactivity, n-pentane has been investigated in experiments and simulations at both low and high temperatures [21-26]. A recent n-pentane model [23] shows a good agreement with experimental results. However, the low and high...
temperature chemistry of n-pentane has not been studied at high pressure to supercritical pressure conditions in both experiments and simulations. It is noted that supercritical combustion has a tremendous potential in gas turbine and air-breathing engines due to its high fuel reactivity, high combustion efficiency, and ultra-lean flammability.

Therefore, the goal of the present study is to understand the low and high temperature oxidation of n-pentane from atmospheric pressure to supercritical pressures (1-100 atm) by using Chemkin software. A recently developed n-pentane model [21] was used to predict the temperature evolutions of major and intermediate species, like n-pentane, O₂, CO, CO₂, CH₃O, C₂H₄, CH₃CHO at varied pressure and temperature conditions.

2. Modelling
A recent literature model recently proposed by Bugler et al. [21] was used to carry on the present simulations and kinetic analysis. All simulations were performed in the perfectly stirred reactor model within CHEMKIN-PRO software employing the transient solver [27], and the numerical results were compared at the following simulation conditions in table 1.

| Case | Equivalence ratio | n-C₅H₁₂ (%) | O₂ (%) | N₂ (%) | Residence time (s) | Temperature range (K) | Pressure(atm) |
|------|-------------------|-------------|--------|--------|---------------------|-----------------------|--------------|
| 1    | 0.5               | 1           | 16     | 83     | 1                   | 350-1050             | 1            |
| 2    | 0.5               | 1           | 16     | 83     | 1                   | 350-1050             | 10           |
| 3    | 0.5               | 1           | 16     | 83     | 1                   | 350-1050             | 100          |

3. Results

![Mole Fraction of NC₅H₁₂](image.png)

(a)

![Mole Fraction of O₂](image.png)

(b)

![Mole Fraction of CO](image.png)

(b)

![Mole Fraction of CO₂](image.png)

(d)
In the reaction, n-pentane \((n-C_5H_{12})\) is the reactant and it has a very active low temperature oxidation property. As shown in figure 1, when the environmental pressure increases, the influence of low temperature chemical property of \(n-C_5H_{12}\) increases. Under the pressure of 1 atm, the oxidation reaction starts to occur at 550K, and the reactivity keeps increasing until the temperature reaches somewhere around 640K. From there the reactivity starts to drop back and finally almost stops oxidation at about 720-730K and remains not reacting due to its low temperature oxidation property until the temperature reaches about 800K. Above 800K, high temperature oxidation starts to occur, and the n-pentane continues to be obviously consumed until it is all gone. But the difference between low and high temperature oxidation weakens because the negative temperature coefficient (NTC) is decreasing (at 10 atm and 100 atm, high temperature oxidation occurs right after low temperature oxidation). Also, as the environmental pressure increases, the initial temperature of high temperature oxidation is lowered.

Formaldehyde \((CH_2O)\) and ethylene \((C_2H_4)\) are two of the main products of low temperature oxidation of \(n-C_5H_{12}\) and they have very similar temperature evolution profile. It was interesting to notice that the typical \(CH_2O\) and \(C_2H_4\) low and high temperature oxidation peaks merged to a single peak at supercritical pressures. According to the graph, in high pressure environments, as the environmental pressure increases, the peak area widens but the maximum value of mole fraction decreased. However, we can see that at the normal pressure (1 atm), when the temperature reached 1000K, the mole fraction of \(CH_2O\) drops down to somewhere near zero. It is because of the decomposition of formaldehyde into aldehyde \((HCO)\) in high temperature. Furthermore, the decomposition continues, producing carbon monoxide \((CO)\) and then carbon dioxide \((CO_2)\). Also, acetaldehyde \((CH_3CHO)\) has similar evolution profile with \(CH_2O\).

As the environmental pressure increases, the difference between high temperature oxidation and low temperature oxidation becomes less obvious. Corresponding to the graph of formaldehyde, under normal pressure (1 atm), the amount of carbon monoxide starts to increase at the time of decomposition of formaldehyde. CO starts to decrease after 850 - 900K due to its combining to
Oxygen (O$_2$) generating CO$_2$. CO$_2$ has very similar properties to CO. Corresponding to the decreasing of CO at the moment, CO$_2$ starts to increase in amount after 850-900K.

According to the pathway analysis at 675K in figure 2 (a), n-pentane reacts with hydroxy and produces three different isomers of n-pentane radical (C$_5$H$_{11}^*$). 23.6% of n-pentane becomes C$_5$H$_{11}$-1, 52.4% becomes C$_5$H$_{11}$-2 and 19.9% goes to C$_5$H$_{11}$-3. And these isomers combine with oxygen,
producing C3H11O2 (known as RO2 in the general reaction trend). In a relatively low temperature environment (675K, for example), the main consumption reaction of C3H11O2 is the isomerization reaction to form C3H10OOH by 90.4% (known as QOOH in the general reaction trend). Under low temperature and high pressure, QOOH mainly combines with oxygen, producing O2QOOH. And the other decomposition path of QOOH is negligible. As a result, we can say that pressure can obviously promote low temperature oxidation.

\[
\begin{align*}
\text{C}_2\text{H}_10\text{OOH}_2-4\text{O}_2 & \rightarrow \text{C}_3\text{H}_11\text{OOH} - 1 - 4, \\
\text{C}_2\text{H}_10\text{OOH}_2-4\text{O}_2 + \text{O}_2 & \rightarrow \text{C}_3\text{H}_10\text{OOH}2-4, \\
\text{C}_2\text{H}_10\text{OOH}_2-4\text{O}_2 + \text{H}_2\text{O} & \rightarrow \text{C}_3\text{H}_10\text{OOH}2-4, \\
\text{C}_2\text{H}_10\text{OOH}_2-4\text{O}_2 + \text{O} & \rightarrow \text{C}_3\text{H}_10\text{OOH}2-4, \\
\text{C}_2\text{H}_10\text{OOH}_2-4\text{O}_2 + \text{C}_2\text{H}_10\text{OOH}_2-4 & \rightarrow \text{C}_3\text{H}_10\text{OOH}2-4, \\
\text{C}_2\text{H}_10\text{OOH}_2-4\text{O}_2 + \text{O}_2 & \rightarrow \text{C}_3\text{H}_10\text{OOH}2-4, \\
\text{C}_2\text{H}_10\text{OOH}_2-4\text{O}_2 + \text{H}_2\text{O} & \rightarrow \text{C}_3\text{H}_10\text{OOH}2-4, \\
\text{C}_2\text{H}_10\text{OOH}_2-4\text{O}_2 + \text{O} & \rightarrow \text{C}_3\text{H}_10\text{OOH}2-4, \\
\text{C}_2\text{H}_10\text{OOH}_2-4\text{O}_2 + \text{C}_2\text{H}_10\text{OOH}_2-4 & \rightarrow \text{C}_3\text{H}_10\text{OOH}2-4.
\end{align*}
\]

Figure 3. (a) (b) Sensitivity analysis of n-pentane at 675 and 825K, respectively, at 100 atm.

Moving onto the reaction paths under higher temperature (825K) in figure 2 (b), same as 625K environment, n-pentane reacts to produce three isomers of its radical, 27.6% becomes C3H11-1, 48.9% becomes C3H11-2 and 18% goes to C3H11-3. It is known that the typical pathway under high temperature is C3H11O2 = HO2 + C3H10, however, at 100 atm, the major consumption reaction of C3H11O2 becomes the isomerization reaction to form C2H10OOH (by 65.2%), which is different from
the typical high temperature oxidation at lower pressures. In addition, the addition reaction between QOOH and oxygen is still more important than the decomposition reaction of QOOH at high temperature and 100 atm. Therefore, at supercritical pressures, the high temperature oxidation is governed by the branching reactions of RO2, and the addition reaction of QOOH with oxygen dominates the reaction paths at both low and high temperature oxidations. It explains why the peaks of intermediate species (such as CH2O, C2H4, CH2CHO, etc.) at low and high temperatures merge to one single peak at supercritical pressures.

In figure 3 (a) at 675K, according to the sensitivity analysis of the mole fraction of n-pentane and the results of the net reaction rate, the reaction C5H11O2-1=><C5H10OOH1-4 is the most sensitive reaction. Other isomerization reactions, such as C5H11O2-2=<><C5H10OOH2-5 and C5H11O2-2=<><C5H10OOH2-4, are also very significant. Meanwhile, the reactions C5H11O2-2=<><C5H10-2+HO2, C5H11O2-2=<><C5H10-1+HO2 and C5H11O2-3=<><C5H10-2+HO2 are decomposition reactions that are the significant promoting ones that will yield HO2, and thus enhance the overall reactivity. Therefore, at low temperature, the branching reactions of RO2 dominate reaction paths. In addition, the H abstraction reaction of n-pentane with OH and HO2 are also impotent. In figure 3(b) at 825K, similarly according to the sensitivity analysis of the mole fraction of n-pentane and the results of the net reaction rate, decomposition reactions, such as C5H11O2-2=<><C5H10-1+HO2, C5H11O2-2=<><C5H10-2+HO2, C5H11O2-3=<><C5H10-2+HO2 and C5H11O2-1=<><C5H10-1+HO2, take the most significant role. The isomerization reactions of RO2, which are generally important at low temperatures, are still sensitive at intermediate temperatures at 100 atm. Therefore, at 825K, the branching reaction of RO2 will dominate the reaction paths. The importance of RO2 branching reactions in both low and intermediate temperatures in the sensitivity analysis is corresponding with the pathway analysis at the same temperatures.

4. Conclusion
The present study is to understand the low and high temperature oxidation of n-pentane from atmospheric pressure to supercritical pressures (1-100 atm) by using Chemkin software. A recently developed n-pentane model [23] was used to predict the temperature evolutions of major and intermediate species, like n-pentane, O2, CO, CO2, CH2O, C2H4, CH2CHO at varied pressure and temperature conditions. As the environmental pressure increases, the difference between high temperature oxidation and low temperature oxidation becomes less obvious because the negative temperature coefficient (NTC) is decreasing (at 10 atm and 100 atm, high temperature oxidation occurs right after low temperature oxidation). At supercritical pressures, the high temperature oxidation is governed by the branching reactions of RO2, and the addition reaction of QOOH with oxygen dominates the reaction paths at both low and high temperature oxidations because the addition reaction between QOOH and oxygen is still more important than the decomposition reaction of QOOH at high temperature and 100 atm. According to the pathway analysis and sensitivity analysis, the branching reactions of RO2 are dominating at both low and intermediate to high temperatures.

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