Mathematical modeling of the propane and propane-propylene cut thermal decomposition process

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Abstract. The article describes the mathematical modeling of the propane pyrolysis process. The developed model is a system of ordinary nonlinear differential equations (SONDE), which describes the changes in the concentrations of the components of the substances involved in the reaction over time. The computer implementation of the mathematical model is based on the MathWorks MATLAB programming environment. The program was used to search for the reaction optimal operating conditions: the temperature and the composition of the raw materials of the pyrolysis process.

1. Introduction
In the world, including Russia, there has been a tendency to increase demand in lower olefins, which are important components in the petrochemical industry. They are mainly obtained by pyrolysis, i.e. due to thermal decomposition of hydrocarbon compounds. The reaction products, ethylene and propylene, are used in the chemical industry to produce plastics, polyethylene and the production of many other substances.

2. Theoretical analysis
Currently, more than half of the raw materials processed are straight-run gasoline (54%) and gas oil (6%), the rest is gases from refineries and condensate fields (ethane - 29%, propane - 6%, butane - 5%) \cite{1-4}. Thus, due to the large reserves of natural gas, there is issue of involving more gases in the pyrolysis process, such as ethane, propane, butane, as well as their mixtures.

On Figure 1 are shown diagrams reflecting the structure of the raw material base for producing ethylene in the USA and Russia.

At the Institute of Catalysis named after G.K. Boreskov of Siberian Branch of Russian Academy of Sciences (SB of RAS) considers ways to create cost-effective processing technology for low productivity by controlling chemical pyrolysis reactions through additional generation of radicals in a reacting gas by laser radiation absorbed by the mixture of reagents \cite{5-8}. For this purpose, a flow-type reactor using microwave radiation was used. Microwave radiation allows for uniform heating throughout the substance bulk. As a result of the experiment with the use of the microwave radiation within the reactor, experimental data of the target products yield at different temperatures were
obtained [9-10]. Microwave radiation allowed to increase the selectivity of the process, due to the process began to take place at higher temperatures.

![Distribution diagram of raw material base for production of ethylene in the United States and Russia.](image)

**Figure 1.** The distribution diagram of the raw material base for the production of ethylene in the United States and Russia.

### 3. Methodology

At the initial stage in the study of the complex reactions mechanisms of thermal decomposition of propane and propane-propylene cut (PPC), chemical transformations without laser exposure are simulated. A compact 30-stage propane pyrolysis model developed by L.N. Nurislamova using sensitivity analysis methods was taken as the basis [11]. The 30-stage propane pyrolysis model is shown in Table 1.

| №  | Stage                                      | $A$, 1/sec OR sm$^3$/mol·sec | $E$, kJ/mol | $N$  |
|----|--------------------------------------------|-------------------------------|-------------|------|
| 1  | $C_3H_8 \rightarrow C_2H_2^* + CH_3^*$     | 2.78E+18                     | 376         | -1.8 |
| 2  | $C_2H_6 + CH_3^* \rightarrow C_3H_8$       | 2.83E+13                     | 0           | -0.5 |
| 3  | $C_2H_2^* \rightarrow C_2H_4 + H^*$        | 4.31E+12                     | 155         | 1.19 |
| 4  | $C_2H_4 + H^* \rightarrow C_2H_2^*$        | 4.09E+12                     | 4.15        | 1.49 |
| 5  | $C_3H_6 + CH_3^* \rightarrow CH_4 + n-C_3H_7^*$ | 2.98E+08                     | 29.93       | 3.65 |
| 6  | $C_3H_6 + CH_3^* \rightarrow CH_4 + iso-C_3H_7^*$ | 5.48E+08                     | 22.95       | 3.46 |
| 7  | $C_3H_6 + H^* \rightarrow H_2 + n-C_3H_7^*$ | 2.55E+12                     | 28.27       | 2.54 |
| 8  | $C_3H_6 + H^* \rightarrow H_2 + iso-C_3H_7^*$ | 1.13E+12                     | 18.71       | 2.4  |
| 9  | $n-C_3H_7^* \rightarrow C_3H_6 + CH_3^*$   | 1.2E+13                      | 126         | 0    |
| 10 | $iso-C_3H_7^* \rightarrow C_3H_6 + H^*$    | 1.6E+13                      | 150         | 0    |
| 11 | $n-C_3H_7^* \rightarrow C_3H_6 + H^*$     | 1.09E+13                     | 149         | 0.17 |
| 12 | $C_3H_6 + H^* \rightarrow n-C_3H_7^*$      | 1.3E+13                      | 13.64       | 0    |
| 13 | $C_3H_6 + C_3H_3^* \rightarrow C_3H_6 + n-C_3H_7^*$ | 9.7E+08                      | 38.25       | 3.65 |
| 14 | $C_3H_6 + C_3H_3^* \rightarrow C_2H_4 + iso-C_3H_7^*$ | 4.79E+10                     | 36.92       | 3.1  |
| 15 | $C_3H_6 + H^* \rightarrow H_2 + C_3H_3^*$  | 2.61E+11                     | 10.39       | 2.5  |
| 16 | $H_2 + C_3H_3^* \rightarrow C_3H_6 + H^*$  | 8.37E+10                     | 79.49       | 2.38 |
| 17 | $C_3H_6 + C_3H_3^* \rightarrow C_3H_6 + n-C_3H_7^*$ | 3.44E+10                     | 83.06       | 3.3  |
It is assumed that 17 substances including 10 individual components and 7 radicals participate in the pyrolysis process (Table 2). For convenience, the numbering of all components involved in the reaction has been adopted.

| Individual substances | Radicals |
|-----------------------|----------|
| $1 - C_4H_8.2 - C_2H_4.3 - CH_4.4 - H_2.5 - C_3H_6.6 - C_2H_6$ | $11 - C_2H_4.12 - CH_3.13 - H^*$. |
| $7 - C_4H_8.8 - C_2H_4.9 - C_3H_2.10 - C_4H_6$ | $14 - n - C_2H_3.15 - 13 - C_2H_3^*$. |
| $16 - C_2H_4.17 - C_2H_4^*$. | |

According to experimental data, a chemical reaction takes place in a closed system, without a change in volume. Such a system is adequately described by the law of acting masses in the form of a system of ordinary nonlinear differential equations defined by the Cauchy problem [12, 13].

$$\frac{dc_1}{dt} = -K_1 \cdot c_1 + K_2 \cdot c_{11} \cdot c_{12} - K_5 \cdot c_1 \cdot c_{12} - K_{4} \cdot c_1 \cdot c_{13} - K_8 \cdot c_1 \cdot c_{13} - K_1 \cdot c_1 \cdot c_{11}$$

$$\frac{dc_2}{dt} = K_4 \cdot c_{11} - K_4 \cdot c_2 \cdot c_{11} + K_9 \cdot c_{14} + K_14 \cdot c_1 \cdot c_{16} - K_4 \cdot c_1 \cdot c_{13} - K_{18} \cdot c_2 \cdot c_{12} + K_{19} \cdot c_3 \cdot c_{16}$$

$$\frac{dc_3}{dt} = K_3 \cdot c_1 \cdot c_{12} + K_2 \cdot c_1 \cdot c_{12} + K_{18} \cdot c_2 \cdot c_{12} - K_{19} \cdot c_3 \cdot c_{16} + K_{20} \cdot c_4 \cdot c_{12}$$

$$\frac{dc_4}{dt} = K_3 \cdot c_1 \cdot c_{15} + K_8 \cdot c_1 \cdot c_{13} + K_{15} \cdot c_5 \cdot c_{13} - K_6 \cdot c_4 \cdot c_{12} - K_{20} \cdot c_4 \cdot c_{12} + K_{25} \cdot c_6 \cdot c_{12}$$

$$\frac{dc_5}{dt} = K_{10} \cdot c_{15} + K_{11} \cdot c_{14} - K_{12} \cdot c_1 \cdot c_{15} - K_{15} \cdot c_5 \cdot c_{13} + K_{16} \cdot c_4 \cdot c_{17} + K_{17} \cdot c_1 \cdot c_{17} - K_{22} \cdot c_5 \cdot c_{11}$$

$$\frac{dc_6}{dt} = K_{13} \cdot c_1 \cdot c_{11} + K_{22} \cdot c_5 \cdot c_{11} - K_{25} \cdot c_6 \cdot c_{13} + K_{28} \cdot c_1 \cdot c_{12}$$

$$\frac{dc_7}{dt} = K_{15} \cdot c_1 \cdot c_{17} + K_{22} \cdot c_5 \cdot c_{17} - K_{25} \cdot c_6 \cdot c_{13} + K_{28} \cdot c_1 \cdot c_{12}$$
\[
\frac{dc_1}{dt} = K_{21} \cdot c_2 \cdot c_{16} - K_{23} \cdot c_1 - K_{24} \cdot c_7 \cdot c_{12}
\]
\[
\frac{dc_2}{dt} = K_{23} \cdot c_{71}
\]
\[
\frac{dc_6}{dt} = K_{26} \cdot c_{17}
\]
\[
\frac{dc_{10}}{dt} = K_{29} \cdot c_{15} \cdot c_{12} - K_{27} \cdot c_{10}
\]
\[
\frac{dc_{11}}{dt} = K_1 \cdot c_1 - K_2 \cdot c_{11} \cdot c_{12} - K_3 \cdot c_{11} - K_4 \cdot c_2 \cdot c_{15} - K_{16} \cdot c_1 \cdot c_{12} - K_9 \cdot c_1 \cdot c_{12} + K_9 \cdot c_4 \cdot c_{12} + K_{19} \cdot c_3 \cdot c_{16} - K_{20} \cdot c_4 \cdot c_{12} + K_{20} \cdot c_1 \cdot c_{12} + K_{27} \cdot c_{10} - K_{28} \cdot c_{12} \cdot c_{12} - K_{29} \cdot c_{12} \cdot c_{17} - K_{30} \cdot c_{12} \cdot c_{16}
\]
\[
\frac{dc_{12}}{dt} = K_3 \cdot c_{11} - K_4 \cdot c_2 \cdot c_{15} - K_3 \cdot c_1 \cdot c_{13} + K_6 \cdot c_1 \cdot c_{15} - K_4 \cdot c_1 \cdot c_{13} + K_{10} \cdot c_{15} + K_{11} \cdot c_4 - K_{12} \cdot c_5 \cdot c_{13} - K_{15} \cdot c_5 \cdot c_{13} + K_{16} \cdot c_4 \cdot c_{12} + K_{20} \cdot c_4 \cdot c_{12} + K_{23} \cdot c_7 - K_{25} \cdot c_6 \cdot c_{13}
\]
\[
\frac{dc_{13}}{dt} = K_5 \cdot c_1 \cdot c_{11} + K_7 \cdot c_1 \cdot c_{13} - K_9 \cdot c_{14} - K_{11} \cdot c_4 + K_{12} \cdot c_5 + c_{13} + K_{13} \cdot c_4 \cdot c_{11} + K_{17} \cdot c_1 \cdot c_{17}
\]
\[
\frac{dc_{14}}{dt} = K_3 \cdot c_4 \cdot c_{17} + K_{20} \cdot c_4 \cdot c_{12} + K_{23} \cdot c_7 - K_{25} \cdot c_6 \cdot c_{13}
\]
\[
\frac{dc_{15}}{dt} = K_3 \cdot c_4 \cdot c_{17} = K_{15} \cdot c_4 \cdot c_{15} - K_{16} \cdot c_4 \cdot c_{17} - K_{17} \cdot c_1 \cdot c_{17} + K_{22} \cdot c_4 \cdot c_{11} - K_{26} \cdot c_{17} + K_{27} \cdot c_{10} - K_{29} \cdot c_{12} \cdot c_{17}
\]
\[
K = A \cdot \left(\frac{T}{298}\right)^{T/E} e^{-\frac{E}{RT}}
\]
where \(A\) is the preexponential factor, \(sm^3/(mol\cdot sec)\); \(E\) is activation energy, \(kJ/mol\); \(R\) is the universal gas constant, \(kJ/mol\cdot K\); \(T\) is temperature, \(K\); \(n\) is the temperature exponent, experimentally determined parameter.

### 4. Experimental part

Based on the resulting system of differential equations describing the pyrolysis process, a program in the MATLAB environment was written, allowing calculating the change in the concentration of components over time (1), as well as the rate constants of each reaction (2).

The purpose of this work was to establish the optimum temperature of the process, at which the maximum yield of ethylene was observed. The system of differential equations using the Gear method was solved [14, 15].

According to the plant data, three variants of the composition of the initial reagents were considered:

1) PPC with a large amount of propylene - 75% and with a propane content of 25%;
2) PPC with equal content of propylene and propane.

Based on the developed mathematical model, a computational experiment in the temperature range of 750 – 900 °C with a step of 50 °C was carried out. This interval and temperature variation step was adopted based on the technological capabilities of industrial reactors.
5. Results and Conclusion

Figure 2 shows the change curve in the yield of ethylene with an increase in the 100% propane pyrolysis temperature from 800 to 950 °C. It can be seen the rise in temperature contributes to an increase in ethylene yield. It was found that the process above 950 °C leads to a decrease in the ethylene yield due to side reactions with the formation of undesirable components. This is confirmed by the hydrogen yield curve, shown on Figure 3, which is an undesirable component that contributes to the ethylene hydrogenation reactions.

**Figure 2.** The ethylene yield curve in dependence on propane pyrolysis temperature increase.

**Figure 3.** The hydrogen yield in dependence on 100%-containing propane pyrolysis over time with temperature increase.

**Figure 4.** The ethylene yield curve in dependence on the PPC pyrolysis temperature increase.
Figure 5. The hydrogen yield curve in dependence on 100%-containing propane pyrolysis over time with temperature increase.

When conducting a computational experiment with a PPC having the same amount of propylene and propane, the results presented on Figures 4 and 5 were obtained. It was also established that an increase in temperature contributes to an increase in the ethylene yield.

The results of the experiment allows determining the best composition of raw materials. The highest yield of the target product is achieved by pyrolysis of propane-propylene cut. The highest yield of ethylene is 44% during the pyrolysis of PPC containing the same amount of propane and propylene at a temperature of 950 °C.

The results obtained allow us to conclude that the pyrolysis of gaseous propanes and propylene lead to a relatively high yield of valuable ethylene.

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