Kinetics of thermal conversion of gaseous products of polypropylene pyrolysis using several detailed kinetic mechanisms

A M Tereza¹, G L Agafonov¹, E K Anderzhanov¹, A S Betev¹, S P Medvedev¹, S V Khomik¹, G N Mokhin¹ and V N Mikhalkin²

¹Semenov Federal Research Center of Chemical Physics, Russian Academy of Sciences, Moscow, 119991, Russia
²Academy of State Fire Service, EMERCOM of Russia, Moscow, 129366, Russia

E-mail: tereza@chph.ras.ru

Abstract. Thermal conversion (TC) of polypropylene pyrolysis gaseous products was studied numerically using three detailed kinetic mechanisms (DKMs) for the initial temperatures $T_0$ ranging from 700 K to 1300 K and the initial pressure of 1 atm. Numerical simulations showed that all DKMs predicted similar qualitative behavior of the reacting mixture, however, they gave significantly different rates of the increase of the mole fractions of CH₄ and H₂ along with simultaneous decrease in C₂⁺ hydrocarbons. The temperature increase in course of TC process was also found to be predicted differently by the three DKMs. Its characteristics depended on the initial temperature, some calculations showed smooth increase while in others explosion-like regimes were observed. The conversion products, along with methane and hydrogen, contained aromatic compounds C₆⁺. Various DKMs gave significantly different TC characteristic times.

1. Introduction

Polypropylene (PP) is present in substantial amounts in industrial and domestic waste and its efficient utilization is an open and important problem [1–3]. The utilization process should be safe for the environment and energy efficient both, but it is also potentially economically beneficial if chemicals produced by the conversion are suitable for further use in industry [4–6]. One of the promising methods of PP utilization is the pyrolysis of plastic waste that produces a variety of gas phase products [7–10]. The exact composition of gas phase depends on the specific method of pyrolysis, and by choosing the optimal conversion conditions energy rich chemicals can be obtained [11]. However the development of the optimal approaches is hindered by a number of factors, including the presence of other elements besides H and C, the large variety of methods and conditions of pyrolysis, and difficulties of monitoring and control of the overall process of the decomposition of initial species and their subsequent transformation [8, 12, 13]. The kinetics of the chemical reactions of the pyrolysis products of different waste and their further conversion after the pyrolysis is also poorly understood [14–16].
In our previous work [16] we studied numerically the TC of gas phase products of PP pyrolysis (hereafter referred to as 'mixture') with several DKMs limited to the lower hydrocarbons up to C3. This approach has been widely used for modeling simplified chemical kinetics and determining the principal pathways of reactions [17, 18]. This simplification was based on the assessment of the mass fraction of C4+ hydrocarbons in the gas phase products of the pyrolysis of various fuels and mixtures, considered to be less than 10%. Moreover, it was difficult to identify precisely all C4+ isomers [19, 20]. However, in our recent work [21] we found that it was important to take into account also C4+ components, that affected both the overall mode of the TC process and the specific outcome of H2. Therefore we decided to analyze the efficiency of different DKMs with more species for the numerical simulation of the mixture TC in terms of the composition of the products and the thermal behavior of the process.

The objective of this work is to study numerically the TC process of a mixture containing major gas phase components recorded at the exit of a pyrolytic reactor with special attention to the components not taken into account previously. The results of this study are useful both for deeper understanding of all the details of chemical reactions in the pyrolytic mixtures and for the development of optimal technologies of the utilization of various wastes in terms of their efficiency and compliance with environmental standards.

2. Numerical simulation

The source data for our study were taken from [22], where pure granulated PP was thermally decomposed and the composition of the gas phase was measured experimentally. The initial composition of the mixture supplied by a gas generator was analyzed chromatographically. The temperature in the sampling zone was about 650 K. C4+ species were identified in [22] mainly as isobutene, while a small fraction of C5+ species — as 2-Me-Buten-1.

| H2 | CH4 | C2H4 | C2H6 | C3H6 | C3H8 | iC4H8 | iC4H10 |
|----|-----|------|------|------|------|-------|--------|
| 5.3| 22.6| 12.3 | 14.3 | 32.8 | 3.2  | 8.9   | 0.6    |

All numerical simulations used same initial mixture composition as per Table. We studied the TC process at different initial temperatures using CHEMKIN III software [23]. The initial temperature was T0 and the initial pressure was 1 atm, volume V assumed to be constant. Time integration was limited to no more than one hour. Only gas phase reactions were considered, thus condensation and soot formation were neglected. The process was assumed to be adiabatic (no heat losses) and heterogeneous reactions were absent.

We chose three DKMs that contained reaction pathways not only for C4 (such as iC4H8), but also for C5 species (such as iC5H10), namely: [24] (version 1412), [25], and [26] (version nbch-mech-062920 developed).

3. Results and discussion

Figure 1 shows the mole fractions of the species and temperature versus time calculated with three DKMs [24-26] at T0 = 900 K. All three DKMs predict that [CH4] and [H2] increase (square brackets denote mole fractions), while C4+ hydrocarbons are depleted. All three DKMs agree that the temperature grows monotonically in the TC process. [H2] grows monotonically, while [CH4] reaches its maximum and then decreases. DKMs [25, 26] predict initial slow growth rate for [CH4] with subsequent acceleration to its maximum value (Fig. 1b, and 1c). DKM [24] predicts smooth monotonic growth of [CH4] (Fig. 1a). Temperature curve follows the pattern of [CH4] curve for all three DKMs. Both temperature and [CH4] reach their respective maximum values almost simultaneously, that is t1, time to the maximum temperature, is almost equal to tc, time to the maximum mole fraction. However, the results of Fig. 1 clearly indicate that the values of tc differ
significantly for three DKMs, therefore, these DKMs have some differences with regards to the TC process modeling.

Contrary to methane, hydrogen mole fraction has no maximum. DKM [24] predicts that both \([\text{H}_2]\) and \([\text{CH}_4]\) increase monotonically, with an S-shaped inflection point, until they reach saturation. The maximum \([\text{H}_2]\) increase rate (corresponding to the inflection point of the curve at the graph) is at \(t_c\) for \([\text{CH}_4]\). According to DKM [25], \([\text{H}_2]\) grows slowly and then sharply accelerates symbasically with \([\text{CH}_4]\) (Fig. 1b). Finally, DKM [25] predicts that \([\text{H}_2]\) slowly decreases at the beginning, but then sharply increases (similar to DKM [25]) and reaches its saturation (Fig. 1c).

**Figure 1.** Species mole fractions vs time for the initial temperature \(T_0 = 900\) K at \(P_0 = 1\) atm for the mixture presented in Table. Black circles represent the temperature. (a) – DKM [24], (b) – DKM [25], (c) – DKM [26].

All three DKMs predict initial slow increase of the \([\text{C}_2\text{H}_4]\) mole fraction. After reaching its maximum value, it drops sharply to less than 1 %. DKMs [25, 26] predict that \(t_c\) for \([\text{C}_2\text{H}_4]\) is very close to \(t_c\) for \([\text{CH}_4]\), however it decreases a little bit earlier (Fig. 1b, and 1c). DKM [24] predicts that \(t_c\) for \([\text{C}_2\text{H}_4]\) is two times lower than \(t_c\) for \([\text{CH}_4]\) (Fig. 1a). Mole fractions of other \([\text{C}_2\text{H}_+\text{ hydrocarbons}]\) present in the initial mixture either tend to zero monotonically or remain almost constant and then drop sharply to almost zero at the moment of \(t_c\) for \([\text{CH}_4]\).

For \(T_0 = 650\) K the shapes of the curves for the temperature, \([\text{CH}_4]\) and \([\text{H}_2]\) according to DKM [24] become similar to their respective shapes for DKMs [25], [26] calculated for higher \(T_0 = 900\) K (Fig. 1b, 1c). On the other hand, the shapes of the curves for DKMs [25], [26] calculated for even higher \(T_0 \geq 1000\) K are similar to the shapes for DKM [24] but for lower values of \(T_0\) (Fig. 1a). Therefore all three DKMs describe the kinetics of the mixture TC in a similar way at least qualitatively. Even though the shapes look similar, numerical values are different.

The increase of \(T_0\) also affects the behavior of heat release. Fig. 2 presents the dependency of temperature vs time in course of TC for \(T_0 = 1000\) K and 1100 K. At the initial stage of the TC the
temperature drop is observed, the higher $T_0$, the more noticeable the decrease. Among the three DKMs, DKM [25] predicts the smallest temperature decrease, while DKM [26] — the largest one, occurring already for $T_0 = 800$ K before the temperature starts to rise and becomes higher than $T_0$ (Fig. 1c). After the temperature reaches its maximum, the mixture cooling rate is different for the three DKMs. DKMs [25] and [26] predict insignificant cooling of the mixture after the maximum. However, DKM [24] shows more pronounced decrease of temperature at the last stage of the TC, eventually to the values slightly higher than $T_0$. The initial decrease of temperature can be attributed to the endothermic reactions of dissociation of propylene, the main component of the initial mixture [27]. Taking into account this initial decrease, the net heat release according to DKM [24] becomes low.

Figure 2. Temperature vs time during the TC for initial temperature $T_0 = 900$ K (solid lines) and $T_0 = 1000$ K (dash lines) at $P_0 = 1$ atm. Black lines correspond to DKM [24], blue lines — DKM [25], red lines — DKM [26].

At the final stage of the TC process [CH$_4$] and [H$_2$] tend to their stationary levels, while C$_2$+ species virtually disappear (Fig. 1). The temperature reaches its maximum. Therefore, $t_T$ can be considered as the characteristic time or the overall duration of the whole TC process. Fig. 3 shows the value of $t_T$ versus initial temperature for three DKMs. For high initial temperatures the duration of TC is almost same for DKMs [24] and [26], but for $T_0 < 900$ K the predictions of the two mechanisms differ greatly, by the order of magnitude. The duration $t_T$ calculated by DKM [25] is about three times lower than that by DKM [26].

Fig. 1 demonstrates that the amount of C atoms in methane accumulated in course of TC is lower than its original amount in C$_2$+ hydrocarbons that are consumed. According to all three DKMs [24-26], the excessive C atoms form a number of aromatic species C$_6$+. However, each DKM predicts different its own variety of species. Only benzene C$_6$H$_6$ is present in all three DKMs. Other species are as follows. For DKM [24], they are: coronulene C$_{20}$H$_{10}$, dimethylbenzanthracene C$_{20}$H$_{16}$, and triphenylethylene C$_{20}$H$_{16}$. For DKM [25] — 1,1-bicyclopropyl C$_8$H$_{10}$ and naphthalene C$_{10}$H$_8$. For DKM [26] — toluene C$_{7}$H$_8$, naphthalene C$_{10}$H$_8$, and phenanthrene C$_{14}$H$_{10}$. Such discrepancy of the results of different DKMs limits us to making but qualitative conclusions with regards to the formation of aromatic species C$_6$+. Because both "light", methane and hydrogen, and "heavy" aromatic compounds C$_6$+ are formed in the TC process, they can be separated by cooling, and C$_6$+ hydrocarbons can be transformed into acetylene and hydrogen as the products of further TC. Further TC of C$_6$+ hydrocarbons can allow to obtain acetylene and hydrogen as products as it occurs in the case of benzene [28]. For this, it will be necessary to significantly increase the temperature in order to reach
those TC conditions where temperature exceeds 2000 K, that leads to the level of the soot particles yield decreasing [29, 30]

Comparison of our calculations using three DKMs [24-26] with other mechanisms limited to C_3+ and lower hydrocarbons proves that the TC process in the absence of oxygen is strongly affected by the presence of C_4+ hydrocarbons. Both the features of the conversion of species and the thermal behavior are different, therefore, more comprehensive DKMs are to be used for better understanding and modeling of the TC.

4. Conclusions

Our numerical simulations of the thermal conversion of the studied mixtures show that all three studied DKMs give qualitatively similar results. However DKMs differ significantly with regards to the time scale of the stages of TC. All calculations show the increase of CH_4 and H_2 and the decrease of higher hydrocarbons (C_2+) initially present in the mixture. The CH_4 concentration reaches its maximum and then drops, while the H_2 concentration rises monotonically to its final value. The temperature is highest at the end of the active stage of TC, when higher hydrocarbons (C_2+) are totally depleted.

Calculations taking into account C_4+ hydrocarbons show more precise results and differ significantly from the calculations using simplified schemes limited to only C_3 and lower hydrocarbons. With the increase of the initial temperature of the mixture the heat release of TC becomes lower due to the endothermic reaction of PP dissociation at the earlier stages of the conversion. In the TC process C_2+ hydrocarbons are depleted, while some aromatic C_6+ hydrocarbons are formed.

Acknowledgments

This study was performed under the Fundamental Research Program of the Russian Academy of Sciences for 2013–2021 at Semenov Federal Research Center for Chemical Physics, Russian Academy of Sciences, topic no. 49.23 (CITIS state registration no. AAAA-A18-118031590088-8) and topic no. 44.8 (CITIS state registration no. AAAA-A21-121011990037-8).
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