Thermodynamic analysis of the plasma-chemical conversion of polymers into synthesis gas

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Abstract. The composition of the gas formed during the decomposition of polyethylene and polyethylene terephthalate in steam-water plasma was calculated. The database includes thermodynamic information of 32 individual substances that can be formed from carbon, hydrogen and oxygen atoms. The calculated temperature range was chosen from 1000 to 2250 K. The conditions for achieving optimal regimes for the conversion of polymers into synthesis gas was analyzed.

1. Introduction
The world production of polymer materials is increasing every year. In the end, all polymer products are converted into consumer waste and pollute the environment. One of the ways of processing waste polymeric materials is plasma-chemical conversion to synthesis gas. The most effective version of the energy carrier for plasma technologies, including plasma-chemical conversion of polymer waste into synthesis gas, is steam-water plasma [1-11]. It is possible to note other positive effects accompanying the practical application of steam-water plasma [12-15].

Determination of the composition of gases formed during the plasma-chemical decomposition of polymers is extremely difficult. In the first approximation, neglecting of the kinetics of plasma-chemical reactions, one can perform a calculation for the case of thermodynamic equilibrium. Despite the conventionality, such a calculation is widely used in the analysis of high-temperature processes of conversion of hydrocarbon raw materials [16]. In this work, a technique developed for inorganic raw materials was used [17]. The validity of this approach is based on the fact that the current structure firstly, is high-temperature; secondly, homogeneous, consisting only of gas components. Condensed phases, i.e. solid or liquid substances are not considered. At the same time, in the composition of which initial substances (organic or inorganic) there were chemical elements from which individual components are formed in the gas phase, which has no fundamental importance.

2. Mathematical model and numerical calculation
When phase and chemical equilibria are established in any closed system, entropy increases. If internal heat sources operate in the system, the entropy increases until the sources are fully exhaustion. Thus, in the equilibrium state, the entropy of a closed system is always maximal. This is the principle of maximum entropy, on which the technique is based [17].

It should be noted that the system becomes equilibrium only if mechanical and energy equilibria with the environment are achieved, i.e. only if the heat is not supplied from the outside and is not
diverted, and the system does not perform mechanical work. Under these conditions, the internal energy is kept constant, and it can not be changed by any phase or chemical transformations within the system itself. Thus, in the absence of internal heat sources for the equilibrium state

\[ dS = 0. \]  

(1)

This condition (1) is the main one in compiling a mathematical model for the maximum entropy principle.

\[ S = \sum_{i=1}^{k} \left[ S_i^i(T) - R \ln \left( \frac{RT}{V} n_i \right) \right] n_i. \]  

(2)

The extremum of this function (2) is found at observance:
- the law of conservation of mass of chemical elements

\[ \sum_{i=1}^{k} v_{ji} n_i - b_j = 0, \]  

(3)
- electroneutrality of the mixture

\[ \sum_{i=1}^{k} v_{ei} n_i = 0, \]  

(4)
- constancy of volume

\[ V = \text{const}, \]  

(5)
- the invariance of internal energy

\[ \sum_{i=1}^{k} U_i(T) n_i = \text{const} \]  

(6)

and also under the condition that the steam-gas mixture is described by the equation of state of an ideal gas

\[ pV - RT \sum_{i=1}^{k} n_i = 0. \]  

(7)

Here \( k \) – is the number of components of the mixture; \( S_i^i(T) \) – the entropy of the \( i \) component at the standard pressure \( p_0 = 0.1013 \) MPa; \( R \) – universal gas constant; \( n_i \) – specific molar content of \( i \) component (mol/kg); \( b_j \) – molar content of the \( j \) of the chemical element in 1 kg of working fluid (mol/kg); \( v_{ji} \) – number of atoms \( j \) of chemical element in \( I \) component (stoichiometric coefficient); \( v_{ei} \) – the multiplicity of ionization of \( i \) component; \( U_i(T) \) – molar internal energy of \( i \)-components.

For numerical calculations the program given in the appendix to [17] was used with small changes. The thermodynamic properties of individual substances are taken from fundamental reference books [18-19]. The database includes thermodynamic information for the following substances: atomic oxygen \( O \), positive ion of atomic oxygen \( O^+ \), negative ion of atomic oxygen \( O^- \), molecular oxygen \( O_2 \), positive ion of molecular oxygen \( O_2^+ \), negative ion of molecular oxygen \( O_2^- \), ozone \( O_3 \), atomic hydrogen \( H \), positive ion of atomic hydrogen \( H^+ \), negative ion of atomic hydrogen \( H^- \), molecular hydrogen \( H_2 \), positive ion of molecular hydrogen \( H_2^+ \), positive hydrogen ion \( H_3^+ \), hydroxyl \( OH \), positive hydroxyl ion \( OH^- \), negative hydroxyl ion \( OH^- \), hydrogen dioxide \( HO_2 \), negative ion of hydrogen dioxide \( HO_2^- \), steam-water \( H_2O \), positive ion of steam-water \( H_2O^+ \), hydrogen peroxide \( H_2O_2 \), positive ion of trihydrogen oxide \( H_3O^+ \), condensed carbon \( C \), carbon in gas phase \( C \), positive carbon ion \( C^+ \), negative carbon ion \( C^- \), carbon monoxide \( CO \), positive carbon monoxide \( CO^+ \), carbon dioxide \( CO_2 \), positive carbon dioxide \( CO_2^+ \), dicarbene oxide \( C_2O \), methine \( CH \), methylene \( CH_2 \), methyl \( CH_3 \), positive carbon dioxide \( CO_2^+ \), dicarbene oxide \( C_2O \), methine \( CH \), methylene \( CH_2 \), methyl \( CH_3 \),
methane \( CH_4 \), acetylene \( C_2H_2 \), ethylene \( C_2H_4 \), ethyl \( C_3H_5 \), ethane \( C_2H_6 \), formyl \( HCO \), formaldehyde \( H_2CO \) and methanol \( CH_3OH \).

3. Results of calculations and their analysis

In the actual process, the products of the plasma-chemical reactions pass through the hardening chamber, where the steam-water condenses. In the hardening chamber there is also the formation of molecular gases from atomic gases and the combination of hydroxyl groups into molecules:

\[
O + O = O_2; \quad (8) \\
H + H = H_2; \quad (9) \\
2OH + 2OH = 2H_2O + O_2. \quad (10)
\]

Due to these processes (8) - (10), the molar composition of the steam-gas mixture significantly changes. At the exit, the "dry" gas consists only of non-condensed phases of individual substances.

The "dry" gas contains saturated steam-water and electrolysis gases: hydrogen and oxygen. As shown estimated calculations by Faraday's law, at a discharge current of \( I = 10 \) A the maximum yield of electrolysis gases does not exceed 0.3 l/min. According to the data presented in [20], the volumetric content of saturated steam at \( T = 300 \) K is \( \sim 3.5 \) %. Thus, for most regimes of the plasmochemical process in the volume of the "dry" gas, steam-water and electrolysis gases are relatively small, and in the design model they can be neglected. In this paper, it is so done.

![Figure 1](image)

**Figure 1.** The volumetric content of the main components with the composition of synthesis gas. Raw material: (a) - polyethylene (PE); (b) - PET. The ratio of "raw materials: steam-water": solid lines - 1: 5; the dotted lines are – 1:100. 1 – \( H_2 \); 2 – \( CO \); 3 – \( CO_2 \).

In the case of polyethylene terephthalate (PET) raw materials, the mass content of the chemical element \( C \) in the original composition is reduced by 10%. This accounts for the formation of a solid residue, which mainly consists of carbon [5, 6].
In the figure 1 shows the graphs based on the results of calculations. As can be seen, the composition of gas synthesis varies considerably with increasing temperature. In the case of raw materials from PE, a more significant change in the composition of the synthesis gas takes place. Apparently, such a regularity is due to the fact that PE in steam-water plasma is almost completely converted to gas [5, 6].

4. Conclusions
1. With a decrease in the molar content of carbon in the original composition of the working fluid (PE + steam or PET + steam), the volumetric yield of the "dry" gas is reduced.
2. To obtain final products of plasma-chemical decomposition only in the gas phase, the amount of steam-water should be in excess relative to the amount of raw materials from the polymers, and in the case of PET this excess should be higher.
3. With increasing excess steam, yield of $CO_2$ and $H_2$ increases, and the volumetric content of CO is reduced.
4. To reduce the ballast gas of $CO_2$ and increase the useful component of CO it is necessary to raise the temperature in the reaction zone. The optimum range is 1500 $\pm$ 2000 K.

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