The material balance of process of plasma-chemical conversion of polymer wastes into synthesis gas

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Abstract. The process of conversion of polymer wastes in the flow of water-steam plasma which are created by the liquid electrodes plasma generators was experimentally studied. The material balance was calculated. The regularities of the participating of hydrogen and oxygen which contained in the water-steam plasma, in formation of chemical compounds in the final products were revealed.

1. Introduction
It is known that the water-steam plasma is the most attractive option of energy carrier of plasma-chemical processes, including plasma waste treatment processes [1, 2]. It provides a number of advantages. Water-steam plasma does not contain the ballast components (such as nitrogen in the composition of the air plasma). Therefore, the thermal efficiency of energy carrier becomes substantially higher. Formation mechanisms of harmful oxides such as oxides of nitrogen and sulfur are suppressed in the water-steam plasma. This ensures the most favourable environmental conditions. The water-steam plasma is enriching synthesis gas by hydrogen due the carbon oxidation of raw materials by water-steam: \( C + H_2O \rightarrow H_2 + CO \). This increases the amount of the final product. There are other positive effects that accompany the practical application of water-steam plasma which are may be noted [3, 4].

Currently arc plasma is used mainly in the processes of recycling [5]. Energy carrier plasma is generated by blowing out the arc discharge using various gases, including water-steam. However, in practice, there are additional technical difficulties at using water-steam in arc plasma torches. In real industrial settings in the first place required an efficient steam generator for obtaining superheated steam. The protection of the refractory electrodes from direct exposure to water-steam needed. And also to take steps to prevent moisture condensation on the surfaces of the conductive elements.

Applying of liquid electrodes plasma generators based on gas discharge with liquid-electrolyte cathode eliminates the above-mentioned negative factors. The plasma stream is forming from electrolytic fumes. Evaporation of electrolyte takes place under the influence of heat coming from the gas discharge.

2. Experiment
In this work, the liquid-cathode plasma generator was used, allowing to create a plasma flow of electrolyte vapor at temperature up to 1800°C and the mass flow rate of up to 3.0 g/s [6, 7]. Previously used pieces of plastic film (PE material) and bottles made of polyethyleneterephthalate (PET material) were as raw material. Processing of raw materials was in a sequence: 1) thermal decomposition in the
environment of water-steam at a temperature of 770-800 K; 2) conversion to synthesis gas in plasma-
chemical reactor in the temperature range 1670-1720 K. Some results of experimental studies
published in [8-13].

The adopted simplifications and source data. In the calculations the balance of the main chemical
elements that make up the reagents was considered. These are: carbon C, hydrogen H and oxygen O.
Material balance implies equality of the masses of individual chemical elements in the primary
components (polymer, raw materials and water) and in the end product in all physical phases: solid,
liquid and gaseous.

The limited options which available direct measurement, do not allow the calculation material
balance in full, taking into account changes of the chemical composition of a reacting mixture during
the whole duration of the process. In this regard, for the calculations selected the steadiest regime,
which in time is located at a sufficient distance from the initial and final stages of the process.
However, even in this case there is an uncertainty in the numerical values of several process
parameters. In particular, remain unknown the exact values of the mass arrival rate of raw material
components (chemical elements C, H and O) in the plasma chemical reactor, where are formed the
final products of plasma chemical reactions. Therefore, the calculation of the material balance is only
possible under certain simplifying assumptions. As such, in this work, we adopted the following
simplifications.

1. Thermal decomposition of the raw material occurs uniformly. The source reagents are received
in the plasma-chemical reactor with mass velocity \( \dot{m} = k \cdot m / \Delta t \). Here \( k \) – is the coefficient taking into
account the formation of solid residue; \( m \) – is the mass of raw material; \( \Delta t \) – is the period of time
during which there is an intensive thermal decomposition of raw materials of volatile components.

2. The mass rate of the chemical elements C, H and O in a plasma-chemical reactor is constant and
their ratio to each other is equal to the atomic mass ratio in a conditional formula of raw materials. For
PE-raw materials (conditional formula \( C_2H_4 \)); \( \dot{m}_C : \dot{m}_H = 24 : 4 \).

It is necessary to consider when compiling a conditional formula of the raw material
polyethyleneterephthalate about forming of a solid residue of carbon. In the plasma-chemical reactor
is received only the volatile components of the thermal decomposition of polyethyleneterephthalate.
Therefore, in the composition of the reagents that acts in plasma-chemical reactor, C atoms less than
the original feedstock. This leads to changes in the stoichiometric coefficients in the chemical formula.
In the experiments, the mass of the solid residue amounted to an average of 10\% from the initial
weight of raw materials. With this in mind, conditional formula is written as \( C_5H_6O_4 \). Thus, for PET-
raw materials: \( \dot{m}_C : \dot{m}_H : \dot{m}_O = 100.8 : 8 : 64 \).

3. Mass rate of \( \dot{m}_C, \dot{m}_H \) and \( \dot{m}_O \) make up a part from proportional of the atomic masses of the
corresponding chemical elements. For polyethylene: \( \dot{m}_C = (24/28)\dot{m} \) and \( \dot{m}_H = (4/28)\dot{m} \). For
polyethyleneterephthalate: \( \dot{m}_C = (100.8/172.8)\dot{m} \), and \( \dot{m}_H = (8/172.8)\dot{m} \) and \( \dot{m}_O = (64/172.8)\dot{m} \).

4. The compositions of the gas phase of end-products and a liquid condensation are unchanged for
the entire duration of the process. These compounds such as those obtained in the analyses of gas and
liquid samples.

5. Mass and volumetric rates of formation of individual substances in the final product are constant,
mass rates of appearance of chemical elements C, H and O in the gas phase (\( \dot{m}_{gC}, \dot{m}_{gH} \) и \( \dot{m}_{gO} \)) are
constant respectively.

| Table 1. Phase composition of the final products. |
|---------------------------------------------|
| **Raw material** | **Solid phase** | **Liquid phase** | **Gas** |
| PE-raw | 0 % | 0.6 % | 99.4 % |
| PET-raw | 10 % | 2.8 % | 87.2 % |

The following are the calculations on the example of two experiments, characteristic for PE-raw
and PET-raw materials. In tables 1 - 3 shows the results of chemical analyses of the final products, as
well as the calculated values of mass rates \( \dot{m}_{gC}, \dot{m}_{gH} \) и \( \dot{m}_{gO} \).
From table 1 follows that the end products in plasma-chemical process are mainly generated in the gas phase. Significant amounts hydrogen, carbon oxides and methane are formed (tables 3 and 4). In small amounts are present acetylene, ethylene and benzene. Thus in the total mass of gaseous end products the content of heavy chemical elements O and C more, than lightweight H.

Table 2. Gaseous end products of the conversion process of PE -raw.

| Component | Volumetric content, vol.% | \( \dot{m}_g \), g/min | \( \dot{m}_{gC} \), g/min | \( \dot{m}_{gH} \), g/min | \( \dot{m}_{gO} \), g/min |
|-----------|--------------------------|-------------------------|-------------------------|-------------------------|-------------------------|
| \( \text{H}_2 \)     | 66.3                     | 0.3966                  | —                       | 0.3966                  | —                       |
| CO         | 9.6                      | 0.8040                  | 0.4346                  | —                       | 0.4594                  |
| \( \text{CO}_2 \)    | 12.0                     | 1.5793                  | 0.4307                  | —                       | 1.1486                  |
| \( \text{CH}_4 \)    | 7.8                      | 0.3733                  | 0.2800                  | 0.0933                  | —                       |
| \( \text{C}_2\text{H}_2 \) | 2.3                     | 0.1789                  | 0.1651                  | 0.0138                  | —                       |
| \( \text{C}_2\text{H}_4 \) | 0.30                    | 0.0251                  | 0.0215                  | 0.0036                  | —                       |
| \( \text{C}_6\text{H}_6 \) | 0.021                   | 0.0049                  | 0.0045                  | 0.0004                  | —                       |
| Summarily   | 98.321                  | 3.3621                  | 1.2464                  | 0.5077                  | 1.6080                  |

\( ^a \) Samples for analysis contain impurities.

Table 3. Gaseous end products of the conversion process of PET-raw.

| Component | Volumetric content, vol.% | \( \dot{m}_g \), g/min | \( \dot{m}_{gC} \), g/min | \( \dot{m}_{gH} \), g/min | \( \dot{m}_{gO} \), g/min |
|-----------|--------------------------|-------------------------|-------------------------|-------------------------|-------------------------|
| \( \text{H}_2 \)     | 51.1                     | 0.2601                  | —                       | 0.2601                  | —                       |
| CO         | 14.7                     | 0.5990                  | 0.2570                  | —                       | 0.3420                  |
| \( \text{CO}_2 \)    | 25.4                     | 2.8430                  | 0.7750                  | —                       | 2.0680                  |
| \( \text{CH}_4 \)    | 4.8                      | 0.1948                  | 0.1460                  | 0.0488                  | —                       |
| \( \text{C}_2\text{H}_2 \) | 0.340                   | 0.0225                  | 0.0208                  | 0.0017                  | —                       |
| \( \text{C}_2\text{H}_4 \) | 0.019                   | 0.0013                  | 0.0011                  | 0.0002                  | —                       |
| \( \text{C}_6\text{H}_6 \) | 0.210                   | 0.0417                  | 0.0385                  | 0.0032                  | —                       |
| Summarily   | 96.569                  | 3.9624                  | 1.2384                  | 0.3140                  | 2.4100                  |

\( ^a \) Samples for analysis contain impurities.

For comparative analysis more informative is the number of atoms, i.e. the molar content, rather than mass. These data are obtained by the recalculation are shown in figures 1 and 2 in the form of diagrams.

**Figure 1.** The mole composition of raw materials at input in plasma-chemical reactor. (a) – PE-raw; (b) – PET-raw.
Figure 2. The mole ratio of chemical elements in the gaseous end products. (a) – PE-raw; (b) – PET-raw.

As seen from the presented diagrams that PE-raw does not contain atoms O, and in the final products they appear. At the same time there is a significant addition of atoms H. Similar patterns are present in the case of PET-raw. In both cases, the atoms H and O are transferred from the steam.

3. Conclusions
Significant amount of hydrogen from water-steam is added to the hydrogen coming to the reaction zone of the plasma-chemical reactor from composition of raw. Therefore, hydrogen volume content is the largest among of all the components in the part of produced synthesis gas.

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