Hydrogen Production from Polymer Waste in a Gas-Flow Reactor

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ABSTRACT

We present a theoretical underpinning of technological and design requirements for a discharge device based on a high-voltage pulse-periodic discharge for the development of a reactor for plasma-chemical recycling of polymer waste into hydrogen and other valuable products. Geometrical parameters, gas flow velocity, power capacity of the discharge power supply, output, and the pulse repetition rate of the discharge device were determined. It was demonstrated that in order to reduce the energy needed for polymer waste recycling, the energy released at the mutual association of the dissociation products and their association with the reagent can be used for partial dissociation of the molecules of the processed materials.

Keywords: Hydrogen, polymer waste, recycling, discharge.

INTRODUCTION

The amount of polymer waste produced all over the world grows every year. This, naturally, adversely affects the environment [1, 2]. In most countries dumping...
and burning are still the most common ways for utilization of polymer waste [3, 4]. It is apparent, however, that dumping cannot be considered as a safe way for utilization of the polymer waste. In fact, only 9% of the polymer waste is recycled, 12% is burned, and 79% is sent to disposal sites or left in the natural environment [5]. The main factor that constrains the use of burning is the emission of toxic vapours and fly ash [6].

Plasma-chemical technologies can be considered as one of the promising methods. These technologies provide massive reactional opportunities as well as optimal parameters for technological processes, and consequently, they ensure ecological safety, cost-effectiveness, and versatility [7–10]. The technologies for plasma-chemical recycling of waste have appeared relatively recently. In spite of their obvious advantages, to date, polymer waste recycling involving the plasma-chemical technique has not been worked out at an industrial scale. This requires the development of reactors. In this respect, accumulation of experimental and theoretical data on the plasma-chemical processes that occur in such reactors is of vital importance for optimization of the reactor operation and prediction of its performance.

For plasma generation, a high-voltage source of pulse-periodic discharge was chosen. This discharge is widely employed in the lasers based on various chemical species [11], and the corresponding dissociation efficiency for different chemical compounds is comparable to that of the other types of discharge commonly employed in nonequilibrium plasma chemistry.

**NUMERICAL EXPERIMENT**

The goal of the present study is to consider the provability of technological characteristics of the device and the operating mode of the reactor for recycling of polymer waste with production of hydrogen and other valuable products. The discharge device suitable for the use in the proposed reactor was a cube with two dielectric walls and an electrode assembly with the working gas mixture pumped through the discharge gap. A similar device was previously used in the experimental constructions of different modules of copper vapour lasers [11]. The conditions for the numerical calculations were chosen based on the analysis of the operating mode of the high-voltage pulse-periodic discharge in copper vapour lasers [11]: the pumped inert gas (helium) involved a flow of polymer waste molecules and the reagent inside the discharge device, the gas temperature was taken to be equal to 1500 K, discharge efficiency was \( \eta = 30\% \), the reagent was calcium, the concentrations of the recycled materials were \( n = 10^{14}, 10^{15}, \text{and } 10^{16} \text{ cm}^{-3} \), the concentration of the inert gas was \( n_g = 10^{17}, 10^{18}, 10^{19} \text{ cm}^{-3} \).

The condition for efficient operation of the discharge device is minimization of the energy losses associated with excitation and dissociation of the association products. For clarity, it was suggested that the minimum times of volume
association \( \tau_{a \text{ min}} \) and diffusion \( \tau_{D \text{ min}} \) of atoms to the walls of the discharge device were 10 times higher than the time \( t = c/u \) the molecules of the recycled materials stayed inside the discharge device: \( \tau_{a \text{ min}} = \tau_{D \text{ min}} = 10t \).

The characteristic time \( \tau_a \) of association was determined by relation (1) [12]:

\[
\tau_a = \frac{1}{a n_Y n_X} ,
\]  

(1)

where \( n_X \) and \( n_Y \) are the concentrations of the dissociated polymer waste molecules, which associate mutually or associate with the atoms of the reagent added into the discharge device, \( \alpha \) is the recombination coefficient.

The characteristic time \( \tau_D \) of diffusion of atoms \( X \) to the walls and electrodes of the discharge device was found according to relation (2) [13]:

\[
\tau_D = \frac{\Lambda^2}{D} ,
\]  

(2)

where \( D = \frac{3}{16 n_g (r_g + r)^2} \left( \frac{2kT}{\pi m_g m} \right) \) is the diffusion coefficient for atoms \( X \) in the inert gas, \( \frac{1}{\Lambda^2} = \frac{2\pi^2}{D} \) is the characteristic diffusion length, \( m_g, r_g \) are the mass and the radius of the inert gas atoms, \( T \) is the temperature of the inert gas, \( m \) and \( r \) are the mass and the radius of atoms \( X \).

The velocity \( v \) of the gas mixture flow through the volume was calculated as:

\[
v = Su = \frac{cS}{0.1\tau_{a \text{ min}}} ,
\]  

(3)

where \( S = ab \) is the cross-section of the gas flow.

The power capacity of the power source and the rate of polymer waste recycling were determined using (4) and (5):

\[
W = \frac{vnQ}{\eta} ,
\]  

(4)

\[
P = vnM ,
\]  

(5)

where \( Q \) is the energy required for breaking all chemical bonds in the molecule, \( M \) is the mass of the molecule of the recycled material.
The repetition rate of the discharge pulses was calculated by (6):

\[ f \geq f_{\text{min}} = \frac{W \eta}{VnQ} , \]  

where \( V \) is the volume of the discharge gap.

The concentration \( n_{Ca} \) of calcium atoms for the considered recycled material was found as (7):

\[ n_{Ca} = \theta \cdot n , \]  

where the value of \( \theta \) specifies the maximum number of Ca atoms capable of reacting with the atoms appearing due to dissociation of the polymer molecule: for polyethylene \( \theta \) is equal to 0.5, for polyvinylchloride – to 1.5, and for polyethyleneterephthalate it is 3 according to [14].

The value of \( \tau_{a \text{ min}} \) was calculated using (1) on the assumption that \( n_X = n_{C2} \), and \( n_Y = n_{Ca} \). The estimate value of the association coefficient \( \alpha \) was taken as \( \alpha = 2.98 \times 10^{-33} \text{cm}^6/\text{s} \), which corresponds to the rate of recombination of Ca and C\(_2\) at a temperature of 1500 K, according to [14]. The value of \( \tau_{D \text{ min}} \) for hydrogen atoms was calculated using (2).

The numerical results are given in TABLE I.

From the technological point of view, the velocities of several tens of m/s can hardly be suitable for a closed reaction chamber. Significant decrease in the gas flow velocity can be achieved by switching to pulse periodic discharges. In this case, the length of the discharge device can be increased greatly with respect to its lateral dimensions. In order to minimize the energy losses at dissociation and excitation of the molecules of the products, which are formed in the processes of mutual association of the dissociation products and association of the latter with the reagent, the duration \( t_{\text{raz}} \) of the discharge must satisfy the following requirements: \( t_{\text{raz}} \ll \tau_a \), \( t_{\text{raz}} \ll \tau_D \). Under these conditions, the time the molecules of the recycled materials stay inside the discharge device can be rather long: \( t = k \cdot \tau_{a \text{ min}}, k \geq 1 \).

Using the data given in TABLE I it is simple to evaluate the output of the plasma-chemical reactor for a particular power source. For example, given that \( n_g = 1 \times 10^{18} \text{cm}^{-3} \) and \( n = 1 \times 10^{16} \text{cm}^{-3} \), we obtain the power capacity of the power source to be 38377 J/s (TABLE I). For these conditions, let us find the output of the reactor using 1.31 kg of CaC\(_2\), and 0.08 kg of H\(_2\) will be obtained per hour, and 0.82 kg of Ca will be required for this. Thus, in the case of polyethylene recycling, the output will be 0.57 kg/h. Under the same conditions, the output of the plasma-chemical reactor will be 1.47 kg/h at polyvinylchloride recycling. For a 50 kW power source, the output of the reactor is 0.74 kg/h for polyethylene, 1.6 kg/h for polyvinylchloride, and 1.11 kg/h for polyethyleneterephthalate. It should be noted that the recycling products include hydrogen.

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TABLE I. YIELDS OF RECYCLING PRODUCTS AND REAGENT CONSUMPTION (KG/H).

<table>
<thead>
<tr>
<th>( n ) (cm(^3))</th>
<th>( n ) (cm(^3))</th>
<th>( \text{polyethylene} )</th>
<th>( \text{polyvinylchloride} )</th>
<th>( \text{polyethyleneterephthalate} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>( 1 \times 10^{17} )</td>
<td>( 1 \times 10^{14} )</td>
<td>13.88</td>
<td>0.82</td>
<td>8.17</td>
</tr>
<tr>
<td>( 1 \times 10^{17} )</td>
<td>( 1 \times 10^{14} )</td>
<td>41.35</td>
<td>2.58</td>
<td>25.83</td>
</tr>
<tr>
<td>( 1 \times 10^{17} )</td>
<td>( 1 \times 10^{14} )</td>
<td>130.8</td>
<td>8.16</td>
<td>81.68</td>
</tr>
<tr>
<td>( 1 \times 10^{18} )</td>
<td>( 1 \times 10^{14} )</td>
<td>0.13</td>
<td>0.008</td>
<td>0.08</td>
</tr>
<tr>
<td>( 1 \times 10^{17} )</td>
<td>( 1 \times 10^{15} )</td>
<td>0.41</td>
<td>0.03</td>
<td>0.26</td>
</tr>
<tr>
<td>( 1 \times 10^{18} )</td>
<td>( 1 \times 10^{16} )</td>
<td>1.31</td>
<td>0.08</td>
<td>0.82</td>
</tr>
<tr>
<td>( 1 \times 10^{19} )</td>
<td>( 1 \times 10^{17} )</td>
<td>0.001</td>
<td>8 ( \times 10^{-9} )</td>
<td>8 ( \times 10^{-9} )</td>
</tr>
<tr>
<td>( 1 \times 10^{19} )</td>
<td>( 1 \times 10^{18} )</td>
<td>0.004</td>
<td>3 ( \times 10^{-9} )</td>
<td>0.003</td>
</tr>
</tbody>
</table>

CONCLUSION

Thus, at present, there is the background for the development and construction of an experimental prototype of a reactor for plasma-chemical recycling of polymer waste with production of hydrogen. In order to reduce the energy required for recycling of the polymer waste, it is possible to partially use the energy, which is released at the mutual association of the dissociation products and their association with the reagent, for dissociation of the molecules of the recycled materials, thus reducing the energy needed for polymer waste recycling.

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REFERENCES