The efficiency of rare elements used for hydrogen production from polymer waste

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Abstract. The authors have proposed the plasma-chemical method of the polymer waste processing and developed a schematic diagram of the reactor. The paper contains the results of the theoretical calculation of the polymer waste processing products. The reagents that allow obtaining hydrogen and other liquid products from polymer waste are selected. It has been proposed to use rare elements for increasing the efficiency of hydrogen production from polymer waste. The results of the calculation of the efficiency of hydrogen production from polymer waste using molybdenum have been revealed in the paper.

1. Introduction

It is well known that the environmental threat to the whole world has become the places of polymer waste (PW) storage. The degradation products of PW are substances that have harmful effects on the environment. Every year about 4.8 million tons of PW is formed in the Russian Federation [1]. World production of plastics is increasing annually by 5–6%, which leads to the increasing of the PW [2].

The universal solution of the PW destruction problem is not found yet, because the destruction of the PW is as complex and expensive as their production [2]. The Russian system of waste utilization is based on waste disposal (more than 80%) in landfills and unorganized dumps [3–5].

Using PW for energy systems and complexes will ensure the prevention of large-scale environmental crisis caused by the lack of PW processing technology that meet the economy and resources saving modern requirements, as well as the expanding the raw material base of energy by using the energy potential of these polymer waste.

Nowadays, an alternative method [6–8] of using the PW for energy systems and complexes is hydrogen production from waste. Hydrogen is a highly environmentally friendly fuel for transport and the development of hydrogen energy. Currently production, storage and using of hydrogen as an
energy fuel receive considerable attention both from the government and large commercial structures [7 – 13].

The evaluation showed that buried PW can annually produce up to 1 million tons of hydrogen. According to various data, summarized in [14], there are two groups of world hydrogen production estimation. According to the first, “the annual world production of hydrogen by the end of 1990 was 40 – 45 million tons or 450 – 500 billion m3” According to the second group, world production of hydrogen was 60 million tons in 1990 and 80 million tons in 1998. As emphasized in [14], “in any case, these amounts are significant, corresponding to 20 – 25% of annual world production of natural gas”.

It is recognized that the advanced PW processing technology is plasma technology (environmentally friendly and cost-effective).

Plasma technology for processing the PW to hydrogen is under active research and development for large-capacity recycling [8, 15, 16]. However, nowadays there is now well-functioning waste processing with the using of plasma chemical methods [16]. According to [16], such plant is in the “setting up” stage in Canada (does not work reliably for a long time), South Korea has a pilot production plant for plasma processing of household and industrial waste up to 1,000 kg per hour. Experimental studies of this area were also conducted in France.

2. Schematic diagram of the plasma chemical reactor for polymer waste processing

Figure 1. A schematic diagram of the reactor for plasma chemical PW processing

The figure 1 shows a schematic diagram of the reactor for plasma chemical PW processing. In the reaction chamber 1 the inert gas enters the valve 2 from the cylinder 3, the operating pressure of which is measured with a vacuum gauge 4. The pump 5 for pumping inert gas from the reaction chamber 1
sets a predetermined pressure of inert gas. Circulation of the inert gas in the reaction chamber 1 in the
direction shown in Figure 1 by arrow occurs via pump 6. PW, converted into the gaseous state by the
heater-cooler 8, adds continuously or portionwise to the inert gas from the reservoir 7 into the reaction
chamber 1. The flow of inert gas entrains and displaces PW vapours at the reaction chamber 1 in the
direction indicated by the arrow. The mixture of inert gas and vapours enters the pyrolysis unit 9. The
initiation of pyrolysis occurs in the pyrolysis initiation device 10 by injection of metal vapour from the
tank 11. The predetermined pressure vapour is provided by the heater 12. Within the movement
of a gas mixture along the heat-resistant channel 13, (14 – thermal insulation) its temperature will
increase and more PW vapours will be pyrolysed. As a result, gas mixture, most of which is PW
processing products, is formed at the end of heat-resistant channel 13 of the pyrolysis unit 9. To
reduce the time of pyrolysis requires preheating of the gas mixture at the inlet or discharge, which will
create products involved in Association with the release of energy.

Processing products with an inert gas flow come into the removable condensation device 15 (16 – 15
device node). Condensed PW processing products from vapour phase accumulate between the
diaphragms 17. Remaining in the reaction chamber 1, gaseous products such as carbon monoxide and
hydrogen move with the inert gas stream in the removable carbon monoxide output device 18 (19 – 18
device node). At node 19 in the interaction of carbon monoxide molecules with a metal insert 20 metal
carbonyl is formed (21 – a filter for removing microparticles that can break away from the walls of
nodes). It is collected and stored in the system 22. The gaseous hydrogen with a stream of an inert gas
comes into hydrogen output device 23 (24 – 23 device node). Hydrogen, that was separated from
membrane 25 (26 – mesh that protects it against aggressive chemicals) and heated by the heater 27
from the gas mixture circulated in the reaction chamber 1, is moved out from the reaction chamber 1 by
pump 28 and is collected in reservoir 29.

3. The results of theoretical studies of the composition of PW procession products

A detailed analysis of PW procession end products requires physical and numerical experiments.
However, the main end-products can be defined for a given character of PW molecules dissociation
with data of the binding energies of the atoms in the molecules of the primary products of processing
and of their ability to react chemically with each other.

Within the analysis (on the base of polyethylene (PE), polyvinyl chloride (PVC) and polyethylene
terephthalate (PET)), it has been suggested that the breaking of chemical bonds, the energy of which is
less than 5 eV is carried out in repetitively pulsed discharge in the polymer waste molecules. Chemical
reagent is calcium vapours.

The table 1 shows the results of evaluation of basic products of PE, PVC and PET processing and
reagent costs for processing of 1 kg PW.

**Table 1.** Of evaluation of basic products of PE, PVC and PET processing and reagent costs for
processing of 1 kg PW

| PW  | Processing products | Reagent cost, kg |
|-----|---------------------|------------------|
| PE  | CaC₂, H₂            | 1.43             |
| PVC | CaCl₂, H₂           | 0.96             |
| PET | CaC₂, CO, H₂        | 0.63             |
4. The efficiency of hydrogen production from PW

To reduce the cost of energy for processing PW proposed to use the energy released during association of the products of dissociation PW with each other and with the reagent.

First, it is necessary to estimate the amount of energy $G_d$ that must be expended on the dissociation of one molecule of PW with $T_{\text{max}}$:

$$G_d = \sum_i (E_i n_i \alpha_i),$$

where $i$ – the type of coupling in the molecule, $n_i$ – number of similar bonds in the molecule, $E_i$ – $i$-type chemical bond breaking energy, $\alpha_i$ – degree of dissociation of bonds of type $i$ at $T_{\text{max}}$.

Then estimate the amount of energy that is released during the formation of refined products from one molecule of PW with $T_{\text{max}}$:

$$G_a = \sum_i n_i \sum_j (E_j n_j (1 - \alpha_j)),$$

where $j$ – bond type of association products, $n_j$ – number of similar bonds in the association products, $E_j$ – bond breaking energy of $j$-type, $l$ – type of molecules resulting from association, $n_l$ – number of similar molecules or radicals in the products of the association, $j$ – degree of dissociation of type $i$ bonds at $T_{\text{max}}$.

The amount of energy stored in the chemical bonds that were not dissociated by pyrolysis, is:

$$G_d = G_{dc} - G_d,$$

$$G_{dc} = \sum_i (E_i n_i),$$

where $G_{dc}$ – energy of complete dissociation of a PW single molecule.

In the paper the maximum temperature ($T_{\text{max}}$), corresponding to the maximum value of the relative amount of products formed as a result of the dissociation products association with each other and reagent, was defined in the pyrolysis for PE, PVC and PET (concentrations $n = 10^{15}$, $10^{16}$, $10^{17}$ cm$^{-3}$) (Table 2). Estimates are made under the assumption that during the pyrolysis such bonds as C = O and C = C are remained and the reagent is calcium.

The assessment of minimum efficiency of hydrogen production (Table 2) is made on the assumption that electrical energy is wasted on gas heating to $T_{\text{max}}$ and unexploded bond dissociation by pyrolysis:

$$\delta'_{\text{H}} = \frac{W_{\text{H}}}{G_n' + G_{\text{Tmax}} - \Delta G'},$$

where $\Delta G = G_a - G_d$ ($G_{dc'}$ – energy that must be expended on dissociation under $T_{\text{max}}$, $G_d$ – energy that is released during the dissociation of association products with each other and the atoms of the reagent), $G_{dc'}$ – energy stored in the undissociated bonds during the pyrolysis, $W_{\text{H}}$ – energy released by burning hydrogen produced during the PW processing, $G_{\text{Tmax}} = \frac{3}{2} k(T_{\text{p}} - T_{\text{i}})(n_{\text{AT}} N + Y N)$ – energy that must be expended in heating the mixture of inert gas and molecules to the PW to $T_{\text{max}}$ ($T_{\text{i}} = 300$ K – initial temperature, $n_{\text{AT}}$ – number of atoms in the molecule, $N$ – number of PW molecules in one kg, $Y = 5$; 10 – ratio of the concentration of inert gas atoms to the concentration of PW software.

Maximum efficiency of hydrogen production (Table 2) is estimated on the assumption that electrical energy is wasted on gas heating to $T_{\text{max}}$:

$$\delta''_{\text{H}} = \frac{W_{\text{H}}}{G_{\text{Tmax}} - \Delta G}. $$

It is clear that the real value of the efficiency of hydrogen production will be between $\delta'_{\text{H}}$ and $\delta''_{\text{H}}$.

**Table 2.** The results of calculation: the maximum temperature $T_{\text{max}}$ reached in the pyrolysis zone (figure 1), the cost of energy $G_d$ for the dissociation under $T_{\text{max}}$, energy $G_d$ that is released during the formation of processed products under $T_{\text{max}}$, the energy $G_d'$, stored in the bonds that are not braked at the result of pyrolysis under $T_{\text{max}}$, power consumption $G_{\text{T}}$ on heating the mixture of inert gas and
molecules of processing substances under \( T_{\text{max}} \), the minimal \( \delta'_{\text{HI}} \) and maximal \( \delta'_{\text{II}} \) efficiency of hydrogen production, based on 1 kg of PW

| PW  | \( n \), cm\(^3\) | \( T_{\text{max}} \), K | \( G_d \), kW-h | \( G_a \), kW-h | \( G_f \), kW-h (\( Y=5 \)) | \( G_f \), kW-h (\( Y=10 \)) | \( \delta'_{\text{HI}} \) (\( Y=5 \)) | \( \delta'_{\text{HI}} \) (\( Y=10 \)) | \( \delta'_{\text{II}} \) (\( Y=5 \)) | \( \delta'_{\text{II}} \) (\( Y=10 \)) |
|-----|-----------------|----------------|-------------|-------------|----------------|----------------|----------------|----------------|----------------|----------------|
| PW  | 10\(^{15}\)      | 2200           | 17.99       | 17.56       | 2.14           | 3.76           | 5.94           | 0.9            | 0.65           | 1.5            | 0.87            |
|     | 10\(^{16}\)      | 2450           | 17.15       | 16.12       | 2.98           | 4.16           | 6.91           | 0.68           | 0.51           | 1.34           | 0.71            |
|     | 10\(^{17}\)      | 2800           | 16.54       | 14.82       | 3.59           | 4.94           | 8.03           | 0.54           | 0.42           | 1.13           | 0.57            |
| PVC | 10\(^{15}\)      | 2200           | 7.62        | 7.33        | 1.70           | 1.16           | 1.7            | 0.63           | 0.54           | 1.71           | 1.00            |
|     | 10\(^{16}\)      | 2500           | 7.62        | 7.05        | 1.69           | 1.34           | 1.69           | 0.55           | 0.47           | 1.48           | 0.79            |
|     | 10\(^{17}\)      | 2850           | 7.36        | 6.55        | 1.95           | 1.56           | 1.95           | 0.46           | 0.39           | 1.3            | 0.65            |
| PET | 10\(^{15}\)      | 2200           | 7.66        | 7.9         | 1.18           | 0.93           | 1.18           | 1.07           | 0.39           | 2.94           | 1.48            |
|     | 10\(^{16}\)      | 2450           | 7.2         | 7.19        | 1.65           | 1.05           | 1.65           | 0.73           | 0.79           | 1.87           | 1.59            |
|     | 10\(^{17}\)      | 2750           | 6.53        | 6.24        | 2.32           | 1.19           | 2.23           | 0.52           | 0.68           | 1.35           | 1.16            |

Thus, the proposed method enables the production of hydrogen from PW with efficiency greater than one. The proposed method for hydrogen production can be used for hydrogen production from fossil hydrocarbons.

5. Improving the efficiency of hydrogen production from PW - rare elements

Improving the efficiency of hydrogen production can be achieved by selection of reagents, providing even greater energy release during the formation of the corresponding processed products, such as molybdenum.

Table 3 shows the calculation results of the same parameters as in Table 2, but with the molybdenum reagent.

The data in Table 3 indicate that at the optimum temperatures the costs to the dissociation by electric discharge of one kilogram of processed materials are significantly reduced as compared with the case discussed above.

Moreover, Table 3 shows that the amount of energy released during the formation of PW processing products in the case of using the molybdenum as a reagent exceeds the total cost of electric power for heating the mixture of inert gas and polymer waste vapour to \( T_{\text{max}} \) and the energy stored in the undissociated links as a result of the energy released in the formation of processed products.

Table 3. The results of calculation: \( G_d \) – energy expended on the dissociation of molecules contained in one kg, \( G_a \) – energy released during the formation of processing products from one kg, \( G_f ' \) – energy stored in unbroken bonds for one kg, the reagent – molybdenum

| PW  | \( n \), cm\(^3\) | \( T_{\text{max}} \), K | \( G_d \), kW-h | \( G_a \), kW-h | \( AG \), kJ-kW-h | \( G_f ' \), kW-h | \( G_f \), kW-h (\( Y=5 \)) | \( G_f \), kW-h (\( Y=10 \)) |
|-----|-----------------|----------------|-------------|-------------|----------------|-------------|----------------|----------------|
| PW  | 10\(^{15}\)      | 2200           | 17.99       | 33.4        | 15.41         | 2.14        | 3.76           | 6.10            |
|     | 10\(^{16}\)      | 2500           | 17.79       | 31.38       | 13.59         | 2.33        | 4.35           | 7.07            |
|     | 10\(^{17}\)      | 2850           | 17.12       | 28.25       | 11.13         | 3.01        | 5.04           | 8.19            |
| PVC | 10\(^{15}\)      | 2250           | 7.99        | 14.02       | 6.03          | 1.32        | 1.19           | 1.73            |
|     | 10\(^{16}\)      | 2500           | 7.62        | 12.74       | 5.12          | 1.69        | 1.34           | 1.95            |
6. Conclusion
The authors have proposed technical solution and found conditions (temperature and concentration are defined) at which efficiency of energy for hydrogen production that required in addition to the heat generated in the process of association is greater than one. Environmentally friendly and high energy efficiency in hydrogen production certainly provides the high competitiveness of the proposed plasma chemical PW processing with hydrogen production with the rare elements using. Moreover, on the base of this method well-functioning, environmental and technical safety mobile unit can be created. Calculations have shown that the performance of the mobile unit capacity of 250 kW/h for 1 hour ensure the production of 8 kg of hydrogen from 55 kg of polyethylene processing, 5.5 kg of hydrogen – from 125 kg of PVC, 8 kg of hydrogen – from 163 kg of PET. It is expediently to use the hydrogen produced in these mobile units to obtain the energy required for dissociation of recyclable materials.

Thus, there are all conditions for a qualitative leap in environmental and energy problems solution with the using of rare elements.

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