Equilibrium analysis of hydrogen production using the steam-plasma gasification process of the used car tires

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Abstract. The paper deals with the treatment of used car tires. The method of used tires plasma gasification is proposed. The investigation of the syngas composition was carried out according to the temperature and plasma flow rate variation. The method of the steam catalytic conversion of CO, which is a part of the syngas, and CaO usage are suggested. The results of the calculation modeling at various temperatures, pressures, and steam flow rates are presented.

1. Introduction
Over 1 billion car tires [1] are produced annually. Thus, their demand constantly increases due to the improved living standards. The used tires practically do not dissolve in the native habitat. The main ways of their processing are: combustion, recapping, recycling and landfilling. According to the research data [2] about 65 % of the used tires are processed in the developed countries. Another part is put on dumps, which is environmentally unfriendly. Therefore a cost effective method of the used tires processing is an important problem.

The used tires generally consist of carbon – 83-89 % and hydrogen – 6-8 %, their ash content makes up 4.4-11.1 %, low calorific value – 32-39 MJ/kg [3]. Tire processing using the gasification technology is promising. In this case the organic part of tires turns into syngas, and inorganic transforms into slag. Syngas is the mixed gas mainly consisting of H₂ and CO. The gasification process divides to allothermal and autothermal by means of a heat supply. Autothermal process is realized due to the partial raw material combustion. Heat is supplied with the external heat carrier in the allothermal method. The low temperature plasma is the most perspective heat supply. Autothermal process is realized due to the partial raw material combustion. Heat is supplied with the external heat carrier in the allothermal method. The low temperature plasma is the most perspective heat carrier [4,5]. It also can be used as an oxidizer, thus high temperatures of the process are reached and the end product yield increases. The plasma usage allows controlling the plasma forming gas flow rate in wide range. The use of steam as a plasma forming gas is considered to be the most effective, as that allows obtaining the syngas which almost does not contain minor components (N₂, CO₂)[6-8].

Syngas can be used for hydrogen production. Thus it is expedient to carry out steam catalytic conversion of CO, which is a part of syngas, on the reaction with CaO [9, 10]:

\[ CO(g) + H_2O(g) + CaO(s) \rightarrow H_2(g) + CaCO_3(s) \]  

(1)

It is necessary to carry out the syngas cleaning [11] to prevent the poisoning of the steam conversion catalyst, since the used tires contain sulfur-containing components which generally turn into H₂S at the gasification process. It is expedient to use ethanolamine (or diethanolamine, or methyl
diethanolamine) as an absorber of sulfur-containing components of the syngas, so that CO₂ also is absorbed [12].

2. The analysis of the process
The composition calculation of gaseous products under the condition of the thermodynamic equilibrium at flow rates of the steam plasma of 0.2-5 kg/kg of tires, temperatures 1150-1500 K and atmospheric pressure for modeling the process of used tires plasma gasification was settled. Chemical WorkBench ver.3.5, Kinetic Technologies, which is based on the principle of entropy maximum, was used for the calculations. Thus it was accepted that the process is adiabatic, and the inorganic part of the used tires does not participate in chemical transformations. The following tire composition was used in calculation: C – 81.48, H – 8.00, O – 3.38, N – 0.47, S – 1.80, ashes – 4.88 % of mass (on working mass). The low calorific value is 36.55 MJ/kg.

The calculation of H₂ concentration in a range of temperatures 650-1000 K, steam flow rate 0.8-3.1 kg/kg of gas and pressure 1-7 atm was carried out for determining the optimum process conditions of steam catalytic conversion of CO in the presence of CaO.

The preliminary calculation of the hydrogenous gas composition was carried out at the mole stoichiometric and excess ratios under the condition of the thermodynamic equilibrium for determining the CaO:C ratio during the steam catalytic conversion of CO. It showed that the excess content of CaO slightly influences on the hydrogenous gas composition. Therefore the stoichiometric mole ratio of CaO:C was used in further calculations.

3. Results and their discussion
Figure 1 shows the calculated H₂+CO content in dependence on the specific (on 1 kg of tires) steam plasma flow rate.

According to the calculations, the formation of the graphite is taking place at the steam plasma flow rate less than ~1.2 kg/kg of tires. The maximum concentration of CO+H₂ is observed at the flow rate close to stoichiometric (~1.2 kg/kg of tires). The stoichiometric flow rate is an oxidizer flow rate when all carbon and oxygen of the fuel and the oxidizer turns into CO, and fuel hydrogen – in H₂. The further increase in the steam plasma flow rate leads to interaction between CO and H₂O with H₂ formation and to syngas yield increasing. Thus the total fuel component quantity does not change. It leads to decrease in their concentration in syngas.

Apparantly from fig. 1 the temperature increase leads to increase in H₂+CO content in the syngas. However at a mode close to stoichiometric at temperatures above 1350 K H₂+CO concentration practically does not change.
The specific energy consumption was calculated from the energy balance:

\[ E_{in} = H_{sg}(1350) \cdot G_{sg} - H_{tires}(298) - H_{H_2O}(298) \cdot G_{plasma} \]  

(2)

where \( E_{in} \) – energy consumption (MJ/kg), \( H_{sg}(1350) \) – gasification products enthalpy at temperature 1350 K (MJ/kg), \( H_{H_2O}(298) \) – enthalpy of formation of water (MJ/kg), \( H_{tires}(298) \) – enthalpy of formation of tires (MJ/kg), \( G_{sg} \) – gasification products yield (kg/kg), \( G_{plasma} \) – steam plasma consumption (kg/kg).

If syngas thermal energy is used to decrease the energy consumption, the steam plasma flow rate in dependence of the energy consumption at temperature 1350 K will be as follows (fig. 2):

![Figure 2](image)

**Figure 2.** The dependence of the energy consumption on the steam plasma flow rate.

It can be seen that when the steam plasma flow rate increases, the energy consumption increases significantly. Thus the \( \text{H}_2+\text{CO} \) yield also raises (fig. 3), at the energy consumption more than \(~11.2\) MJ/kg (steam plasma flow rate is \(~1.2\) kg/kg of tires and more) the maximum total yield of \( \text{CO}+\text{H}_2 \) is observed.

![Figure 3](image)

**Figure 3.** The dependence of total \( \text{H}_2+\text{CO} \) yield on energy consumption.

Therefore, the gasification process is expedient to carry out at 1350 K and at steam plasma flow rate of \(~1.2\) kg/kg of tires. It is possible to produce \( 4.2\text{Nm}^3 \) syngas, consisting of \( \text{H}_2 - \text{60.3}\% \) and \( \text{CO} - \text{39.0}\% \), from 1 kg used automobile tires at such process organization. Thus it is necessary to obtain
steam plasma with ∼14 MJ/kg enthalpy, taking into account the heat of vaporization. The energy consumption on the steam plasma gasification of 1 kg used tires is 11.2 MJ/kg of tires.

Figure 4 shows the calculated hydrogen content, which is produced at steam conversion of CO, in dependence of the temperature at steam flow rate 0.8-3.1 kg/kg syngas.

![Figure 4](image)

**Figure 4.** The dependence of hydrogen content on the temperature at various steam flow rates in the atmospheric pressure.

Findings in Fig. 4 show that the steam plasma flow rate growth promotes more complete process progress. However, the H₂ concentration reaches maximum and practically does not change at flow rates higher than ∼2.0 kg/kg of tires and at temperatures ∼725-850 K. Low H₂ concentration at temperatures less than ∼725 K is connected with reactions course with the formation of CH₄. The efficiency of CO₂ absorption considerably decreases at temperatures more than ∼850 K that also leads to the H₂ content decrease in hydrogenous gas.

Figure 5 shows the dependence of H₂ yield on temperature and pressure at the steam flow rate 2 kg/kg syngas.

![Figure 5](image)

**Figure 5.** The dependence of H₂ yield on the temperature at steam flow rate 2 kg/kg syngas for various pressures.

Pressure growth promotes the reactions course with the methane formation that leads to considerable decrease in the H₂ yield (fig. 5) at temperatures lower than ∼850 K.
As was said, the process of CO steam conversion is exothermic. The released energy amount considerably decreases with the temperature growth and rises with the pressure increase (fig. 6) at CO conversion.

Thus, it is most convenient to carry out the process of steam catalytic conversion of CO at steam flow rate ~2 kg/kg syngas, at temperature ~725-750 K and at atmospheric pressure. The energy released at the stage of steam catalytic conversion of CO in this process mode is ~1.6-1.8 MJ/kg syngas. It is possible to produce ~4.2 Nm\(^3\) of hydrogenous gas from 1 kg of the used tires under such conditions. The gas composition will be the following: H\(_2\) – 99.5-99.7 %, CH\(_4\) – 0.2-0.4 % and N\(_2\) – 0.1 %. The conversion level of CO according to the calculation reaches ~99.99 %.

It is possible to use the Fe-Cr-Cu-oxide catalyst as the catalyst of the CO steam conversion at such process organization [13].

The total energy consumption on 1 Nm\(^3\) of H\(_2\) production without calculation of expenditures on the absorbent reactivation and the syngas cleaning is ~0.6 kW.

4. Conclusion
The calculation shows that it is possible to produce ~4.2 Nm\(^3\) of the syngas, consisting of H\(_2\) – 60.3 and CO – 39.0 %, when processing 1 kg of the used tires by the steam plasma gasification process at the temperature 1350 K and the steam plasma flow rate of ~1.2 kg/kg of tires.

It is possible to produce ~4.2 Nm\(^3\) of the hydrogenous gas, consisting of H\(_2\) – 99.5-99.7, CH\(_4\) – 0.2-0.4 and N\(_2\) – 0.1 %, with the subsequent steam conversion of CO, which is a part of syngas, at the process temperature of ~725-750 K, at the steam flow rate of ~2 kg/kg syngas and at atmospheric pressure.

The energy consumption quantity on 1 Nm\(^3\) of H\(_2\) production without calculation of expenditures on the absorbent reactivation and the syngas cleaning is ~0.6 kW.

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