High pressure plasma reactor for thermal dissociation of carbon dioxide

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Plasma reforming systems are considered as one of the possible solutions to overcome several drawbacks related to reformation of pollution gases and hydrocarbons since they provide compactness and high reactivity. Developed plasma chemical reactor at VSE permits to study the energy efficiency of direct and/or assisted plasma reforming/synthesis.

An increased utilization of fossil fuel has caused the atmospheric accumulation of carbon dioxide, which induces significant climatic changes. Conversion of CO$_2$ into more valuable chemicals is a very attractive idea and a number of researches worldwide have been performed. The plasma-assisted methods developed for reducing CO$_2$ emission are: RF plasma; corona; dielectric barrier discharge; glow discharge; gliding arc and thermal plasma.

Carbon dioxide can be decomposed by itself or by reacting with H$_2$, C and CH$_4$ under high temperatures. This high temperature can be obtained by using thermal plasma as well as non equilibrium plasma. The difference between these two methods consists in how the electric energy is delivered to the reacting substances. For plasmas in thermal equilibrium the most of supplied electrical energy is transformed into translation motion of particles and only small part intended for excitation, dissociation, ionization, etc. In the case of non-equilibrium plasmas the principal part of electrical energy is converted into excitation of vibrational layers of molecules.

Simultaneously with direct reaction $CO_2 \rightarrow CO + 1/2O_2$ ($\Delta H = 2.9$ eV/molecule), a reverse reaction of CO$_2$ formation is also occurring. Thus, the thermal dissociation process must include two phases – heating and fast quenching to stabilize the reaction products from reverse reactions. Taking into account the data of the reversibility and equilibrium of the reaction it is possible to obtain conditions for increased yield of CO$_2$ decomposition.

The quenching is the principal factor, which determines the distribution of final product. Moreover, the final product distribution depends on the rates of competing reactions during the quenching. Thus, the control of the quenching temperature is very important for the thermal plasma processing. The quenching is not effective if the quenching rate is less than $10^5$ K/s [1]. Most commonly used technologies are contact with a cold wall, contact with a liquid spray, injection into a fluidized bed, and mixing with a cooler gas.

A plasma chemical reactor, based on DC plasma torch (described in [2]), is presented. A reverse vortex diminishes thermal losses and increases discharge power per unit of arc length that gives rise to high temperature in arc column and high enthalpy of the plasma. Plasma torch thermal efficiency versus enthalpy of plasma jet is presented in Fig.1 for carbon dioxide and air as plasma forming gases. For low plasma jet enthalpies the thermal efficiency of plasma torch attains 86%. The thermal efficiency of plasma torch working with CO$_2$ is above of the air for high enthalpies due to an earlier onset of thermal dissociation.

The quenching chamber consists of a system of refrigerated discs, equipped with a flow turbulators. Estimated quenching rates are up to $10^7$-10$^8$ K/s and can be changed by means of varying of the volume of the post processing chamber. The experimental setup fulfill principal requirements of plasma chemical reactors: ability to working for a long time under high temperature conditions and with elevated thermal efficiency; assure a uniform distribution of temperature and reagent densities in the reaction zone; guarantee an adequate residence time of the reforming/synthesis products and provide the required conditions for product quenching.

The setup performance can be described by an energy efficiency parameter $\eta$, which is determined by the ratio of the dissociation enthalpy of the process, $\Delta H$, to the energy $E$ consumed for one molecule of carbon monoxide (CO) produced in a plasma system, i.e. $\psi = \frac{\Delta H}{E}$. 

Thermodynamic equilibrium composition was calculated by software CHEMKIN [3]. A solid line in Fig. 2 shows theoretical estimations of the energy efficiency due to thermal decomposition only. A maximum energy efficiency of 46% can be attained at the energy of 4 eV/molecule stored in the gas, which corresponds to ~3200 °C and composition: CO$_2$ – 14%; CO – 51%; O – 19% and O$_2$ – 16%.

Design of full factorial experiments was performed to maximize the energy efficiency of the plasma chemical reactor. Three principal factors were taken into account: quenching rate $dT/dt$, gas flow rate $G$ and arc current $I$. Some results are shown in Fig. 2. The data marked by open triangle (item 2) was obtained from the least favorable conditions, i.e. large volume of the reactor post discharge chamber and, respectively, low quenching rate. The same set of the arc currents and gas flow rates were applied for small volume of chamber and high quenching rate (item 3). As it was expected, the quenching rate has the main effect on the energy efficiency. Second in importance is the gas flow rate and the arc current is the last one. The set of experimental data marked with open stars (item 4) was obtained for chosen values of $G$ and $I$, after a virtual walking along the gradient on the surface “current”- “gas-flow-rate”. The maximum energy efficiency of about 30% (at maximum 46%) was achieved. Subsequent advance was limited by the availability of the gas supply systems.

The reaction rate in thermal plasma is so fast that thermodynamic equilibrium can be completed in a very short time. But the quenching rate is technically limited and the equilibrium composition of exit gas is, normally, “rollback” to lower equilibrium temperature $T_e$. For evaluation of the reactor quenching efficiency a parameter $\Theta = T_e/T_h$ can be useful. Here, $T_h$ is the exit gas temperature obtained from the mean flow enthalpy. For item 3 in Fig.2 $\Theta = 0.7 - 0.86$ and $\Theta = 0.9$ for item 4.

The conversion rate of 25–27% was obtained in direct decomposition of CO$_2$ and there is the way for improvement.

References