

NONEQUILIBRIUM PLASMA CHEMISTRY FOR CONCEPT OF SUSTAINABLE DEVELOPMENT

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Abstract. This work is devoted to the exploration of the compatibility of the hybrid plasma-catalytic conversion of liquid hydrocarbons into syngas with the concept of sustainable development. The results of experimental investigations indicate the high efficiency of plasma-catalytic conversion of ethanol to syngas and the small amount of waste (a few percent of feedstock weight). The results of the simulation of the kinetics using ZDPlasKin code for thermochemical and hybrid plasma-catalytic conversion.

Keywords: sustainable development, non-equilibrium plasma chemistry, rotating gliding discharge, conversion.

1. Introduction

The scale on which modern industry uses materials and energy not only led to the substantial depletion of fossil resources but also caused the accumulation of the large amount of wastes, which are hazardous to the environment. In 1980, International Union for Conservation of Nature, United Nations Environment Program and World Wildlife Fund addressed this problem by developing the World Conservation Strategy for Sustainable Development. In September of 2015, the UN proposed 17 goals of sustainable development, which were adopted by 70 countries [1].

The minimization of the use of fossil fuels and their replacement with the renewable energy sources is one of the most important sustainable development goals for ecology, society, and economics. The switch to the renewable biomass can lead to an ecologically beneficial reduction in the emission of carbon, chemicals, and liquid fuels. However, it is widely recognized that the use of first-generation biomass raw materials, such as corn or edible oilseeds, is not a sustainable option in the long run because it competes directly or indirectly with the production of food. Therefore, the European Union is aimed at the use of second-generation biomass raw materials, such as lignocellulose, waste oils and fats [2].

A major barrier to increasing the scale of biofuels production lies in the disadvantages of two main ways of processing lignocellulosic biomass: thermochemical and biotechnological. The biotechnological method of biofuel production is based on using the microorganisms for the processing of biomass into the desired product. This technology is used successfully to obtain ethanol from plant sugars and starches, but it faces significant challenges in the transition to the more complex raw materials, such as lignin and cellulose,

and while attempting to produce more sophisticated biofuels than ethanol [3]. At this stage of technological development, the performance of the biotechnological processing of lignocellulosic feedstock is low and is not able to provide the required rate of biofuel production growth.

The modern thermochemical technology of lignocellulosic biomass processing requires much higher temperatures than biotechnological methods (over 700 °C for pyrolysis and 1000 °C for gasification). A significant disadvantage of the thermochemical technologies is low energy efficiency. It is also worth noting that the use of high temperatures not only complicates the design of processing devices and requires the increase of safety requirements, but also decreases the selectivity of the raw materials conversion and leads to the emergence of byproducts. Therefore, the traditional thermochemical (temperature > 700 °C) and traditional plasma-chemical (thermochemical conversion using plasma torches; temperature > 1000 °C) processing of biomass lead to the appearance of the unwanted byproducts and wastes. In the case of catalytic conversion, a high content of impurities in the initial raw biomass negatively affects the yield and longevity of catalysts.

As of today, the discussion is open on the development of principles behind the construction of new technologies for the conversion of substances, which are known as "green chemistry". This is a departure from the traditional evaluation of the effectiveness based on the chemical yield towards the cost-effectiveness evaluation based on the lack of hazardous waste and toxic and/or hazardous substances. "Green chemistry" has to transform the raw materials (preferably renewable), exclude hazardous waste, and use no toxic agents in the production of chemical products and in their application [4]. There should be the development of

processes involving H_2 , O_2 , CO , CO_2 , NH_3 as a direct source of atoms H, O, C and N in the production of fine chemicals. The quantitative measure of the environmental acceptability of chemical technology is E factor, which is defined as the ratio of waste weight to the weight of a target product. Waste includes everything that is not a target product [4].

This work is devoted to further experimental research of hybrid plasma-catalytic system with the gas discharge generator of the wide-aperture flow of non-isothermal plasma. Some features of the kinetics in plasma of a wide-aperture rotating gliding discharge are investigated using numerical modeling. The comparison between the model of chemical kinetics during thermochemical reforming and the results of experimental research is provided.

2. Methods and experimental setup

Partial oxidation reforming of hydrocarbons is the most energy-efficient and economical reaction pathway for use in the conversion methods that utilize electric energy. This is especially important for the plasma-chemical reforming methods that use electric energy. The reason for this is that in modern power plants the production of one unit of electrical energy requires three units of chemical energy. Fig. 1 shows the schemes of two hydrocarbon conversion approaches present in plasma-chemistry: plasma reforming and plasma-catalytic reforming.

In plasma approach, the hydrocarbon and oxidant are introduced directly into the discharge area after which the activated mixture is injected into the reaction chamber. Such approach leads to the appearance of the exothermal reactions in the discharge area, which increase the rotational temperature of heavy plasma components and cause the decrease of plasma non-isothermality and drop in the yield of desired products [5]. In plasma-catalytic approach, only a part of the oxidant is introduced into the discharge area and the activated oxidant is injected in a form of radicals into the reaction chamber, which has the separate injection of hydrocarbon. This approach results in the generation of the non-isothermal plasma, which provides the increased selectivity of desired product. Discharge can be used to activate a part of the oxidant while the rest of the oxidant is introduced into the reaction chamber together with the hydrocarbon. The plasma-catalytic approach uses the active species (OH, H, O), which are produced inside plasma from the non-toxic and/or safe reagents, to initiate the chain reactions of renewable biomass conversion at a low temperature ($\approx 250\text{--}350\text{ }^\circ\text{C}$).

A discharge chamber, which is attached to the reaction chamber [6], is designed for the plasma-catalytic approach to the hydrocarbon conversion. Plasma is generated using wide-aperture rotating gliding discharge [7, 8]. The discharge is powered using DC power source. Fig. 2 shows the discharge chamber,

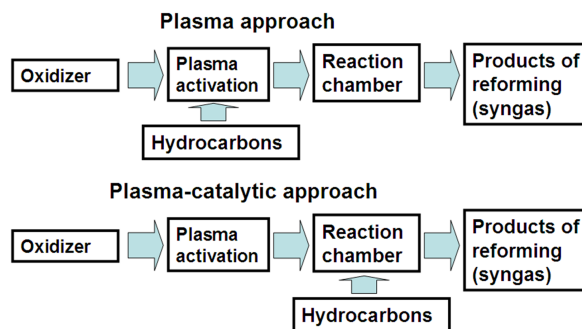


Figure 1. Schematic representation of plasma and plasma-catalytic approaches to hydrocarbon conversion.

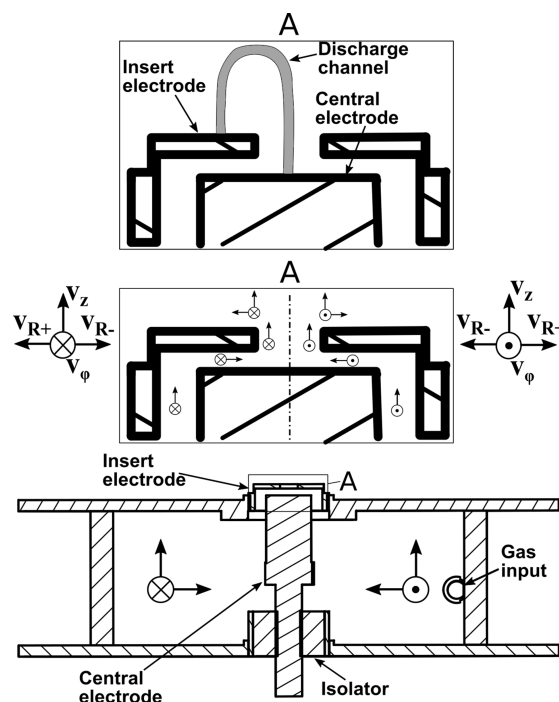


Figure 2. Scheme of discharge chamber, directions of gas flows and wide-aperture rotating gliding discharge during plasma-catalytic reforming of hydrocarbons.

gas flow directions, and wide-aperture rotating gliding discharge.

96% ethanol was used as a model hydrocarbon during the plasma-catalytic reforming of hydrocarbons, atmospheric air, which was supplied using a compressor, was used as an oxidant. The system for plasma-catalytic reforming of hydrocarbons into the synthesis gas was designed for the output power of 25 kW and tested using 53.3 g min^{-1} (25 kW) ethanol flow. The experimental laboratory studies of hybrid plasma-catalytic reforming of ethanol were conducted at lower output power. Optical emission spectroscopy was used for the study of plasma. Gas chromatography was used for the study of gas-phase products.

3. Experimental results

The efficiency of the reforming system in terms of hydrogen production can be evaluated from its hydrogen

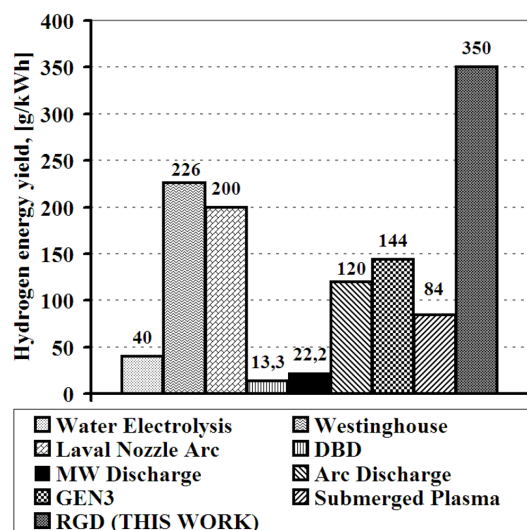


Figure 3. The hydrogen energy yield of reforming of ethanol for different methods of hydrogen production using electrical energy.

energy yield. It corresponds to the flow of produced H_2 divided by the electric power spent on plasma generation and is commonly expressed in $g kWh^{-1}$. Hydrogen energy yield provided in this work corresponds to $4.3 g min^{-1}$ (2 kW) ethanol input and 24 W input into plasma generation. Based on H_2 concentration in reforming products provided by gas chromatography, the flow of produced H_2 was $\approx 8.4 g h^{-1}$. Resulting hydrogen energy yield was $\approx 350 g kWh^{-1}$.

Fig. 3 shows the comparison between the hydrogen energy yields and conversion efficiency of the hybrid plasma-catalytic reforming of ethanol (this work) and other methods of hydrogen production that utilize electrical energy: Water Electrolysis [9], Westinghouse [10], Laval Nozzle Arc [11], DBD [11], MW Discharge [11], Arc Discharge [12], GEN3 [13], Submerged Plasma [14].

The hydrogen energy yield of hybrid plasma-catalytic ethanol reforming is the highest in comparison with the other methods [9–14]. The ratio of the reactor power output to its volume is approximately $100 kW l^{-1}$. The hybrid plasma-catalytic approach can be used to solve the existing problems of the traditional renewable biomass reforming methods.

4. Results of numerical modeling

The kinetics of plasma-chemical processes in the plasma of wide-aperture rotating gliding discharge and chemical kinetics of ethanol conversion into synthesis gas were calculated via ZDPlasKin program code [15]. ZDPlasKin allows the simulation of plasma kinetics from the preliminary set of input parameters of the studied system (temperature, pressure, the initial concentration of reagents etc.). During the calculation fulfilled for the plasma of moist air, the database used for the calculation comprised of 900 chemical and electron-molecular reactions involving

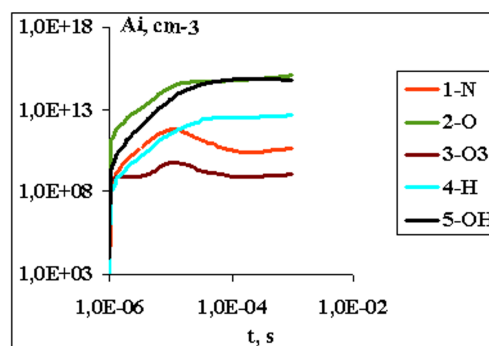


Figure 4. Typical time dependencies of the concentrations of N, O, O_3 , H, OH at 2500 K, $400 V cm^{-1}$ for $0.9Air/0.1H_2O$ gas.

83 components. Time sampling step was 10^{-12} s. The time interval for the calculation of changes in the concentration of plasma components at the time evolution was 10^{-3} s. It is significantly higher than the time of the exposure of gas to the current channel of gas discharge considering the experimental data: the rate of gas flow was $\approx 10^3 cm s^{-1}$, wide-aperture rotating discharge is a transverse discharge with the diameter of current channel $\approx 10^{-1} cm$, respectively the time of gas exposure to the current channel is $\approx 10^{-4}$ s.

This list of reactions is based on a mechanism proposed in [16]. Because the experimental data confirms that the rotational temperature, determined using optical emission spectroscopy, is high enough ($\approx 2500 K$), all the reaction of the oxidation of atmospheric nitrogen were included to the list of reactions. The mechanism was complemented by the reactions, which involved such species as N_2O , NO_2 , NO_3 , N_2O_5 , N_2O^+ , NO_2^+ , N_2O^- , NO_2^- , NO_3^- , the rates of chemical and electron reactions were taken from [17]. According to the experiment, the electric field in the plasma zone varied in the range of $100-500 V cm^{-1}$, which necessitated the addition of dissociation reactions by electron impact of such components as H_2O , NO_2 , and HO. At the same time, in this type of conversion, the air with the addition of H_2O is the plasma gas, which is why the list of reactions involving H_2O and its derivatives was added to this mechanism. The list of reactions involving H_2O was composed using [18].

Typical time dependencies of the concentrations of N, O, O_3 , H, OH, which are calculated for the plasma of gas discharge – $[Ai](t)$, are shown in Fig. 4. Provided dependences $[Ai](t)$ show that during the experiment the setting time of the fixed values $[Ai]$ of O, H, and OH radicals corresponds to $\approx 10^{-4}$ s, and the degree of the dissociation of molecular oxygen O_2 and water H_2O is $\approx 10^{-2}$.

During the calculation of chemical kinetics in the reactor zone of the experimental system [7], the database contained 130 chemical reactions involving 30 components [19]. Time sampling step was 10^{-6} s. The time interval for the calculation of changes in the concentration of plasma components was 10^{-3} s. The time

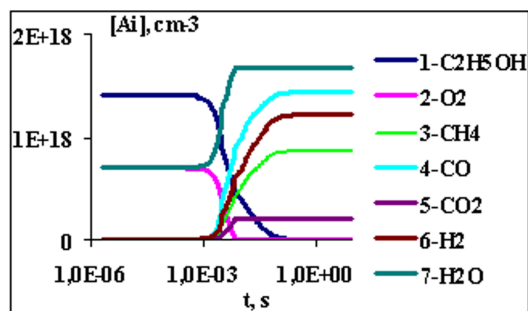


Figure 5. Time dependence of concentrations for the thermochemical conversion of ethanol at 1300 K for $1C_2H_5OH/0.5O_2/0.5H_2O/2N_2$ initial mixture.

interval for the calculation of changes in the concentration of the gas components at the outlet of the reactor zone (Fig. 5) was equal to 10 seconds.

Time dependence of concentrations for the thermochemical partial oxidative conversion of ethanol indicates the existence of two conversion stages: with oxygen and without oxygen. Fig. 5 shows that the ratio between H_2 and CO changes in time.

Product concentrations were calculated for 523–823 K temperature range. Syngas ratio depended on the temperature and changed from 1.6 to 0.7.

5. Conclusions

1. Plasma-catalytic approach is an emerging alternative to the traditional conversion technologies. Plasma-catalytic approach uses active species generated in the plasma from non-toxic and/or non-hazardous reagents to initiate the chain reactions of renewable biomass conversion at low temperature (≈ 500 – 600 K).

2. Plasma-catalytic approach confirms the concept of sustainable development with the production of small amounts of waste.

3. Studies of chemical kinetics revealed differences in the mechanism of the conversions that result in significant changes in syngas ratio ($[H_2]/[CO]$).

4. Partial oxidative conversion of ethanol has two conversion stages: with oxygen and without oxygen.

5. Temperature dependences of the conversion products concentrations point at the change of syngas ratio caused by the rise of CO concentration with the increase of reforming temperature. In addition, CH_3CHO production correlates with sharp oxidant (O_2) concentration decrease in the system, indicating that reforming is conducted through the chain reactions.

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