KINETICS OF PYROLYSIS OF ETHANOL-AIR MIXTURE

O.M. Tsymbaliuk, V.Ya. Chernyak, E.V. Martysh, T.S. Donchenko, A.O. Fayzulin

[1]Taras Shevchenko National University of Kyiv, Kyiv, Ukraine

E-mail: tsimbaluk.alexander@gmail.com, chernyak_v@ukr.net

The article presents the results of studying the high-temperature zone (about 1100 K) of ethanol pyrolysis at atmospheric pressure. Physical model is proposed for this zone and its validation is done. ZDPlaskin software package was used for numerical modeling of chemical reactions in this zone. It was shown with obtained results that pyrolysis has several stages and molecular oxygen has strong influence on the process staging. Oxygen influence on the chemical reactions during reforming was studied. The main channels of generating of ethanol reforming aimed components such as H_2 and CO, were examined. The most important reforming reactions are determined.
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INTRODUCTION

There are two main approaches for the conversion of liquid hydrocarbons in plasma chemistry: plasma and plasma-catalytic. During the first approach the conversion takes place because of the plasma chemical transformations in plasma itself. All required reagents, such as hydrocarbon and various gases (H_2O, O_2, CO_2, air) are injected into the plasma. The peculiarity of the second approach is that main conversion transformations occur in the high-temperature chemical reactor. Plasma is used as a catalyst of the chemical transformations. The distinct reforming products and their mixtures can be used as plasma gases. At the same time, the plasma can be used to activate only a part of the reagents.

Various reforming techniques were examined under the experimental studies [1, 2]. The reagents composition at the system inlet and outlet was controlled and the plasma emission spectra were measured during the experiments. So, these measurements do not give a complete pattern what is going on inside the reactor volume. Due to this, the numerical modeling of the kinetics is required for the more complete understanding of the physical and chemical processes in plasma and plasma-catalytic systems.

Nowadays, the numerical kinetics of conversion is more researched for the plasma reforming, while for the plasma-catalytic approach it was not conducted. This is despite the knowledge that it is more promising based on energy efficiency and productivity [3]. This is why this work considers the available approaches to the numerical modeling of the conversion of the hydrocarbon vapors in the plasma-catalytic system with the vortex injection of the reagents. The model hydrocarbon was ethanol, which is a promising "green fuel".

1. PHYSICAL MODEL

Numerical modeling of the kinetic is performed for the ethanol reforming in the plasma-catalytic systems. Fig. 1 presents the scheme of one of the experimental systems, which are used for studying the liquid hydrocarbon reforming in the plasma-catalytic scheme [4].
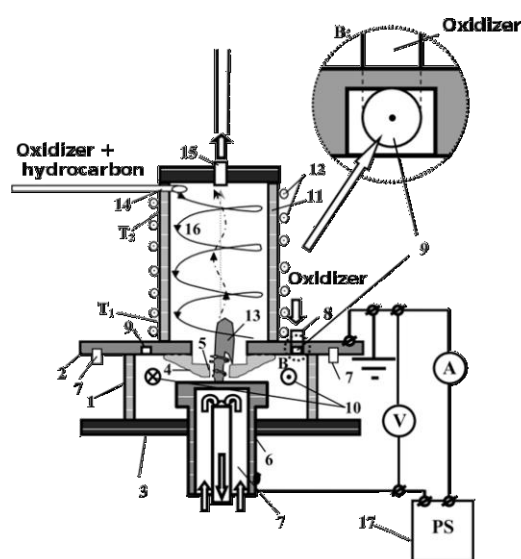

Fig. 1. Scheme of experimental setup: 1 – quartz chamber; 2, 3 – flanges; 4,5 – sleeves; 6 – t-shaped electrode; 7 – water cooling; 8 – oxidant inlet; 9 – directing channel; 10 – gas flow direction; 11 – pyrolytic (reaction) chamber; 12 – heater; 13 – plasma torch; 14 – hydrocarbon inlet; 15 – reforming products outlet; 16 – gas flow direction; 17 – power source

The main goal of the numerical modeling of kinetics is the study of the processes that take place in the pyrolytic (reaction) chamber volume. The mixture of the hydrocarbon vapors and a part of the oxidant was introduced into the chamber tangentially to its wall via the inlet 14 (see Fig. 1.) and formed "tornado"-type reverse vortex flow. Rotating mixture descended to the bottom of reaction chamber, moved to the axis, where plasma-activated oxidant is introduced into reaction chamber, and then the mixture moves upwards and leaves through the aperture 15. Thus, the volume of reaction chamber can be separated into several zones: chemical reforming process or pyrolytic part; plasma part; main reforming zone.

The first zone has constant high temperature, the mixture of the initial hydrocarbon and a part of the oxidant is injected into this zone.

The second zone is filled with the discharge plasma. A part of the oxidant is injected and activated in this zone. The peculiarity of the kinetics calculations in plasma zone is ability to set reduced electric field according to the experimentally measured field and a gas temperature, which can be evaluated from the plasma emission spectra [5].

The third zone is the main reaction zone of the reactor, which receives the final products of the first and second zones. The main processes of the initial hydrocarbon reforming take place in this zone.

This work contains the numerical modeling of the kinetics in the first zone. 130 chemical reaction between 30 components are examined [6]. Because there is no plasma in the studied zone, the investigation can be limited to the chemical reactions. The mixture temperature in this zone was 1100 K and considered to be stable. The modeling time was in the range of $10^{-2} \dots 1$ s. This range was selected because it is close to the time that the mixture spends in the conditions of the first zone in the hybrid plasma-catalytic reactors with power less than 50 kW.

ZDPlaskin software package was used for numerical modeling of chemical reactions in this zone [7, 8]. This software code allows investigating the evolution of component concentrations in time for the non-thermal plasma with the freely set processes between the components while taking into account the chemical reactions.

2. RESULTS AND DISCUSSION

Fig. 3 shows the results of the numerical modeling of the components concentration change with time. The modeling was performed at T=1100 K, P = 1 atm, and with 10^{-5} s discreet modeling time step. The ratio between the ethanol and oxygen was 4 to 1. This ratio was chosen because during the plasma catalytic reforming part of the oxidant is introduced with ethanol and other part is activated by plasma and only then it is mixed with the main mixture. Only part of the oxidant has to be taken into account because only the first zone is modeled.

The changes in the dependence of H_2 and CO concentrations on time are shown in Fig. 2. Rather sharp decrease (approximately during 0.15 s) of O_2 can also be seen. The concentrations of H_2, CO and H_2O start to increase with the beginning of the decrease of O_2 concentration. After the decrease of oxygen concentration by an order of magnitude the concentrations of H_2O and CO achieve stable value, and almost do not change after that.

As we can see from Fig. 2, the decrease of O_2 concentration correlates with the increase of H_2O concentration. Aside from that, after the significant decrease of O_2 concentration the increase of H2O concentration stops and remains stable. This allows us to assume that H_2O is one of the final products that are generated using O_2.

From the conducted analysis of the rate of the chemical reaction we can conclude that the decrease of O_2 concentration is caused by the reactions:

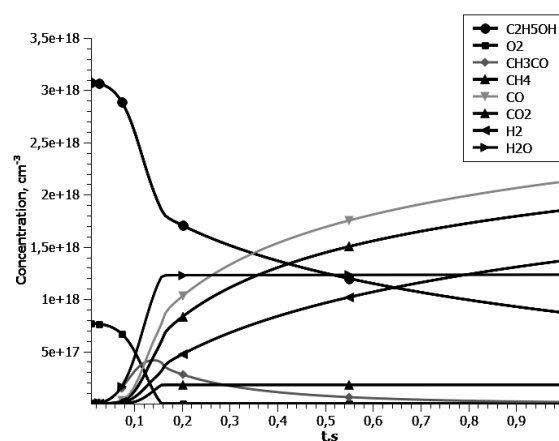$$C_2H_5OH + O_2 \rightarrow CH_3CHO + HO_2. \qquad (1)$$

Fig. 2. The results of the numerical modelling of the dependence of some components concentrations on time

The domination of this reaction explains the decrease of HO_2 concentration after the decrease of O_2 concentration. After the generation, HO_2 becomes an important link in the reforming reaction chain.

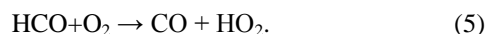For the whole time the most important H_2 generation reactions are :

$$CH_2O + M \rightarrow CO + H_2 + M. \qquad (2)$$
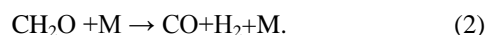
Also important is H component. The main channels of its generation are the reactions like:

$$CH_3O + M \rightarrow CH_2O + H + M, \qquad (3)$$
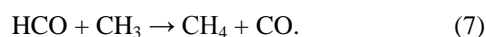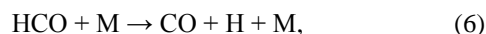
$$HCO + M \rightarrow CO + H + M. \qquad (4)$$
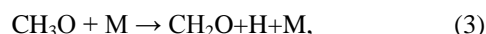
But before 0.15 s the dominant generation reaction is (5), and after that (6).

CO generation can be also separated into two stages. Before the stage of sharp O_2 concentration decrease the main reaction for CO generation is:

$$HCO + O_2 \rightarrow CO + HO_2. \qquad (5)$$

After the decrease of O_2 concentration, following reactions become dominant:

$$HCO + M \rightarrow CO + H + M, \qquad (6)$$

$$HCO + CH_3 \rightarrow CH_4 + CO. \qquad (7)$$

HCO is also the important component for the generation of CO during the whole time. The main channels of its generation are:

$$CH_3CHO \rightarrow CH_3 + HCO, \qquad (8)$$

$$CH_2O + CH_3 \rightarrow CH_4 + HCO. \qquad (9)$$
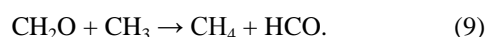
CONCLUSIONS

The numerical modeling of the high-temperature pyrolysis of the reach ethanol and oxygen mixture (4 to 1 ratio) was performed with usage of ZDPlaskin software complex. The obtained results were analyzed.

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According to modeling results the reforming has several stages.

The active radicals are produced during the first stage via the reactions of C_2H_5OH with oxygen. Their products turn after several transformations into H_2O_2. It fractures onto OH radicals and they create new link of reaction chain.

The period of rapid decrease of oxygen concentration can be considered as the second stage. It can be characterized as a start of oxidizing dry reforming. The role of H_2O_2 during this reforming stage should be noted. This component is the important link that supports the reforming chain. The period after the almost complete "burning" of oxygen, during which the sufficient amount of water is produced (which can point out at the beginning of steam reforming) can be considered as the third stage.

The disappearance of oxygen decreases the production rate of the desired reforming components.

REFERENCES

1. A. Czernichowski. Further development of plasma sources: the glidarc-iii/ A. Czernichowski, M. Czernichowski // *Pap. 17th International Symposium on plasma Chemistry*. 2005, p. 1-4.
2. O.V. Solomenko, O.A. Nedybaliuk, V.Ya. Chernyak, V.V. Iukhymenko, Iu.P. Veremii, K.V. Iukhymenko, E.V. Martysh, V.P. Demchina, I.I. Fedirchyk, D.S. Levko, O.M. Tsymbalyuk, A.I. Liptuga, S.V. Dragnev. Hybrid plasma-catalytic reforming of ethanol aerosol // *Problems of Atomic Science and Technology*. 2015, № 1, p. 231-234.
3. V.Ya. Chernyak, O.A. Nedybaliuk, E.V. Martysh, et al. Plasma catalysis of chemical reactions// *Problems of Atomic Science and Technology*. 2014, № 6, p. 124-129.
4. O.A. Nedybaliuk, V.Ya. Chernyak, V.V. Kolgan, V.V. Iukhymenko, et al. Plasma-Catalytic Reforming of Liquid Hydrocarbons // *Problems of Atomic Science and Technology*. 2015, № 1, p. 235-238.
5. O.A. Nedybaliuk, O.V. Solomenko, E.V. Martysh, I.I. Fedirchyk. Plasma-liquid system with rotational gliding discharge with liquid electrode // *Problems of Atomic Science and Technology. Series "Plasma Physics"*. 2014, № 6 (20), p. 191-194.
6. A.N. Tsymbalyuk, D.S. Levko, V.Ya. Chernyak, E.V. Martysh, O.A. Nedybalyuk, and E.V. Solomenko. Influence of the Gas Mixture Temperature on the Efficiency of Synthesis Gas Production from Ethanolin a Nonequilibrium Plasma // *Technical Physics*. 2013, v. 58, № 8, p. 1138-1143.
7. S. Pancheshnyi, B. Eismann, G.J.M. Hagelaar, L.C. Pitchford. Computer code ZDPlaskin // University of Toulouse, LAPLACE, CNRS-UPS-INP, Toulouse, France, 2008. *http://www.zdplaskin.laplace.univ-tlse.fr*.
8. R. Snoeckx, R. Aerts, X. Tu, A. Bogaerts. Plasma-Based Dry Reforming: A Computational Study Ranging from the Nanoseconds to Seconds Time Scale // *J. Phys. Chem. C*. 2013, v. 117 (10), p. 4957-4970.

КИНЕТИКА ПИРОЛИЗА СМЕСИ ЭТАНОЛ-ВОЗДУХ

А.Н. Цымбалюк, В.Я. Черняк, Е.В. Мартыш, Т.С. Донченко, А.А. Файзулин

Приведены результаты исследования зоны высокотемпературного (около 1100 К) пиролиза этанола при атмосферном давлении. Для этой зоны предложена физическая модель, и дано её обоснование. Проведено численное моделирование течения химических реакций с помощью программного пакета ZDPlaskin. Используя полученные результаты, показано, что пиролиз протекает в несколько стадий. Показано значительное влияние молекулярного кислорода на стадийность процесса. Исследовано его влияние на ход химических реакций в процессе реформирования. Рассмотрены основные каналы генерации целевых компонентов реформирования этанола, а именно H_2 и CO. Определены наиболее важные реакции реформирования.

КІНЕТИКА ПІРОЛІЗУ СУМІШІ ЕТАНОЛ-ПОВІТРЯ

О.М. Цимбалюк, В.Я. Черняк, Є.В. Мартиш, Т.С. Донченко, А.О. Файзулін

Наведено результати дослідження зони високотемпературного (приблизно 1100 К) піролізу етанолу при атмосферному тиску. Для цієї зони запропонована фізична модель та дано її обґрунтування. Проведено числове моделювання перебігу хімічних реакцій за допомогою програмного пакету ZDPlaskin. Використовуючи результати, які отримані, показано, що піроліз протікає в декілька стадій. Показано значний вплив молекулярного кисню на стадійність процесу. Досліджено його вплив на перебіг хімічних реакцій в процесі реформування. Розглянуто основні канали генерації цільових компонентів реформування етанолу, а саме H_2 та CO. Визначено найбільш важливі реакції реформування.