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Theoretical study of partial oxidation of methane by non-equilibrium oxygen plasma to produce hydrogen rich syngas

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ABSTRACT

Modeling study of the partial oxidation of methane and methane-steam blend in a model flow reactor with given length in order to produce hydrogen rich syngas via activation of oxygen by specially arranged electric discharge is presented. It has been shown that the minor length of methane and methane-steam conversion into syngas is achieved at reduced electric field of 10 Td, when excited $O_2(a^1\Delta_g)$ and $O_2(b^1\Sigma_g^+)$ molecules are preferably generated in a discharge. The major yield of syngas due to methane partial oxidation takes place at CH_4/O_2 equivalence ratio $\phi = 3$ and can be as large as 89%, whereas the greatest ratio of H_2 mole fraction to CO one in syngas can be achieved at $\phi = 4$, when the yield of syngas is notably smaller ~69–76%. The addition of steam to methane delays the conversion process and does not allow increasing the syngas mole fraction and H_2/CO ratio significantly at the flow reactor exit. The estimates of energy efficiency of the process showed that the major value of energy returned on energy invested is achieved for the plasma-chemical approach based on methane partial oxidation or a combination of partial oxidation with steam conversion.

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Introduction

One of the principal problems of modern civilization is the reduction of fuel consumption in engines of various transportation systems, power plants and industrial processes. This can be achieved via the usage of fuels with higher mass heating value and increasing combustion rate compared to traditional hydrocarbon fuels widely utilized, today, for heat and electricity production. Nowadays, hydrogen and

synthesis gas (or syngas) consisting mostly of H_2 and CO are considered as perspective alternative fuels [1,2]. In fact, for example, the mass heating value ΔH_T of hydrogen is equal to 121 kJ/g, whereas for methane we have $\Delta H_T = 50$ kJ/g. Syngas with high hydrogen content also possess higher mass heating value than methane. Therefore, in order to ensure the identical temperature in the combustion exhaust upon burning of syngas with air, one can use the leaner fuel/air mixture compared to methane burning and, thus, reduce fuel consumption. The higher is the concentration of hydrogen in

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Nomenclature

Roman symbols

C_i	mass fraction of species i ,
E	electric field strength, [V/cm]
E_s	energy put into the gas in the discharge at normal conditions: $P_0 = 1$ atm and $T_0 = 298$ K, [J/nm ³]
E/N	reduced electric field, [Td] (1 Td = 10^{-17} V cm ²)
ΔH_T	mass heating value, [kJ/g]
ΔH_{syngas}	energy released during combustion of produced syngas in air, [kJ/mol]
L_{in}	induction zone length, [cm]
N	number density of molecules, [cm ⁻³]
P_0	pressure, [atm]
Q_h	energy spent on heating the mixture from 300 K to the value T_0 , [kJ/mol]
Q_c	energy released during the conversion process, [kJ/mol]
$Q_{\text{in}} = Q_h + E_s$	energy spent on reforming process, [kJ/mol]
t	time, [s]
T	gas temperature, [K]
T_0	initial temperature of CH ₄ –H ₂ O and O ₂ flows, [K]
T_e	equilibrium temperature, [K]
T_{ex}	temperature at flow reactor exit, [K]
T_d	temperature of the oxygen plasma at the discharge outlet, [K]
T_{mix}	gas temperature just after the mixing of CH ₄ –H ₂ O and oxygen plasma flows, [K]
T_v	vibrational temperature of O ₂ (X ³ Σ _g ⁻) molecules at the discharge outlet, [K]
U	velocity, [m/s]
U_{in}	gas velocity at flow reactor entrance, [m/s]
x	spatial coordinate along the flow reactor, [cm]

Greek symbols

$\beta = \gamma_{\text{H}_2}^{\text{ex}} / \gamma_{\text{CO}}^{\text{ex}}$	ratio of H ₂ and CO mole fractions at flow reactor exit,
$\beta^e = \gamma_{\text{H}_2}^e / \gamma_{\text{CO}}^e$	ratio of H ₂ and CO equilibrium mole fractions,
$\delta = (C_{\text{H}_2}^{\text{ex}} + C_{\text{CO}}^{\text{ex}}) / C_{\text{CH}_4}^0$	ratio of mass of produced syngas to mass of reformed CH ₄ ,
$\varepsilon = \gamma_{\text{H}_2\text{O}}^0 / \gamma_{\text{CH}_4}^0$	ratio of H ₂ O and CH ₄ mole fractions at flow reactor entrance,
γ_i	mole fraction of species i ,
γ_i^e	equilibrium mole fraction of species i ,
γ_i^{ex}	mole fraction of species i at flow reactor exit,
γ_s	mole fraction of syngas at flow reactor exit,
γ_s^e	equilibrium mole fraction of syngas,
$\eta = \frac{\Delta H_{\text{syngas}} \gamma_s}{Q_{\text{in}}}$	energy efficiency of the process (energy returned on the energy invested),
ϕ	fuel to oxidizer equivalence ratio.

syngas, the greater is the mass heating value of such synthetic fuel. The ratio of the concentrations of hydrogen and carbon oxide in syngas depends on the method of its production and can vary within rather broad limits.

In addition, the velocity of flame propagation in the syngas–air mixture even at H₂/CO = 25/75 is noticeably higher than that in the methane–air mixture [2] (the velocity of flame propagation in the fuel-lean syngas–air mixture is the same as in the methane–air mixture only in the case of a low fraction of hydrogen in syngas H₂/CO = 5/95), syngas combustion can be expected to be stable even in a leaner mixture than in the case of methane combustion, i.e., it is possible to provide a smaller fraction of NO and CO in combustion products. That is why for past years a great attention has been paid to the development of combustors operating on syngas [3].

One of the most promising ways to obtain syngas with high H₂/CO ratio is the partial oxidation of hydrocarbons via subjecting the fuel-rich hydrocarbon/oxygen(air) mixture to non-equilibrium specially arranged electric discharge [4–8]. Such a discharge produces highly reactive atoms and radicals or excited molecules that can enhance chain mechanism of hydrocarbon oxidation and, thus, intensify the conversion of primary hydrocarbon to syngas. The conversion of organic fuels to syngas is frequently called as fuel reforming. The key problem in fuel reforming is the achievement of highest energy efficiency in the conversion process. The conversion level of any hydrocarbons to syngas reaches the essential value only after the ignition event. Therefore, it is needed to provide a successful ignition of the fuel-rich hydrocarbon–oxygen(air) mixture at an appropriate distance in a flow reactor used for fuel reforming. Moreover, this process must be occurred with minor energy consumption and must allow one to ensure the composition of syngas with major mass heating value. Nowadays, plasma-assisted fuel reforming is considered as a very promising technology both for onboard generation of hydrogen for fuel cell vehicles and for the production of syngas in a large scale for its further usage to produce heat and electric energy or to utilize it for preparing fuel blends [7,9–13].

It should be emphasized that, for past years, a large number of researches were focused on the analysis of the intensification of ignition/combustion and fuel reforming by thermally equilibrium and thermally non-equilibrium plasmas (see, for example, overviews [14–16] and original works [17–32]). Such plasmas can be produced by various types of discharges [15,16]. It is known that the composition of plasma, generated by an electric discharge, depends on specific energy put into the gas, reduced electric field E/N (E is the electric field strength and N is the number density of molecules) and, certainly, the composition and parameters of the mixture subjected to an electric discharge [15,32]. Depending on the E/N value, the discharge energy can preferably spent on heating the gas or on the excitation of vibrational and electronic states of molecules and production of highly reactive atoms and radicals.

This paper does address the numerical analysis of the efficiency of plasma-chemical methods used for the conversion of hydrocarbons into syngas in a flow reactor as well as an extensive study of kinetic processes responsible for methane or methane–steam mixture partial oxidation stimulated by non-equilibrium oxygen discharge plasma comprising such highly reactive species as O₂(a¹Δ_g) and O₂(b¹Σ_g⁺) molecules and O atoms.

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