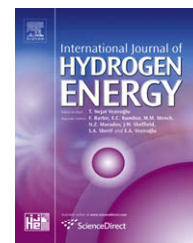


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Kinetic model of homogeneous thermal decomposition of methane and ethane

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ABSTRACT

In this paper, the homogeneous decomposition of methane and ethane is modeled in a well stirred flow reactor. The kinetics of this process is represented by a reaction mechanism of 242 reactions and 75 species, based on a mechanism developed for hydrocarbon combustion and soot formation. It is shown that this model correctly predicts the hydrogen yield from pyrolysis in a temperature range of 600–1600 °C, and pressure range of 0.1–10 atm. Furthermore, the effect of temperature, pressure and residence time on the amount of hydrogen produced from the decomposition of methane, ethane, natural gas, and a mixture of methane and argon is studied. The model predicts that the use of ethane or its addition to methane increases the speed of hydrogen production at low temperatures and pressures. The addition of a noble gas like argon also increases the yield of hydrogen at high pressures.

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1. Introduction

The use of hydrogen as fuel has been a major topic for energy research mainly because of environmental concerns and rising gas prices [1,2]. Hydrogen is a clean fuel, and reduces the amount of greenhouse gas emission considerably [3]. It can be produced from different substances, such as water [4,5] and biomass [6–8], however, due to economic and technical constraints, its main source is currently natural gas (NG) [9,10]. The base methods of hydrogen production from natural gas are reforming and pyrolysis. Steam reforming is the most established process in large-scale production of hydrogen [11,12]. It involves an endothermic reaction between steam and natural gas, producing carbon dioxide as a by-product. The separation of carbon dioxide from hydrogen and its subsequent sequestration are complex and increase the cost of the overall process. An alternative production method is the

direct thermal decomposition of natural gas [13–18]. This method eliminates the production of carbon dioxide. It is therefore more appropriate with regard to environmental concerns, and also simplifies the overall process. Comparison between these two technologies shows that pyrolysis is an appropriate method for hydrogen production and an attractive alternative to the established reforming process [19,20].

In order to produce a reasonable amount of hydrogen, thermal decomposition of natural gas is performed either at high temperatures [20,21] or with a catalyst [22–24]. Correct prediction of the kinetics of these cases requires the gas phase of the process to be properly modeled. The kinetic model of the gas phase of the decomposition of light hydrocarbons has been studied in multiple cases as part of hydrocarbon fuel combustion [25–29]. However, it should be noted that due to the nature of the combustion reactions, the mechanisms of decomposition in these studies were developed with the

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oxidation of hydrocarbons, at high temperatures. The reaction mechanisms for the pyrolysis of methane and ethane were investigated by Hidaka et al. [30,31]. While these mechanisms have been validated for the pyrolysis process, and not as part of the combustion process, they do not include polycyclic aromatic hydrocarbons (PAHs). These gas species are presumed to be the precursor of solid carbon formation [18,32] and have therefore been taken into consideration in the current study. Another mechanism available for homogeneous decomposition of natural gas is the one presented by Gupta et al. [33] for low temperature pyrolysis (600–900 °C) in fuel cells, with around 1150 elementary reactions among 190 species. A drawback of this mechanism is the significant increase in computation time due to the large number of reactions and species. In the present paper, the homogeneous decomposition of methane, ethane, and natural gas is modeled with a relatively small number of elementary reactions, including polycyclic aromatic hydrocarbon species. The model predicts the hydrogen yield with a good accuracy for temperatures ranging from 600 to 1600 °C, and pressures between 0.1 and 10 atm. The model is then used to study the effect of temperature, pressure and residence time on hydrogen yield from pyrolysis of methane, ethane, natural gas, and a mixture of methane and argon in a well stirred flow reactor.

2. Model description

The reactor considered in this study is a well stirred flow reactor at constant temperature and pressure. The time-dependent continuity equation for each gas species in this reactor is expressed as follows:

$$\frac{dY_k}{dt} = \frac{1}{\tau}(Y_{k,in} - Y_k) + \frac{\dot{\omega}_k MW_k}{\rho}$$

where Y_k and $Y_{k,in}$ are the mass fractions of the k th species at the exit and inlet of the reactor, respectively, τ is the residence time, ρ is the overall density, and MW_k is the molecular weight of the k th species. Also $\dot{\omega}_k$ is the k th species molar production rate, which is calculated using the rates of different reactions in the mechanism.

The combination of continuity equations of all the species in the reactor forms a system of initial value ordinary differential equations (ODEs). This set of equations is solved with a variable coefficient ODE solver, Dvode [34], to determine the composition of the exhaust mixture in different times. At steady state, the left side of the continuity equation is equal to zero, and the exhaust mixture composition is obtained by solving the resulting set of algebraic equations. It can be observed from the continuity equation that the composition of the exhaust mixture depends on the residence time, while the temperature and pressure also affect this value through the species molar production rate and density.

3. Reaction mechanism

The elementary reactions considered in this study to model the homogeneous decomposition of natural gas are based on

those used by Appel et al. [26]. The latter mechanism was developed for modeling soot formation in the combustion of hydrocarbons. It includes the reactions of C_1 and C_2 species from the GRI-Mech 1.2 mechanism [35], the formation of higher linear hydrocarbons, and also reactions resulting in the formation of polycyclic aromatic hydrocarbons (PAHs) up to pyrene. Appel's mechanism is modified using available experimental data for homogeneous pyrolysis of methane and ethane [36,37]. The reactions containing species with oxygen atom are removed, leaving the remaining mechanism with 242 elementary reactions and 75 species. Furthermore, the rate of reaction $C_2H_5 + H = C_2H_4 + H_2$, which is one of the main reactions in ethane pyrolysis, is replaced by that used in the Hidaka mechanism [31]. As a result, the rate coefficient of this reaction is increased to about 22.5 times its initial value.

The rate coefficients of reverse reactions are calculated using the equilibrium constant and forward reaction rates. The thermodynamic data used are obtained from the soot formation model [26], based on the NASA-Lewis Thermodynamic Database [38], and are in the form of polynomials.

The kinetics of the decomposition of methane and ethane can be described using the resulting mechanism as follows. In the first step, the bonds between the atoms of methane and ethane are broken and the gases are decomposed to smaller molecules and radicals, such as H, H_2 , CH and other combinations of carbon and hydrogen. The main reactants and the resulting products are then combined in a set of reactions to form larger hydrocarbons up to C_6 , comprising the precursors of aromatic species. The next step is the formation of the first aromatic ring, which is a six-membered ring of benzene or phenyl radical, and is mainly produced from the recombination of propargyl radicals, as well as the reaction of $n-C_4H_3$ or $n-C_4H_5$ with acetylene. These single-ring molecules grow to polycyclic aromatic hydrocarbons (PAHs) through the H abstraction- C_2H_2 addition mechanism. It is noted that pyrene, which consists of four fused benzene rings, is the largest PAH species considered in this mechanism. The solid carbon particles are produced by the coalescence of two PAH molecules and the formation of dimers. Since the kinetics of the homogeneous decomposition of methane and ethane is aimed in this paper, the particle inception and further particle phase processes of the solid carbon are not considered.

4. Validation

The kinetic model of the decomposition of methane and ethane was validated by comparing the results with a number of experimental data from the literature [16,36,39–41]. Investigation in different temperatures shows that the current mechanism correctly predicts the amount of methane and ethane consumption. However, the concentration obtained for acetylene at high temperatures (>1375 K) is found to be overpredicted compared to the experimental results. Fig. 1 shows the comparison of experimental data [40,41] with the results of the kinetic model using the current mechanism and the Hidaka mechanism [30] at 1038 K and 0.58 atm, as a function of time. This figure shows that the results of the current

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