Numerical Study of a Laser-induced Ethane Pyrolysis in a Wall-less Reactor using a Reduced Kinetic Scheme

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1 Introduction

Ethylene, as the most important feedstock, is widely used in chemical industry to produce various rubbers, plastics and synthetics. A recent study found the IR-laser irradiation induced ethane pyrolysis yields 25% higher ethylene production rates compared to the conventional steam cracking method [1]. A schematic for such a reactor is illustrated in Fig. 1 in which a laser beam is used to induce the pyrolysis reaction along the axis of the reactor. The pyrolysis reaction is endothermic, and requires external heating source to maintain the process. Therefore, the conventional pyrolysis reactors employ a heating jacket to heat up the wall temperature. To achieve a high yields, it requires a quite large reacting zone, usually the inner wall surface of reactor. This causes extra thermal energy waste. Whereas the pyrolysis in a laser induced reactor occurs within the core region where the laser beam passes. This allows relatively high conversion rate within a small reactor. Thus, such kind reactors are also called wall-less reactor.

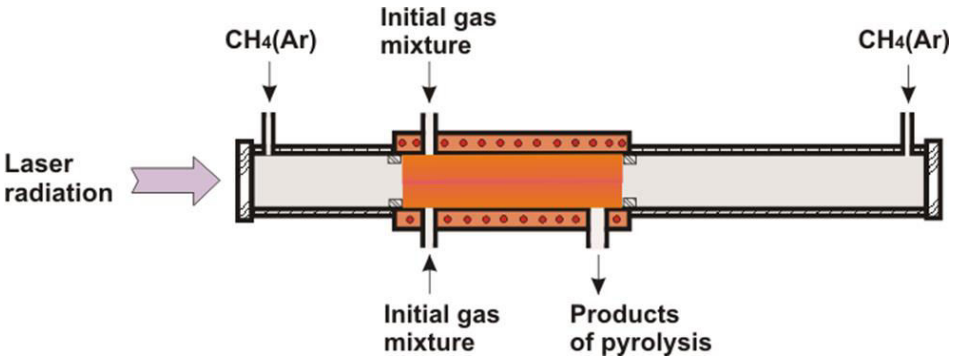

Figure 1. Schematic illustration of a laser-induced ethane pyrolysis reactor 190 mm long with 21 mm diameter, the initial gas mixture is C_2H_6/C_2H_4, CH_4 is the buffer gas to cooling the glass window at the right/left end of reactor, the reaction zone is in orange color is pre-heated up to 975 K.

Laser induced pyrolysis is initiated by the generation of radicals upon heating of the ethane, then, followed by ethane/ethylene autocatalytic reaction in which ethane is converted into ethylene and other light hydrocarbons. Radicals propagate radially to the edges. The main drawback of convectional steam cracking method includes e.g. coking, high molecular products waste and wastewater, high capital costs associated with the complex process of post-reaction separation of the reaction products.

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Whereas, the laser-induced the ethane pyrolysis method avoids these problem and have other advantages, e.g. lower wall temperatures, cheaper construction materials, no need of external cooling of products, smaller size reactors allow conversion of stranded gas. The current experimental researches on such kind of reactors are mainly in the laboratory scale. In order to scale up to the pilot and industrial plants, the 3D CFD numerical model is necessary for developing a compact, cost effective reactor for the pyrolysis of light hydrocarbons using lasers. Thereafter, the present work attempts to develop and validate a reduced chemical kinetic to describe ethane pyrolysis process, then implement it into the CFD code and perform a set of 3D CFD simulations on current laboratory scale reactor. Based on the numerical results, the flow field and temperature field and species concentration inside the reactor has been analyzed. The ethane conversion rate has been studied under various conditions, e.g. different laser power, different wall temperatures.

2 Numerical Models

2.1 Ethane pyrolysis kinetics

To study the ethane pyrolysis, the ethane oxidation has been widely studies under various conditions. The corresponding combustion chemical kinetics has been generated e.g. NIST database, GRI mechanism, Konnov's mechanism, Leeds mechanism, LLNL database and CNRS EXGAS database [2-6]. Some of them contain the ethane pyrolysis kinetics at high temperature. However, the majority of these pyrolysis kinetics have not been validated against the experimental data. A reduced chemical kinetic scheme for steam cracking ethane pyrolysis has been developed recently and validated against the measurement [7]. But, it's hardly applying this kinetics for laser induced pyrolysis because the major species H_2O which plays a role in steam cracking does not exist in the current reactor. Ideally, the detailed kinetic mechanism describing the most essential aspects of the mechanism of a chemical process are needed. But, the detailed mechanisms, which include hundreds of elementary steps, lead to unacceptable calculation time of 3D CFD simulations even on advanced supercomputers. Thus, a reduced chemical kinetic scheme which is equivalent in some respect to the initial system and describes in a similar way the changes in concentrations of the target substances for the modeled process is essential. Recently, a reduced chemical mechanism containing 10 species involving 15 reactions for laser induced ethane pyrolysis has been developed from experimental measurements and quantum-chemical calculations [8]. This kinetic autocatalytic scheme describing the radical chain reactions of ethane pyrolysis includes the chain initiation, chain propagation and chain termination. The kinetic rate constants for elementary reactions and thermodynamic properties for each species were taken from NIST database. The Lindemann theory was applied to calculate the kinetic constants for ethylene biradical reactions.

2.2 Computational models

Inside the reactor, the reacting system is multicomponent laminar gas mixture. To model such a system, the Navier-Stokes equations (mass conservation and momentum conservation) needs to be solved for the flow field and pressure field. To obtain the temperature field, the energy equation needs to take into account the incident irradiation source term as below.

$$\underbrace{\frac{\partial \rho E}{\partial t}}_{\text{unsteady}} + \underbrace{\nabla \cdot [\mathbf{V}(\rho E + P)]}_{\text{convection}} = \nabla \cdot \Big[\underbrace{k_{\text{eff}} \nabla \mathrm{T}}_{\text{conduction}} - \underbrace{\sum_j h_j \mathbf{J}_j}_{\text{Species diffusion}} + \underbrace{\tau_{\text{eff}} \cdot \mathbf{V}}_{\text{Viscous dissipation}} \Big] + \underbrace{S_n}_{\text{Source term}}$$

E is the total energy includes internal energy, kinetic energy and field energy contribution. The source term S_n coming from radiation is the algebraic sum of heat source from change in radiation intensity,

radiation absorption, in- and out- scattering and gas emission. The radiation transfer equation at position $\vec{r}$ in the direction $\vec{s}$ is written as

$$\nabla \cdot (I(\vec{r},\vec{s})\vec{s}) + (a+\sigma_s)I(\vec{r},\vec{s}) = an^2\frac{\sigma T^4}{\pi} + \frac{\sigma_s}{\pi}\int_0^{4\pi} I(\vec{r},\vec{s}')\,\Phi(\vec{s},\vec{s}')d\Omega'$$

I is the radiation intensity depending on location and direction, a is the absorption coefficient for a mixture, σ_s is the scattering coefficient, n is the refractive index, σ is the Stefan-Boltzmann constant, T is the local temperature, Φ is the phase function, Ω' is solid angle, $\vec{s}'$is the scattering direction vector. To obtain the variable-absorption-coefficient for the mixture, a weighted-sum-of-gray-gases model (WSGGM) is used, see below

$$a = \sum_{i=1}^{m} a_{\varepsilon,i} p K_i$$

where, $\alpha_{\varepsilon,i}$ is the temperature/composition dependent emissivity weight factor, p is the partial pressure, K_i is the composition dependent absorption coefficient for ith gray gas, m is the total number species in the mixture

2.3 Physical domain and boundary conditions

The copper tubular reactor has a diameter 21 mm with a length 190 mm and the wall thickness is about 2 mm. The 3D geometry of the reactor was constructed using the ICEM CFD mesh generator. The computational domain consists of about 5 million unstructured tetrahedral cells, see Fig. 2.

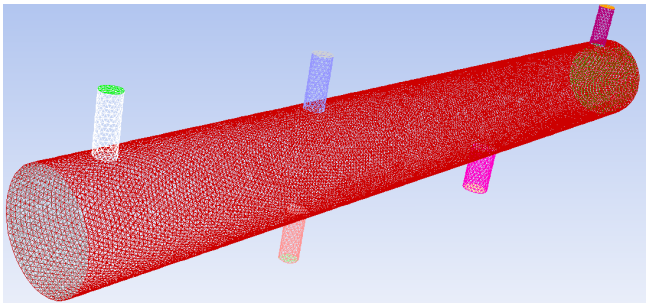

Figure 2. The 3D computational domain, consisting of ~5 million unstructured tetrahedral elements for a lab-scale reactor as illustrated in Fig. 1.

The left and right ends of reactor are glass windows (SiO2). Hence, the boundary condition of these two sides is specified as semi-transparent walls allowing the laser radiation passing through. The laser source was place outside the domain at the center of left end. The other surfaces were assigned as velocity inlet (buffer gas, reacting gas), pressure outlet (products) and opaque solid wall (cylindrical surface of the reactor).

The aforementioned reduced chemical kinetics, incident irradiation model, computational domain and boundary conditions were incorporated into the commercial CFD solver ANSYS Fluent ver. 15.0 [9]. A set of 3D CFD simulations have been performed on a HP-Z820 24-core 3.4 GHz workstation run in parallel.To ensure accuracy, the global Courant number was kept to less than 0.25 by choosing a fixed time step of 0.0001 s and a maximum number of 20 iterations for each time step.

3 Modeling Results and Discussions

3.1 Analysis on reaction pathway and sensitivity

To estimate the adequacy of the reduced scheme to a real process, the reaction pathway and sensitivity analysis have been conducted using CHEMKIN-Pro [10]. The results are displayed in Fig. 3. As shown in reaction pathway, the ethylene triplet biradical can attack ethane on either a carbon atom or a

hydrogen atom. The sensitivity analysis shows the chain propagation cycle (steps 3-5) as well as ethylene biradical generation and death (steps 13-15) greatly affects the ethane pyrolysis.

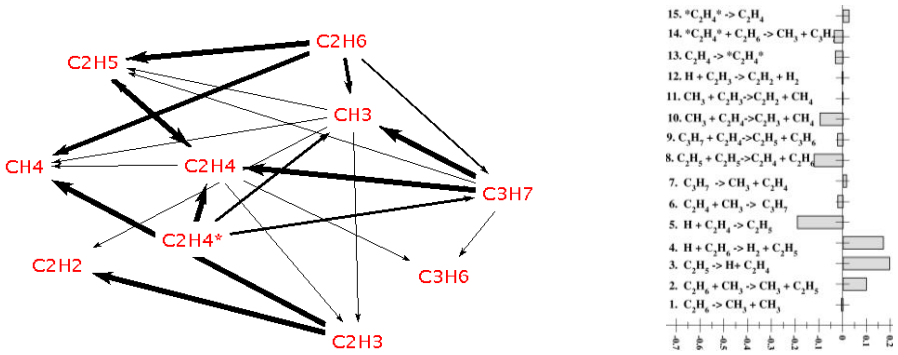

Figure 3. Kinetic analysis using reduced scheme, Left, reaction pathway; Right, normalized sensitivity coefficients at the temperature 1000 K and pressure 1 atm.

3.2 Ethane thermal pyrolysis without laser radiation

Prior to applying the laser radiation, a preliminary 3D CFD simulation that considers a solely thermal pyrolysis of ethane has been carried out to exam the temperature and flow field in the reactor. The instantaneous contours of temperature, heat of reaction, velocity, density and major species concentration have been illustrated in Fig. 4.

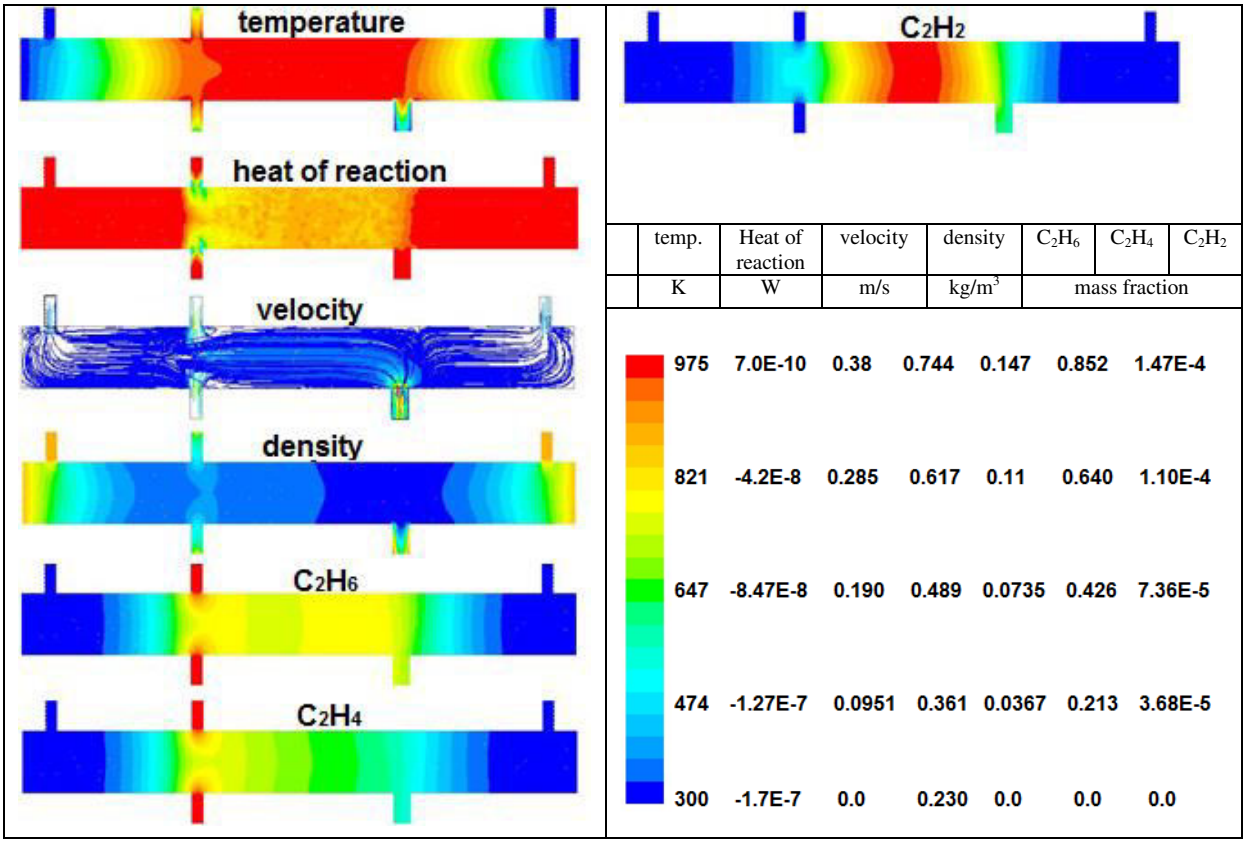

Figure 4 Instantaneous contour of temperature, heat of reaction, velocity, density and species concentration for thermal pyrolysis of ethane by heating the reaction zone to 975 K. The initial gas mixture (C_2H_4:C_2H_6, 85.3:14.7 wt%) flows into the reactor at a rate of 0.75 mg/s at temperature 600 K. The buffer gas stream consists of CH_4 flowing at 0.32 mg/s at temperature 300 K. The operating pressure for this reactor is about 1 atm. The cylindrical wall temperature in reaction zone (as indicated in Fig. 1) was pre-heated up to 975 K.

As can be seen, the region adjacent to wall of reaction has a relative lower heat of reaction due to the endothermic reaction of ethane pyrolysis. It means the major pyrolysis reaction occur at that zone since it has the highest temperature. The velocity streamline clearly demonstrates the initial gas and buffer gas flow into the reactor and push products out.

3.3 Laser-induced ethane pyrolysis

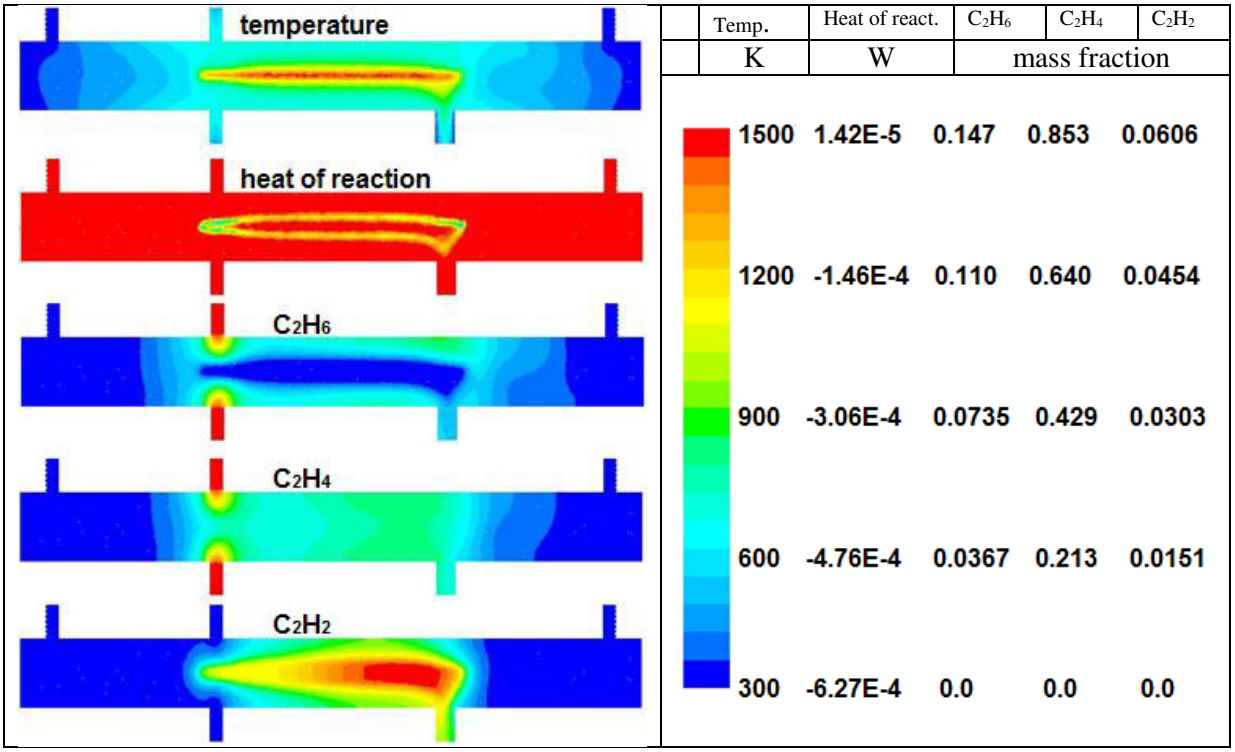

Figure 5. Predicted contours of temperature, C_2H_6 concentration and heat of reaction, and species mass fractions for laser induced ethane pyrolysis with continuous wave CO_2 laser, radiation power 50 W and laser beam diameter 1 mm. The operating conditions (initial gas and buffer gas flow rates, gas and wall temperature, pressure) were taken as the same as those in Fig. 4.

When the laser radiation was applied in the reactor, the predicted contours are looking different, see Figure 5. Compared to the conventional reactor, the new, laser induced, technique produces a higher temperature zone in the core region of reactor. Around this region, ethane pyrolysis yields a higher conversion rate. As shown, the highest temperature locates in the central of reaction zone since the laser beam pass through this region. That's because the absorption spectrum of ethylene that is the major component of reactants coincides with the lasing region. So, the radiation energy of laser beam can be absorbed by ethylene and creates a locally high temperature region, hence accelerating the thermal decomposition of ethane. Aside from thermal absorption, the ethylene tends to reach its electronically excited state due to the effect of radiation on the molecular bonds. Reaction (reaction No. 14 in Fig. 3) between ethylene biradical and ethane produces methyl radical and propyl radical that decomposes then into ethylene and methyl radical. This autocatalytic route accelerates the chemical pyrolysis of ethane significantly. In addition, the reaction zone has a lower heat of reaction due to enhanced endothermic reaction overlapping with the high temperature region.

4 Conclusion

This work attempts to investigate laser induced ethane pyrolysis process in a wall-less reactor using computational fluid dynamics approach. As prior of CFD simulation, a reduced chemical kinetics which contains 10 species involving 15 reactions has been analyzed using sensitivity method and

implemented into CFD code. To model the laser radiation effect, the discrete ordinates radiation model that solves the radiative transfer equation for a finite number of discrete solid angles has been employed. The laser beam was model as incident radiation source (located at the center of glass window) passing through the buffer gas (CH_4) and be transmitted to reactants (C_2H_6/C_2H_4).

The 3D CFD numerical experiments have been carried out according the practical experimental setup. The instantaneous contour for flow field, temperature field and species concentration have been plotted and compared for two different configuration of the reactor. It's observed that the new reactor adopting laser induced technique yields a higher ethane pyrolysis rate than that of traditional reactor. The mechanism for this conversion growth is two-fold: enhanced ethane thermal decomposition due to radiation absorption of ethylene, and enhanced ethane chemical pyrolysis caused by autocatalytic route involving ethylene biradical. In order to prove this hypothesis, the fraction of hydrocarbon radicals needs to be measured quantitatively in the future work.

In addition, these modelling results could be applied to optimize the reactor design and operating conditions for the upscaling reactor in which the reactor dimensions (diameter and length) and mass flow rate of reactants need to be increased and matched properly to obtain highest ethane conversion rate.

5 Acknowledgement

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