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# ON NONEQUILIBRIUM OF PYROLYSIS PROCESS IN THE MANUFACTURE OF ETHENE\*

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**ABSTRACT**: Nonequilibrium process for cracking ethane and n-buthane in the manufacture of ethene has been analytically and numerically investigated in a Heaviside function temperature field and through a normal shock wave. The results demonstrate that, while the reaction temperature increases, the maximum value of ethene yield is increased, and the optimal reaction duration is sharply shortened. For the identical initial reaction temperature, the maximum value of ethene yield through a stationary normal shock wave is less than that in a Heaviside function temperature field. However, the ethene consumption after the maximum value in the former case is less than that in the latter. Higher ethene yield will be obtained by using the gasdynamic heating method than by using the current methods.

KEY WORDS: ethene, pyrolysis, gasdynamic heating

Ethene is one of the most important feedstocks of the petrochemical industry. Many petrochemical products are made from ethene. Ethene is obtained through cracking alkane (ethane, propane, buthane,  $\cdots$ ) in the natural gas or the petroleum distillate (naphtha, diesel oil,  $\cdots$ ) in high temperatures. Ethane, propane, and buthane, etc., belong to light feedstock; naphtha, kerosene, light diesel oil, heavy diesel oil, heavy oil, and crude oil belong to heavy feedstock. For heavy feedstock, fraction is very complicated, and reaction is too many to analyze in detail. For light feedstock, reactions of high-carbon fractions are also complex. However, the pyrolysis reaction of the alkane with low-carbon, such as ethane and buthane, is clear, and their nonequilibrium is representative for the pyrolysis of all kinds of feedstocks in the manufacture of ethene.

Ethene is the intermediate product of nonequilibrium pyrolysis. We can get a high ethene/product ratio through controlling the heating or quenching and reaction rate. Because the products/feedstock ratio is dependent on the quality of feedstock and pyrolysis condition, it is essential to arrange the appropriate reaction condition in order to get a high ratio. In order to develop a new efficient pyrolysis technique, based on the simplified model of the ethane and buthane pyrolysis system, nonequilibrium is investigated in a Heaviside function temperature field and through a normal shock wave. The defects of current technology are analyzed, and then the investigation of a new method on how to improve the pyrolysis technology is conducted.

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### **1 PYROLYSIS REACTION SYSTEM OF ETHANE AND N-BUTHANE**

At present, the methods simulating pyrolysis reaction systems are divided into three models:

(1) Empirical Model: This model lacks not only the essential assumption, but also the differential equations as the function of the furnace length or the duration time. It just gives the mass and heat conservation. This model used to be employed in the manufacture of alkene.

(2) Molecular Model: This model only considers the molecular reaction, which greatly reduces the number of rate equation.

(3) Mechanism Model: This model describes the complex pyrolysis reaction system, based on a number of radical reactions and the data of kinetics and thermodynamics.

During the pyrolysis, the whole reaction system consists of both the molecular reaction and the radical reaction. And the system becomes more complex while the conversion ratio increases. Understanding the radical reaction is helpful to the petrochemical industrial techniques. But it is hard to describe a pyrolysis reaction system by using the radical reaction because of its complication. From the engineering point of view, we can employ the simplified method , i.e., we only consider the molecular reaction and do not involve the details of radical reaction. This method is widely used in industry<sup>[1]</sup>. Many researches demonstrate that the molecular models applied in the pyrolysis of ethane, propane, and buthane, as well as their mixtures are successful. Therefore, the molecular model in Ref.[1] is employed in this paper.

And it should be mentioned that, although this model is in agreement with the real situation at a short distance after the shock wave, it has error immediately after the shock wave. But the value of ethene yield reaches the maximum, to which we pay attention, in about several millisecond, so it has no effect to the conclusions of this paper.

#### 1.1 Pyrolysis System of Ethane

$$C_2H_6 \xrightarrow{k_{1a}} C_2H_4 + H_2 \tag{1a}$$

$$C_2H_6 \xrightarrow{k_{1b}} \frac{1}{2}C_2H_4 + CH_4$$
(1b)

$$C_2H_4 \xrightarrow{k_{2b}} C_2H_2 + H_2 \tag{2}$$

$$C_2H_2 \xrightarrow{k_3} 2C + H_2 \tag{3}$$

The above reactions are first-order,  $k_{1a}$ ,  $k_{1b}$ ,  $k_{2b}$  and  $k_3$  are the reaction rate constants,

 $k_{1a} = 10^{14} \exp(-288.7/RT)$   $k_{1b} = 1.6 \times 10^{12} \exp(-280.3/RT)$   $k_{2b} = 2.57 \times 10^8 \exp(-167.4/RT)$  $k_3 = 9.7 \times 10^{10} \exp(-259.2/RT)$ 

R is the gas universal constant, R = 8.31 J/(mol K).

The rate equation of each fraction:

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Vol.15, No.1 For C<sub>2</sub>H<sub>6</sub>,

$$\frac{\mathrm{d}N_{26}}{\mathrm{d}t} = -(k_{1a} + k_{1b})N_{26}$$

For  $C_2H_4$ ,

$$\frac{\mathrm{d}N_{24}}{\mathrm{d}t} = \left(k_{1a} + \frac{k_{1b}}{2}\right)N_{26} - k_{2b}N_{24}$$

For  $C_2H_2$ ,

$$\frac{\mathrm{d}N_{22}}{\mathrm{d}t} = k_{2b}N_{24} - k_3N_{22}$$

For C,

$$\frac{\mathrm{d}N_{10}}{\mathrm{d}t} = 2k_3N_{22}$$

For CH<sub>4</sub>,

 $\frac{\mathrm{d}N_{14}}{\mathrm{d}t} = k_{1b}N_{26}$ 

For H<sub>2</sub>,

$$\frac{\mathrm{d}N_{02}}{\mathrm{d}t} = k_{1a}N_{26} + k_{2b}N_{24} + k_3N_{22}$$

 $N_{26}$ ,  $N_{24}$ ,  $N_{22}$ ,  $N_{10}$ ,  $N_{14}$ , and  $N_{02}$  are the respective gram moles of  $C_2H_6$ ,  $C_2H_4$ ,  $C_2H_2$ , C,  $CH_4$ , and  $H_2$ , and t is the reaction time.

## 1.2 Pyrolysis System of N-buthane

$$C_4 H_{10} \xrightarrow{k_{1a}} C_2 H_6 + C_2 H_4 \tag{4}$$

$$C_2H_6 \xrightarrow{k_{2\alpha}} C_2H_4 + H_2$$
 (5a)

$$C_2H_6 \xrightarrow{k_{2b}} \frac{1}{2}C_2H_4 + CH_4$$
(5b)

$$C_2H_4 \xrightarrow{k_3} C_2H_2 + H_2 \tag{6}$$

$$C_2H_2 \xrightarrow{k_4} 2C + H_2$$
 (7)

The above reactions are first-order,  $k_{1a}$ ,  $k_{1b}$ ,  $k_{2b}$ ,  $k_3$  and  $k_4$  are the reaction rate constants,

$$k_{1a} = 2.5 \times 10^{14} \exp(-339.5/RT)$$
  

$$k_{2a} = 10^{14} \exp(-288.7/RT)$$
  

$$k_{2b} = 1.6 \times 10^{12} \exp(-280.3/RT)$$
  

$$k_{3} = 2.57 \times 10^{8} \exp(-167.4/RT)$$
  

$$k_{4} = 9.7 \times 10^{10} \exp(-259.2/RT)$$

and R is the gas universal constant,  $R = 8.31 \text{ J/(mol \cdot K)}$ .

The rate equations of each fraction:

For  $C_4H_{10}$ ,

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For  $C_2H_6$ ,

$$\frac{\mathrm{d}N_{26}}{\mathrm{d}t} = -(k_{2a} + k_{2b})N_{26} + k_{1a}N_{410}$$

For  $C_2H_4$ ,

$$\frac{\mathrm{d}N_{24}}{\mathrm{d}t} = k_{1a}N_{410} + \left(k_{2a} + \frac{k_{2b}}{2}\right)N_{26} - k_3N_{24}$$

For  $C_2H_2$ ,

$$\frac{\mathrm{d}N_{22}}{\mathrm{d}t} = k_3 N_{24} - k_4 N_{22}$$

 $\frac{\mathrm{d}N_{410}}{\mathrm{d}t} = -k_{1a}N_{410}$ 

For C,

$$\frac{\mathrm{d}N_{10}}{\mathrm{d}t} = 2k_4 N_{22}$$

For  $CH_4$ ,

$$\frac{\mathrm{d}N_{14}}{\mathrm{d}t} = k_{2b}N_{26}$$

For  $H_2$ ,

$$\frac{\mathrm{d}N_{02}}{\mathrm{d}t} = k_{2a}N_{26} + k_3N_{24} + k_4N_{22}$$

 $N_{410}$ ,  $N_{26}$ ,  $N_{24}$ ,  $N_{22}$ ,  $N_{10}$ ,  $N_{14}$ , and  $N_{02}$  are the respective gram molecules of  $C_4H_{10}$ ,  $C_2H_6$ ,  $C_2H_4$ ,  $C_2H_2$ , C, CH<sub>4</sub>, and H<sub>2</sub>, and t is the reaction time.

### 2 NONEQUILIBRIUM PYROLYSIS OF ETHANE AND N-BUTHANE IN MANUFACTURE OF ETHENE

### 2.1 Pyrolysis in Heaviside Function Temperature Field

Illustrated as Fig.1 is the constant temperature field, which is the Heaviside function.

$$T = \begin{cases} T_1 & \text{when } t < t_0 \\ T_2 & \text{when } t \ge t_0 \end{cases}$$

where  $T_0$  is the critical temperature for cracking reaction. When  $t < t_0$ , there is no reaction; when  $t \ge t_0$ , the ethane and the nbuthane crack, and the reaction temperature keeps constant during pyrolysis.

For the pyrolysis reaction system of ethane, the initial conditions are as follows:

When t = 0,  $N_{26} = N_0$ ,  $N_{24} = N_{22} = N_{10} = N_{14} = N_{02} = 0$ .



Fig.1 The variation of reaction temperature vs. reaction time

To solve the simultaneous rate equations of the fractions, the relation between the ethene yield and the reaction time for cracking the ethane can be written as follows:

$$\frac{N_{24}}{N_0} = \frac{k_{1a} + k_{1b}/2}{k_{2b} - k_{1a} - k_{1b}} \exp[-(k_{1a} + k_{1b})t] - \exp(k_{2b}t)]$$

For the pyrolysis reaction system of n-buthane, the initial conditions are as follows: When t = 0,  $N_{410} = N_0$ ,  $N_{26} = N_{24} = N_{22} = N_{10} = N_{14} = N_{02} = 0$ .

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To solve the simultaneous rate equations of the fractions, the relation between the ethene yield and the reaction time for cracking the n-buthane can be written as follows:

$$\frac{N_{24}}{N_0} = \frac{k_{1a}}{k_{2a} + k_{2b} - k_{1a}} \frac{2k_{2a} + 3k_{2b}/2 - k_{1a}}{k_3 - k_{1a}} \exp(-k_{1a}t) - \frac{k_{1a}(k_{2a} + k_{2b}/2)}{k_{2a} + k_{2b} - k_{1a}} \frac{\exp[-(k_{2a} + k_{2b})t]}{k_3 - k_{2a} - k_{2b}} - \frac{k_{1a}(k_{2a}k_3 + k_{2b}k_3 - k_{1a}k_3 - 2k_{2a}^2 - 7k_{2a}k_{2b}/2 + 2k_{2a}k_{1a} - 3k_{2b}^2/2 + 3k_{1a}k_{2b}/2)}{(k_{2a} + k_{2b} - k_{1a})(k_3 - k_{2a} - k_{2b})(k_3 - k_{1a})} \cdot \exp(-k_3t)$$

Figures 2 and 3 show the variation of the ethene yields against the reaction time for cracking the ethane and n-buthane respectively. When  $t = t_0$ , the pyrolysis reaction begins, and the ratio  $N_{24}/N_0$  increases while the reaction time prolongs. During a short period after the pyrolysis reaction begins, reactions (1a)(1b) of the ethane pyrolysis reaction system and reactions (4)(5a)(5b) of the n-buthane pyrolysis reaction system dominate. Near the peak point of the ratio  $N_{24m}/N_0$ , the ethene generated is equal to the ethene consumed. While the reaction time prolongs after the peak point, the consumption reactions of the ethene (reactions (2)(3) in the ethane pyrolysis reaction system and reactions (6)(7) in the n-buthane pyrolysis reaction system) dominate, and the ethene consumed is greater than the ethene generated, and the ratio  $N_{24}/N_0$  is decreased.



reaction time in different constant reaction temperature (feedstock: ethane)



For the different reaction temperatures, the maximum values of the ethene yields are different, and the optimal reaction times  $t_m$  are different. The higher the reaction temperature is, the higher the peak value of ethene yield is, and the shorter the optimal reaction time is. In order to get a high ratio  $N_{24}/N_0$  near the peak point, the reaction time should be controlled near the optimal reaction time in the manufacture.

#### 2.2 Pyrolysis Reaction after a Normal Shock Wave

After ethane and n-buthane passing through a normal shock wave, their temperature

fields are shown as Fig.4. The gases are passing through the shock wave at  $t = t_0$ , and their temperatures rise from  $T_1$  to  $T_2$ (at that time the pyrolysis reactions have not initiated). Then the ethane and the nbuthane crack. Because the cracking is an endothermal reaction, the temperature decreases while the reaction runs. The reaction temperature of this process varies with the reaction time, so this system is more complicated than the Heaviside function system.

stock: ethane)



Fig.4 The variation of reaction temperature vs. reaction time

In resolving this problem, the variable temperature process is simplified as many constant temperature processes, i.e., the variable temperature process is approximated by the piecewise constant temperature process. The key point of this method is to determine an appropriate time stepsize. If the time stepsize is too big, the calculation error will not be acceptable; if the time stepsize is too small, the calculation will take too long. The variation of the ethene yield and the reaction temperature against the reaction time are illustrated in Fig.5 in different time stepsize after the ethane passed through a normal shock wave. The time steps are  $5\mu$ s and  $0.5\mu$ s, and the initial temperature is  $T_2 = 1500$  K. Between the two cases, the results are a little different only in the initial stage, and are identical in the rest of the region, including the peak region, which demonstrates that it is feasible to use the constant temperature process to approximate the variable temperature process piecewise. Through synthesizing the calculation results at different time stepsizes, the time stepsize is chosen to be  $1 \mu$ s for the following calculations.



Figures 6 and 7 show the variation of the ethene yield and the reaction temperature against the reaction time. Compared with the system with the Heaviside function temperature field, there are several differences: (1) Starting from the same initial reaction

(feedstock: ethane)

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temperature, the maximum value of ethene yield in the varying temperature process is lower than that in the constant temperature process. (2) The optimal reaction duration corresponding to the maximum value of ethene yield obviously prolongs, especially in the high temperature. (3) After the peak point, the ratio drops slowly. In order to get the same ethene yield, the initial enthalpy of feedstock should be increased. The increase of  $t_m$  and the slow drop after the peak point are beneficial to manufacture technology.





# ture vs. reaction time in different initial reaction temperature (feedstock: n-buthane)

#### **3 DISCUSSION**

The above investigations demonstrate that, in order to promote ethene yield, the pyrolysis reaction temperature should be as high as possible. In the meantime, the duration in the high reaction temperature should be strictly controlled. At present, more than 99% ethene is produced by using the vertical pyrolysis furnace, and both the high reaction temperature and the heat are transferred to the feedstock from the outside of the furnace to the inside through the furnace wall. This kind of facility doesn't satisfy the requirements to get a high ethene/feedstock ratio, and has several defects. First, the heating is slow, and the duration in high temperature is very long. Second, the reaction temperature is not high enough. Although the upper temperature resistance limit of the alloy making the furnace is as much as 1500 K, the temperature of feedstock in the middle of the furnace is not high enough, because the difference of temperature between two sides of the furnace wall is more than 200 K in order to keep a high thermal current, and there exists the difference of temperature due to boundary layer, and the furnace can't run in the upper temperature resistance limit for a long time.

In addition, the heat promoting the feedstock temperature is transferred through the furnace wall. Owing to the boundary layer, the temperature of the feedstock in the boundary layer is higher than that in the middle of the furnace. However, the speed of the former is slower than that of the latter. As a result, the feedstock in the boundary layer stays too long in the high reaction temperature, and the secondary reactions greatly increases. The carbon accumulates easily near the furnace wall. To clean out the carbon will increase the production cost.

In order to overcome the defects of external heating pyrolysis furnace, Idemitsu's Chiba ethylene plant, one of Japanese company, and American Allied-Carbon Company utilized Kamm patent<sup>[3]</sup> to develop ACR internal heating pyrolysis facility. The combustion gases of high temperature between hydrogen or methane and oxygen are employed to mix with the feedstock to promote its temperature. The reaction temperature can reach  $1200^{\circ}C \sim 2000^{\circ}C$ . But the time of mixing process is hard to be shortened, and the feedstock stays in high reaction temperature too long. Gorislavets & Mayorov<sup>[4]</sup>, the Russian scientists, proposed another plan on the internal heating, more than needed methane and oxygen are injected into the combustor simultaneously, the combustion gases of high temperature between methane and oxygen will promote the temperature of the surplus methane. The mixing gases are accelerated by the nozzle to be the supersonic flow, their temperature will be elevated by a stationary shock wave, and then the reaction products are quenched by the cooling water. It is obvious that, after the feedstock passes through the shock wave, its temperature and duration can be controlled to meet the requirements to get a high ethene/feedstock ratio. However, this plan ignores such a fact, that the temperature in the combustor is higher than that after the shock wave, and the duration in the combustor may be too long, so the pyrolysis has taken place in the combustor.

Inspired by Gorislavets & Mayorov's research work, Hertzberg<sup>[5]</sup> & H-R Yu<sup>\*</sup> proposed the similar novel suggestion, on the pyrolysis in the manufacture of ethene by means of gasdynamics heating. The relevant issues are being studied in the Institute of Mechanics, Chinese Academy of Sciences.

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