

PYROLYSIS OF ETHANE: EQUILIBRIUM AND KINETIC MODELS AND THE REDUCTION OF REACTION MECHANISM

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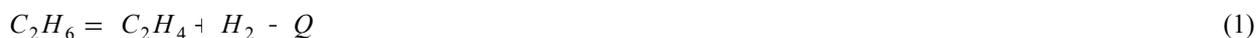
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Abstract Is considered the reaction mechanism of the ethane pyrolysis, utilized in petrochemical industry to obtain ethylene (basic species for production of polyethylene). "Complete" reaction mechanism includes 63 reactions. The zone of the parameter alterations corresponds to conditions of industrial pyrolysis: $T = 900 \dots 1200\text{K}$, $P = 2 \dots 8 \text{ atm}$, $C_2H_6 / H_2O = 1 \dots 2$. Using the scheme of perfect stirred reactor, were carried out numerical simulations on the chemically equilibrium and kinetic models. The results, obtained by these models are different. In the equilibrium approach ethane is decomposed almost completely, and methane is basic pyrolysis product, while in the kinetic approach ethane is decomposed partially, and the basic pyrolysis products are: C_2H_4 and H_2 . The engagement method, developed in the previous works, is applied for reduction of "complete" mechanism. The reduced mechanism includes 18 reactions and with the satisfactory accuracy allows computing the composition of the pyrolysis products.

Keywords: ethane pyrolysis, reaction mechanism, reduction of mechanism, chemical equilibrium and chemical kinetics

1. INTRODUCTION

In the petrochemical industry for obtaining ethylene (C_2H_4 – basic component for production of polyethylene) the ethane pyrolysis is widely used (Albright *et al.*, 1983, Buffenour *et al.*, 2004). This process arises in the tube furnaces at: temperature $T = 900 \dots 1200\text{K}$, pressure $P = 2 \dots 10 \text{ atm}$, with addition to the reagent flow of significant quantity of water vapor ($r_{H_2O} = 0,5 \dots 0,65$). It is known that the ethane transformation in the pyrolysis products (C_2H_4 , H_2 , CH_4 , etc.) occurs with absorption of significant quantity of heat. For example, the reaction:



is essentially endothermic (Albright *et al.*, 1983) with $Q = 4567 \text{ kJ/Kg}$. Therefore the pipes, into which reagents and the pyrolysis products flow, are necessary to heat (usually this occurs by the radiation heat transfer). The ethylene fraction at output ($r_{C_2H_4}^f$) depends on temperature, pressure, vapor concentration and the pipe length (residence time). Varying these parameters, it is possible to reach the maximum of ethylene yield. For the actual industrial plants is typical the composition of the pyrolysis products, given in Table 1.

Table 1. Typical composition of the pyrolysis products (without water vapor), obtained in the actual plants for production of ethylene.

Species	H_2	CH_4	C_2H_4	C_2H_6	C_2H_2	C_3H_6
$r_i(\%)$	3,51	4,30	48,00	39,36	0,30	1,33

Numerous works (Buffenour *et al.*, 2004; Edwin and Balchen, 2001; Prior and Lopes, 2000; Stell, 2003; Marinov *et al.*, 1998; Jones and Lindstedt, 1988; etc) describe different aspects of the ethane pyrolysis. Two aspects, which relate to this problem, are considered in present work:

- deviation of composition of the pyrolysis products from the chemical equilibrium;
- reduction of chemical reactions.

It is known, that for simulation of the ethane pyrolysis for industrial plants is used the approach of the ideal displacement reactor (Krioukov *et al.*, 1997). But for solution of indicated problems it is possible to use also the perfect stirred reactor, that is more convenient for research (Spilimbergo *et al.*, 2007).

2. EQUATION OF CHEMICAL EQUILIBRIUM AND OF CHEMICAL KINETICS

We will consider that the pyrolysis process arises in reactor, showed in Fig. 1. Gaseous reagent (C_2H_6) and water vapor enter into reactor and instantly are mixed with the pyrolysis products (with $P = \text{const}$ and equality of flows $m^+ = m^-$). In state of chemical equilibrium the rates of forward and back reaction are equal $W_j^+ = W_j^-$, and they approach to infinity with the condition:

$$\frac{k_j^+}{k_j^-} = K_j^c \quad (2)$$

where K_j^c – equilibrium constant, k_j^+ , k_j^- the rate constant j -th reaction.

For the equilibrium conditions the reactor temperature (T_o) is prescribed and is ensured by heat transfers regard, to the reagent mass unit ($Q_{eq} [J/kg]$). This value is determined from the formulae:

$$Q_{eq} = \sum_i h_i(T_o)g_i^{eq} - [h_{C_2H_6}(T_{en})g_{C_2H_6} + h_{H_2O}(T_{en})g_{H_2O}] \quad (3)$$

where $h_i(T_o)$, g_i^{eq} – specific mass enthalpy and mass fraction of i -th pyrolysis product species; T_{en} , g_{H_2O} , $g_{C_2H_6}$, h_{H_2O} , $h_{C_2H_6}$ – temperature, mass fractions and the enthalpies of the input flow species.

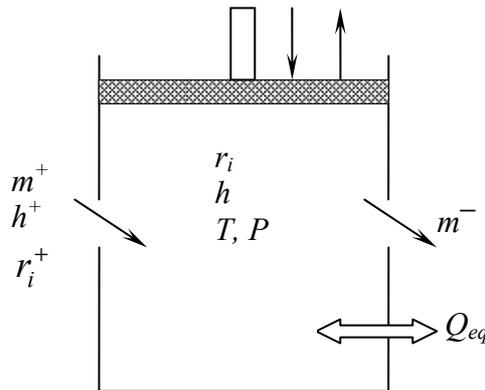


Figure1. Scheme of the perfect stirred reactor.

The calculation of chemical equilibrium was accomplished, using the known model (Alemassov *et al.*, 1971), which includes the following equations:

a) dissociation of molecules:

$$\ln P_j - \sum_{i=1}^n a_{ij} \cdot \ln P_i + \ln K_j = 0 \quad j = 1, \dots, m \quad (4)$$

where

$$\ln K_j = \frac{\sum_{i=1}^n a_{ij} \cdot S_i^o - S_j^o}{R_o} - \frac{\sum_{i=1}^n a_{ij} \cdot H_i - H_j}{R_o T} \quad (5)$$

b) conservation of atoms:

$$\ln \left(\sum_{j=1}^m a_{ij} \cdot P_j + P_i \right) - \ln M_p - \ln b_{ip} = 0 \quad i = 1, \dots, n \quad (6)$$

c) Dalton:

$$\ln \left(\sum_{q=1}^{m+n} P_q \right) - \ln P = 0 \quad (7)$$

where: P_i, P_j, P_q – the partial pressures of atoms (i), of molecules (j) and any ($q = i + j$) species; a_{ij} – the number of i -th atoms in j -th molecule; K_j – the dissociation constant j -th molecule (this constant is function of enthalpy (H_j) and of entropy (S_j^o)); M_p – incognita constant; R_o – universal gas constant; b_{ip} – the number of atoms in conditional formula of reagent species.

In this work the calculation of non – equilibrium processes is accomplish by model of perfect stirred reactor with $P, m = const$ (m is the flow in reactor), which is described by following equations:

1) The chemical kinetics in the exponential form (Kriukov *et al.*, 1997):

$$\frac{d\gamma_i}{d\tau} = -e^{\gamma} \left(\sum_j v_{ij} \Omega_j + \frac{r_i^+ \mu_{\Sigma}}{\mu^+ \tau_p} \right) + \sum_q \sum_j v_{qj} \Omega_j + \sum_q \frac{r_q^+ \mu_{\Sigma}}{\mu^+ \tau_p} \quad i, p, q = 1, \dots, n_c; \quad j = 1, \dots, 2m_c; \quad (8)$$

where: $\Omega_j = k_j \left(\frac{P}{R_o T} \right)^{\bar{m}_j} \exp \left(- \sum_p n_{pj} \gamma_p \right)$; $\bar{m}_j = m_j + \sum n_{pj} - 1$; $\gamma_i = - \ln r_i$;

$v_{ij} = v_{is}'' - v_{is}'$; $n_{ij} = v_{is}'$; $j = s$; $s = 1, \dots, m_c$;

$v_{ij} = v_{is}' - v_{is}''$; $n_{ij} = v_{is}''$; $j = s + m_c$; $s = 1, \dots, m_c$;

v_{is}', v_{is}'' – stoichiometric coefficients in set of reversible reactions:



B_i – symbol of i -th species; m_j – index of participation of third body M ($m_j = 1$ if particle M participates in j -th reaction, otherwise $m_j = 0$); k_j – rate constant of j -th reaction; r_i and r_i^+ – molar fractions of i -th species in reactor and in input flow (the flow of reagents); $n_c \in m_c$ – numbers of species and of reactions in the reacting medium; τ_p – residence time; μ_{Σ} – average molecular mass in reactor; μ_i – molecular mass of i -th specie; μ^+ – average molecular mass of the reagents.

2) The energy equation, in integral form:

$$h_{C_2H_6} g_{C_2H_6} + h_{H_2O} g_{H_2O} + Q_{eq} = \sum_i h_i(T) g_i \quad i = 1, \dots, n_c \quad (10)$$

where: Q_{eq} it is determined from formulae (2).

The integration of equations (8) – (10) is carry out until the steady-state values of temperature (T_f) and composition (r_f - molar fractions), which differ from the appropriate equilibrium values (T_o, r_i^{eq}) and approach to them with $\tau_p \rightarrow \infty$.

3. FORMING OF REACTION MECHANISM. COMPARISON OF KINETIC AND EQUILIBRIUM COMPOSITIONS

The reaction mechanism, necessary to accomplish the kinetic calculations (C-mechanism), was formed from databases (Marinov *et al.*, 1998; LEED's, 2004; Glarborg *et al.*, 1986) and includes the species: $H, H_2, H_2O, CH, CH_2, CH_3, CH_4, C_2H, C_2H_2, C_2H_3, C_2H_4, C_2H_5, C_2H_6, C_3H_2, C_3H_4, C_3H_5, C_3H_6, C_3H_7, C_3H_8$ and selected reactions, given in Tab. 2. It is observed, that these mechanisms (and also the mechanism of Konnov (2007)) include both the pyrolysis reactions and the oxidation (combustion) reactions, and only the pyrolysis reactions were selected in C-mechanism.

The thermodynamic properties of species $H_i = f_i(T)$ $S_i^o = f_i(T)$ were taken from the databases (Marinov *et al.*, 1998 and LEED's, 2004). Reactions of variable order in the general case written, for example, in the form:



were used in version for high pressure in the Lindemann form (Kee *et al.*, 2000). Chemically equilibrium and kinetic calculations were carried out by code RISTV (Spilimbergo *et al.*, 2007).

Table 2. Reaction mechanism of the ethane pyrolysis (C-mechanism).

N	Reaction	N	Reaction	N	Reaction
1R	H+H+M=H2+M	22R	C2H5+H=C1H3+C1H3	43R	C2H2+M=C2H1+H+M
2R	CH3+M=CH+H2+M	23R	CH3+CH3=C2H4+H2	44R	C2H+H2=C2H2+H
3R	CH2+H=CH+H2	24R	CH3+CH2=C2H4+H	45R	C3H8=C2H5+CH3
4R	CH+C2H2=C3H2+H	25R	C2H6+H=C2H5+H2	46R	C3H8+H=C3H7+H2
5R	CH4+M=CH3+H+M	26R	C2H5+H=C2H4+H2	47R	C3H8+CH3=C3H7+CH4
6R	CH4+H=CH3+H2	27R	C2H5+H=C2H6	48R	C3H8+C2H3=C3H7+C2H4
7R	CH4+CH2=CH3+CH3	28R	C2H4+CH3=C2H3+CH4	49R	C3H8+C2H5=C3H7+C2H6
8R	CH3+M=CH2+H+M	29R	C2H6+CH3=C2H5+CH4	50R	C3H8+C3H5=C3H6+C3H7
9R	CH3+H=CH2+H2	30R	C2H6+CH2=CH3+C2H5	51R	C3H7=C2H4+CH3
10R	CH2+H=CH+H2	31R	C2H5+M=C2H4+H+M	52R	C3H6+H=C3H7
11R	CH2+CH=C2H2+H	32R	C2H4+M=C2H2+H2+M	53R	C3H7+H=C2H5+CH3
12R	CH2+CH2=C2H2+H2	33R	C2H4+M=C2H3+H+M	54R	C3H6=C2H2+CH4
13R	CH+H=C+H2	34R	C2H4+H=C2H3+H2	55R	C3H6=C3H4+H2
14R	CH+CH3=C2H3+H	35R	C2H3+M=C2H2+H+M	56R	C3H5+H=C3H6
15R	CH+CH4=C2H4+H	36R	C2H3+H=C2H2+H2	57R	C3H6+H=C2H4+CH3
16R	CH+C2H4=CH2+C2H3	37R	C2H3+CH2=C2H2+CH3	58R	C3H6+H=C3H5+H2
17R	CH+C2H6=C2H4+CH3	38R	C2H3+C2H=C2H2+C2H2	59R	C3H6+CH3=C3H5+CH4
18R	C+CH4=CH+CH3	39R	C2H3+CH=CH2+C2H2	60R	C3H5+H=C3H4+H2
19R	C+CH3=C2H2+H	40R	C2H3+CH3=C3H5+H	61R	C3H5+CH3=C3H4+CH4
20R	C+CH2=C2H+H	41R	C2H3+CH3=C2H2+CH4	62R	C3H4+H=CH3+C2H2
21R	CH3+CH3=C2H6	42R	C2H2+CH3=C2H+CH4	63R	C3H4+H=C3H5

Comparative calculations were performed in the parametric domain, corresponding of industrial pyrolysis, namely:

$$T = 900 \dots 1200\text{K}; P = 2 \dots 8 \text{ atm}; r_{H_2O} = 0,5 \dots 0,65; \tau_p = 0,1 \dots 1 \text{ sec} \quad (12)$$

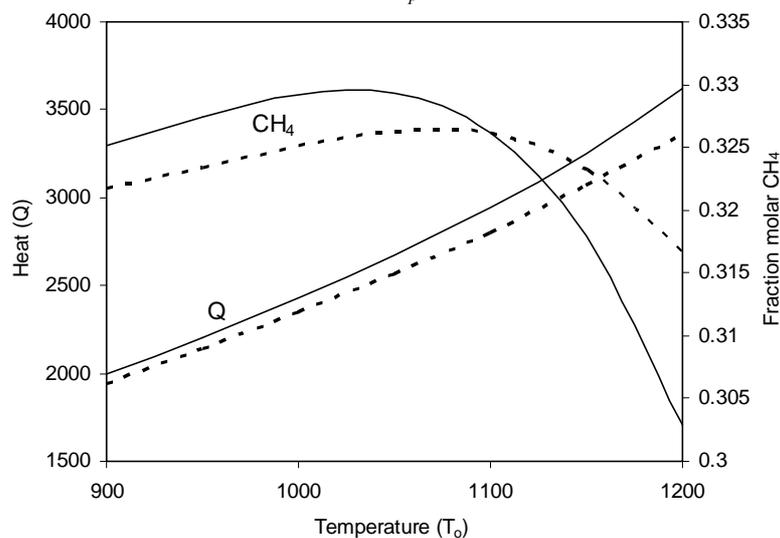


Figure 2. Equilibrium values Q_{eq} and $r_{CH_4}^{eq}$ depending on temperature T_o ($r_{H_2O} = 0,625$; — 2 atm; - - - 6 atm).

For example, the interval of values τ_p (necessary for fulfilling the kinetic calculations) corresponds to the residence time of ethane into the furnace pipes. The initial reagent temperature had value $T_{en} = 298K$. In course of equilibrium calculations were determined the values $Q_{eq} = f(T_o, P)$, showed on Fig. 2. Is evident, that with increase T_o a quantity of required heat increases and it is expended on reagent heating (from 298K to T_o) and on the transformation C_2H_6 in the pyrolysis products (C_2H_4 , H_2 , CH_4 and etc.). Main of them in the equilibrium conditions is methane (CH_4), and its concentration weakly depends on temperature. The small fraction of reagent is converted in C_2H_4 , H_2 , C_2H_2 . For example, for the conditions $P = 2$ atm, $r_{H_2O} = 0,625$, with alteration of temperature in interval $T = 900 \dots 1200K$, the molar fractions $r_{C_2H_2}^{eq}$ and $r_{H_2}^{eq}$ increase from 1% to 5% (Fig. 3). The composition of the pyrolysis products weakly depends on pressure. For the selected domain of parameters were carried out also the calculations by kinetic model. Some obtained results and their comparison with chemically equilibrium data depending on T_o , (this actually corresponds depending on Q_{eq}) are shown in Figs. 4 - 7.

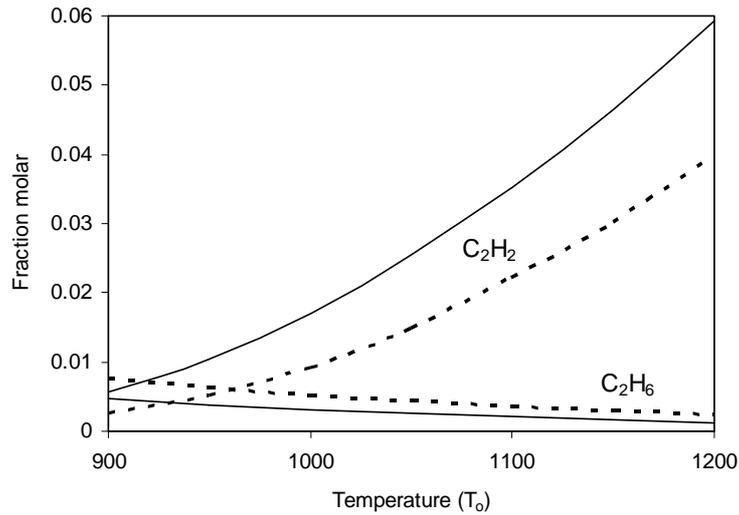


Figure 3. Equilibrium values $r_{C_2H_2}^{eq}$ and $r_{C_2H_6}^{eq}$ depending on temperature T_o ($r_{H_2O} = 0,625$; — 2 atm; - - - 6 atm).

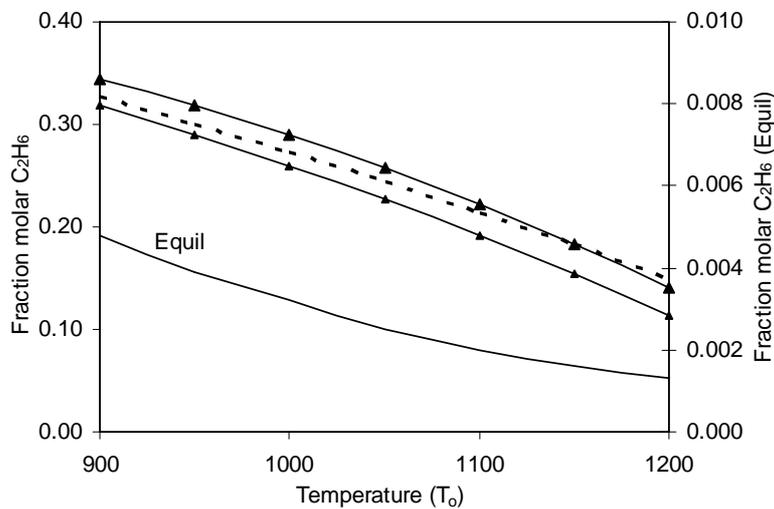


Figure 4. Alteration of molar fractions $r_{C_2H_6}^f$ and $r_{C_2H_6}^{eq}$ in depending on T_o ($r_{H_2O} = 0,625$).

▲ - P = 2 atm, $\tau_p = 0,1$ sec; ■ - P = 2 atm, $\tau_p = 1$ sec; - - - P = 6 atm, $\tau_p = 1$ sec

Analyzing these results it is necessary to note the following moments:

- temperature influences considerably and pressure influences weakly in composition of the pyrolysis products;
- with increase of residence time from $\tau_p = 0,1$ sec to $\tau_p = 1$ sec the pyrolysis depth increases and therefore T_f (0,1sec) > T_f (1sec);
- in comparison with the equilibrium calculations the kinetic calculations show considerably higher concentration C_2H_6 , i.e. $r_{C_2H_6}^f \gg r_{C_2H_6}^{eq}$, but with increase of temperature value $r_{C_2H_6}^f$ falls, because the pyrolysis reactions are accelerated;

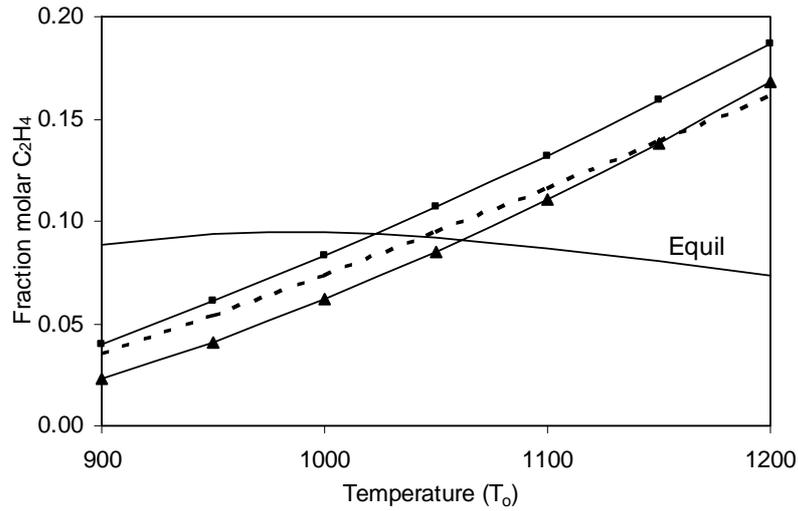


Figure 5. Alteration of molar fractions $r_{C_2H_4}^f$ and $r_{C_2H_4}^{eq}$ in depending on T_o ($r_{H_2O} = 0,625$).
 ▲ - P = 2 atm, $\tau_p = 0,1$ sec; ■ - P = 2 atm, $\tau_p = 1$ sec; ---- P = 6 atm, $\tau_p = 1$ sec

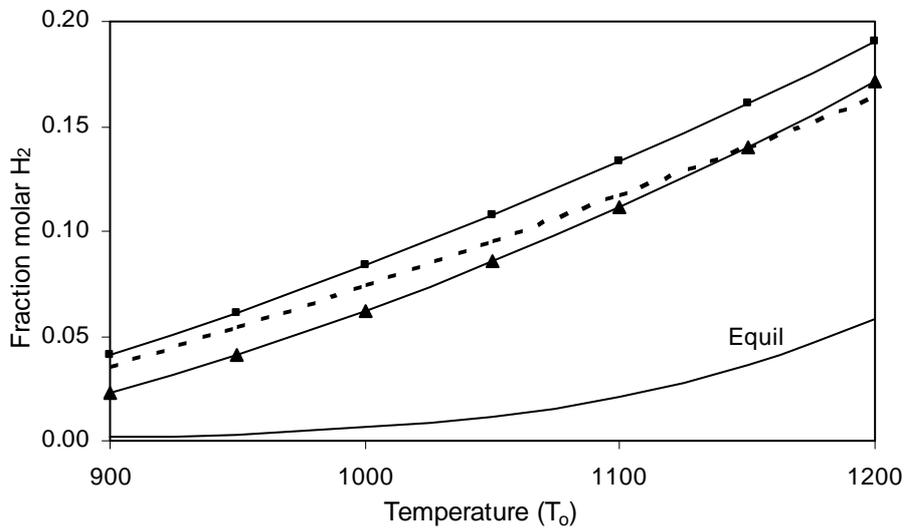


Figure 6. Alteration of molar fractions $r_{H_2}^f$ and $r_{H_2}^{eq}$ in depending on T_o ($r_{H_2O} = 0,625$).
 ▲ - P = 2 atm, $\tau_p = 0,1$ sec; ■ - P = 2 atm, $\tau_p = 1$ sec; ---- P = 6 atm, $\tau_p = 1$ sec

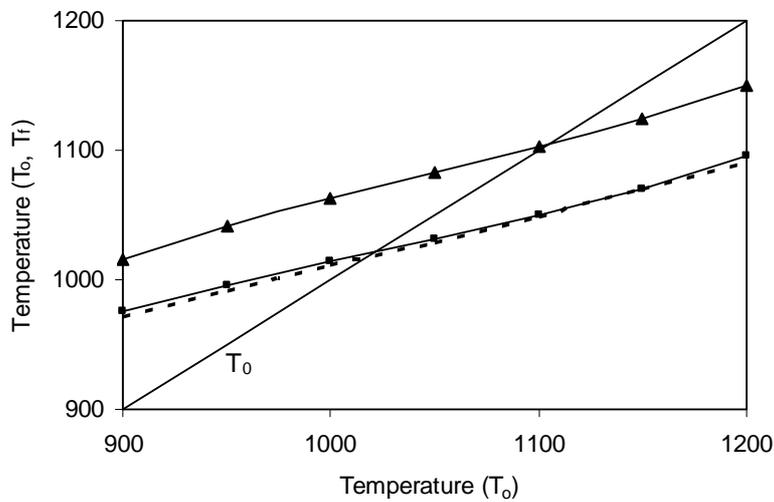


Figure 7. Alteration of temperature T_f in depending on T_o ($r_{H_2O} = 0,625$).
 ▲ - P = 2 atm, $\tau_p = 0,1$ sec; ■ - P = 2 atm, $\tau_p = 1$ sec; ---- P = 6 atm, $\tau_p = 1$ sec

- in the selected temperature interval, according to kinetic model the methane practically is not formed ($r_{CH_4}^f < 1\%$) in contrast to the equilibrium data;
- in the equilibrium model the fraction C_2H_4 weakly depending on T_o ($r_{C_2H_4}^{eq} = 8...9\%$), but according to kinetic model the concentration C_2H_4 considerably increases from 3% (when $T_o = 900K$) to 18% (when $T_o = 1200K$);
- with increase T_o according to kinetic model concentration H_2 considerably increases from 2% (when $T_o = 900K$) to 18% (when $T_o = 1200K$), essentially exceeding the appropriate equilibrium values;
- with the low values T_o (small Q_{eq}) the temperature $T_f > T_o$ (Fig 7), that is caused by insignificant formation C_2H_4 by comparison with equilibrium data. But with high T_o , concentration C_2H_4 becomes above equilibrium data ($r_{C_2H_4}^f > r_{C_2H_4}^{eq}$), that leads to the significant energy expenditures for the ethane pyrolysis and then T_f becomes less than T_o .

4. REDUCTION OF THE PYROLYSIS REACTION MECHANISM

The reduction of complete mechanism of reactions (C-mechanism) was carried out by the engagement method, given in the work (Spilimbergo *et al.*, 2007). According to this method the calculations of processes in the reactor begin from chemical equilibrium state (with temperature T_o) until establishment of same stationary state (temperature T_f), with chemical non-equilibrium composition. In result of the reaction rate analysis of the complete mechanism (C-mechanism) in the stationary state, the engagement method forms a reduced mechanism (S-mechanism) only with the notable reactions. In method is used the reduction indicator, which is established by the user and is located in interval $\zeta = 0, \dots, 1$. If the value of $\zeta = 1$, the reduced mechanism is only constituted by reactions with maximum rates. If the value of $\zeta = 0$, the reduced -mechanism is equal to the C-mechanism.

If the reduction is realized for:

- a point in the space $\{r_{H_2O}, P, T_o, \tau_p = \text{const.}\}$, then the reduced mechanism is called LS-mechanism;
- a line $\{r_{H_2O}, P, \tau_p = \text{const.}, T_o = \text{var.}\}$, then the reduced mechanism is called ST-mechanism;
- a limited zone $\{r_{H_2O}, P, T_o, \tau_p = \text{var.}\}$, then the reduced mechanism is called GS-mechanism.

In all calculation variants the initial data are: the reduction indicator ζ , the reagent symbols, the symbols of main combustion products and species interesting for the user.

The additional initial data in LS-mechanism are: r_{H_2O}, P, T_o and τ_p . Thus, initially, the LS-mechanism is constituted only by same species (without reactions) and it is formed step by the step using the following algorithm:

P1. For each i -th species that is already included in the LS-mechanism, it is considered all reactions with this species.

P2. The maximums for these reactions are obtained:

$$\Omega_{im} = \max[abs(v_{ij}\Omega_j)] \quad j = 1, \dots, 2m_c; \quad (13)$$

$$\Omega_{id} = \max[abs(v_{is}(\Omega_s - \Omega_{s+mc}))] \quad s = 1, \dots, m_c; \quad (14)$$

where Ω_{im} is the maximum value by module among the terms $v_{ij}\Omega_j$ of the forward and back directions of reactions with i -th species; Ω_{id} is the maximum value by module of differences between the forward and back directions of these reactions.

P3. Among the reactions with i -th species are selected those that satisfy one of relations:

$$abs(v_{ij}\Omega_j) \geq \zeta \Omega_{im} \quad j = 1, \dots, 2m_c; \quad (15)$$

$$abs(v_{is}(\Omega_s - \Omega_{s+mc})) \geq \zeta \Omega_{id} \quad s = 1, \dots, m_c. \quad (16)$$

P4. Each reaction selected by relations (15) and (16) is included in LS-mechanism, if it was not included previously.

P5. Each species of each reaction selected by step P3 is also included in LS-mechanism, if was not included previously. So a species (initially included) "engages" others reactions and species.

To form a ST-mechanism, the additional initial data are: r_{H_2O}, P, τ_p and the temperature interval $[T_o(\max), \dots, T_o(\min)]$. This interval is divided by n_T parts, with width: $\Delta T = (T_o(\max) - T_o(\min))/n_T$. For each point $r_{H_2O}, P, \tau_p, T_o(\min) + k\Delta T$, where ($k = 1 \dots n_T$), is formed the LS- mechanism. Then, to obtain the ST-mechanism, joining all LT-mechanisms.

To form a GS-mechanism, the additional initial data are: the intervals: of temperature $[T_o(\max), \dots, T_o(\min)]$, of molar fractions $[r_{H2O}(\max), \dots, r_{H2O}(\min)]$ and of pressure $[P(\max), \dots, P(\min)]$. In this case is necessary to choose different values $r_{H2O,m}$ and P_j and to carry out the calculations (each time in interval $[T_o(\max), \dots, T_o(\min)]$) generating the ST-mechanisms for each point $(r_{H2O,m}, P_j)$ and then, to obtain the GS(ζ)-mechanism, joining all ST-mechanisms.

In the present work reduction of C-mechanism is executed for domain of parameters T, P, r_{H2O} and τ_p , corresponded to working conditions in of industrial plants (12). As reagents were naturally considered: C_2H_6 and H_2O . As the basic pyrolysis products were selected CH_4 and C_2H_2 (from the equilibrium model) and C_2H_4, H_2 (from the kinetic model). In course of precomputations was selected the reduction indicator of mechanism ($\zeta = 0,05$). In result of application of the engagement method was obtained GS- mechanism, which includes 18 reactions (Tab. 3) and substances: $H, H_2, H_2O, CH_3, CH_4, C_2H_2, C_2H_3, C_2H_4, C_2H_5, C_2H_6, C_3H_4, C_3H_5, C_3H_6$ and C_3H_7 .

Table 3. Reduced reaction mechanism (GS - mechanism) of pyrolysis C_2H_6 ($\zeta = 0,05$).

N	Reaction	N	Reaction	N	Reaction
9R	$C1H4+H=C1H3+H2$	34R	$C2H5+M=C2H4+H+M$	59R	$C3H5+H=C3H6$
24R	$C1H3+C1H3=C2H6$	35R	$C2H4+M=C2H2+H2+M$	60R	$C3H6+H=C2H4+C1H3$
25R	$C2H5+H=C1H3+C1H3$	37R	$C2H4+H=C2H3+H2$	61R	$C3H6+H=C3H5+H2$
28R	$C2H6+H=C2H5+H2$	38R	$C2H3+M=C2H2+H+M$	63R	$C3H5+H=C3H4+H2$
31R	$C2H4+C1H3=C2H3+C1H4$	54R	$C3H7=C2H4+C1H3$	65R	$C3H4+H=C1H3+C2H2$
32R	$C2H6+C1H3=C2H5+C1H4$	55R	$C3H6+H=C3H7$	66R	$C3H4+H=C3H5$

Then in accordance with the estimation, given in (Spilimbergo *et al.*, 2007), the calculation volume with GS-mechanism is decreased in $\left(\frac{63}{18}\right)\left(\frac{19}{14}\right)^3 = 8,8$ times in comparison with the C-mechanism. Results, obtained by these mechanisms, were comprises for all selected lines of domain (T, P, r_{H2O}, τ_p) . Examples of comparison for the lines: $T=900\dots 1200K, P = 2atm, r_{H2O} = 0,625, \tau_p = 1sec$ and $T = 900\dots 1200K, P = 6atm, r_{H2O} = 0,5; \tau_p = 1sec$ are presented in Figs.8 and 9. Is evident, that values $T_f, r_{C_2H_4}^f$ and $r_{C_2H_6}^f$, obtained by the complete and reduced mechanisms are close. For concentrations of other species analogous results were obtained. Thus, the formed reduced mechanism can be used to predict the characteristics of the ethane pyrolysis process.

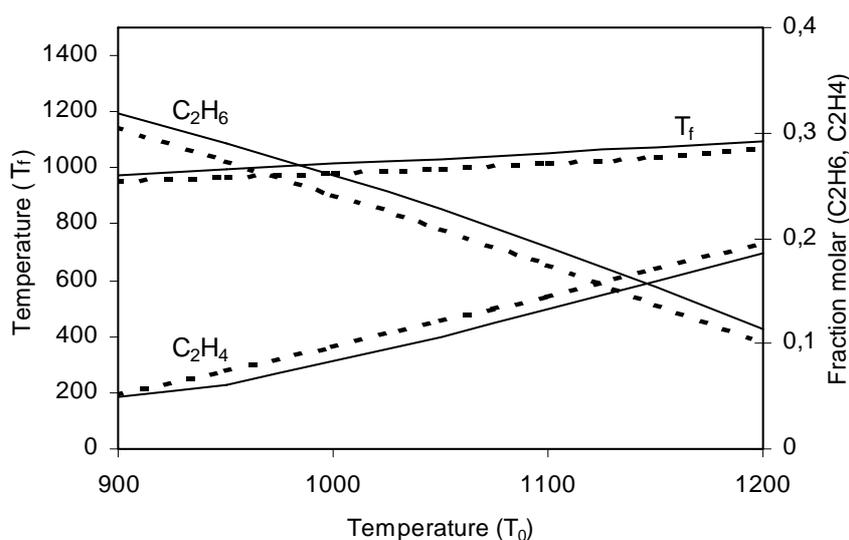


Figure 8. Comparison of values $T_f, r_{C_2H_4}^f$ and $r_{C_2H_6}^f$ obtained by the complete and reduced mechanisms with $P = 2atm, r_{H2O} = 0,625; \tau_p = 1sec$ (— C-mechanism; - - - GS-mechanism).

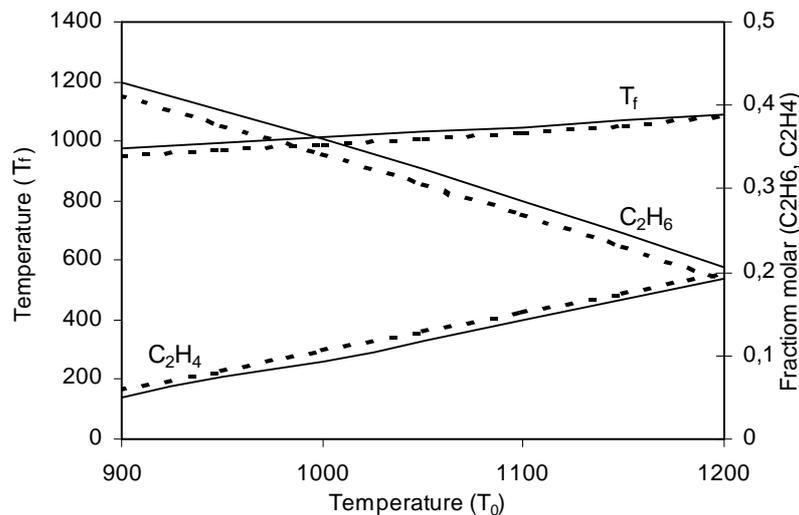


Figure 9 Comparison of values T_f , $r_{C_2H_4}^f$ and $r_{C_2H_6}^f$ obtained by the complete and reduced mechanisms with $P = 6\text{atm}$, $r_{H_2O} = 0,5$; $\tau_p = 1\text{sec}$ (— C-mechanism; - - - GS-mechanism)

5. CONCLUSION

Are considered the chemical aspects of the ethane pyrolysis, widely utilized in the petrochemical industry for the production of ethylene.

The numeric simulation of the pyrolysis processes with the use of the equilibrium and kinetic approaches was carried out for conditions of the perfect stirred reactor. In the investigated temperature interval the results, obtained on these approaches, significantly differ from each other. According to equilibrium model the pyrolysis products contain, mainly, methane, and also the small concentrations C_2H_4 , C_2H_2 and H_2 , which little alter in the interval $T=900\dots1200\text{K}$. But according to kinetic model by the main products of pyrolysis are C_2H_4 and H_2 , whose concentrations depend on temperature. Furthermore, at output from reactor in significant concentration can contain reagent (C_2H_6). Its decomposition determines the stationary temperature T_f in reactor: for the small degrees of decomposition $T_f > T_o$, and for the significant degrees $T_f < T_o$.

The numeric simulations were accomplished for industrial conditions of the ethane pyrolysis $T = 900\dots1200\text{K}$; $P=2\dots8\text{atm}$; $r_{H_2O} = 0,5\dots0,65$; $\tau_p = 0,1\dots1\text{sec}$ with reduction of indicator $\zeta = 0,05$. The complete C-mechanism was reduced: in relation of reactions in 3,5 times and in relation of species in 1,3 times.

It is necessary to note that the created model is intended for: comparison of compositions of the pyrolysis products, obtained by chemically equilibrium and kinetic approach and reduction of mechanism of the pyrolysis reactions; and this model is considerably simple, than complex model of the pyrolysis processes in industrial plants. Subsequently, it is planned to create and to examine this complex model by comparison with the experimental data.

6. REFERENCES

- Albright, L.F., Cruns, B.F. and Corcoran, W.H., 1983, "Pyrolysis: Theory and Industrial Practice", Ed. Academic press, New York, 516 p.
- Alemassov, V.E., Dregalin, A.F. and Tishin, A.P., 1971, "Thermodynamic and Thermophysical Properties of the Combustion Products", Survey, Vol. 1, Ed. VINITI, Moscow, 302 p.
- Buffenour, M.H., Aubry, J.M. and Hurstel, X., 2004, "Large Ethylene Plants Present Unique Design, Construction Challenges", Oil and Gas Journal, Vol. 102, No. 3, pp. 60–65.
- Edwin, E. and Balchen, J., 2001, "Dynamic Optimization and Production Planning of Thermal Cracking Operation", Chem. Eng. Science, Vol. 56, pp. 989-997.
- Glarborg, P., Miller J.A. and Kee R.J., 1986, "Kinetic Modeling and Sensitivity Analysis of Nitrogen Oxide Formation in Well-Stirred Reactors", Combustion and Flame, Vol. 65, pp. 177-202.
- Jones W.P. and Lindstedt R.P., 1988, "Global Reaction Schemes for Hydrocarbon Combustion", Combustion and Flame, Vol. 73, pp. 233-242.
- Konnov A., 2007, "Alexander Konnov's combustion mechanisms", [http:// hemepages.vub.ac.be/~akonnov/](http://hemepages.vub.ac.be/~akonnov/)
- Kee R.J., Rupley F.M., Meeks, E. and Miller J.A., 2000, "CHEMKIN: A Software Package for the Analysis of Gas-Phase Chemical and Plasma Kinetics", Sandia National Laboratories Report SAND96-8216, CA.
- Krioukov, V.G., Naoumov V.I., Abdullin, A.L., Demin, A.V. and Trinos T.V., 1997, "Combustion and Flow in Propulsion and Power Generation Systems: Modeling, Energy, Ecology", Ed. Yanus, Moscow.
- LEED's - Reaction Kinetics Database, 2004, School of Chemistry, University of Leeds.

- Marinov, N.M., Pitz, W.J., Westbrook, C.K. and Melius, C.F., 1998, "Aromatic and Polycyclic Aromatic Hydrocarbon Formation in a Laminar Premixed n- Butane Flame", *Combustion and Flame*, Vol. 114, pp. 192-213.
- Prior, D. and Lopes, S., 2000, "Ethylene Plant Closed-loop optimization", *Hydrocarbon Processing*, No. 6, pp. 81-84.
- Spilimbergo, A.P, Veloso, G.O., Krioukov, V.G. and Iskhakova, R.L., 2007, "Engagement Method: Application in Area of Alteration of the Parameters of the Reacting Medium", *Proceedings of the XXVIII CILAMCE (Iberian Latin American Congress on Computational Methods in Engineering)*, Porto, Portugal.
- Stell, J., 2003, "International Survey of Ethylene from Steam Crackers", *Oil and Gas Journal*, Vol. 101, No. 3, pp. 47-53.

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