MODELLING OF STEAM CRACKING. I. SIMPLIFIED MATHEMATICAL MODEL OF STEAM CRACKING FURNACE AND ITS IDENTIFICATION

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A simplified mathematical model of a steam cracking furnace was constructed. The model involves adjustable parameters, values of which are to be evaluated on the basis of measurements available in industrial reactors. The following adjustable parameters are considered: the effective radiative heat transfer coefficient, the convective heat transfer coefficient, the mean relative reactivity of the reaction mixture. The sources of information which can be utilized in the model identification are discussed. A numerical procedure was developed for finding the best set of the adjustable parameters. The procedure is based on the analogy with single-input single-output control loops.

The aim of this research was to develop a simplified mathematical model of a steam cracking furnace which can be used in computer-aided control of industrial units. As some technological properties of the furnaces are changing during the operation cycle, the model involves adjustable parameters, values of which reflect the instantaneous state of the equipment.

The changes of technological properties result from formation of coke deposites on the inner wall of the reactor tube. The impact of the coke layer growth on the reactor properties is complex: The growing coke layer reduces the reactor void volume, thereby affecting the residence time. It reduces the tube void cross-section, which affects the heat transfer area between the reaction mixture and the tube wall, the surface-to-volume ratio of the tube and the flow velocity of the reaction mixture, hence, the convective heat transfer coefficient reaction mixture–tube wall. Furthermore, the coke layer represents an additional heat transfer resistance to that of the tube wall.

Another type of changes is connected with changes of properties of the external surface of the tubes and the surface of the furnace wall. Changes of radiative properties of these surfaces affect the radiative heat transfer between the radiation chamber and the reactor tube.

THEORETICAL

Classification of Information Available for the Model Identification

Information used in identification can be classified into two groups: (i) Direct (internal) information is obtained by a direct measurement on the controlled furnace at the time of identification. It characterizes the instantenous state of the equipment. (ii) Indirect (external) information is based on a long-term experience on the process control, on laboratory measurements, physico-chemical data from literature, etc. It describes general properties of the system.

Structure of the Model

Reaction kinetics. Description of the reaction kinetics is introduced as external information. The steam cracking was described by a system of rate equations[1] of general form

$$r_{\mathrm{j}} = r_{\mathrm{j}}(C_{\mathrm{j}}, T_{\mathrm{r}}, P_{\mathrm{r}})\,. \qquad (1)$$

The rate of heat consumption by chemical reactions then is

$$r_{\mathrm{h}} = \sum^{l} r_{\mathrm{l}} H_{\mathrm{l}}\,. \qquad (2)$$

Pressure drop. Description of the longitudinal profile of the reaction pressure was introduced as external information (Eq. (*3*)),

$$\mathrm{d}P_{\mathrm{r}}/\mathrm{d}z = f_{\mathrm{p}}(C_{\mathrm{j}}, T_{\mathrm{r}}, P_{\mathrm{r}}, F_{\mathrm{r}}) \qquad (3)$$

with the initial condition: if $z = 0$ then $P_{\mathrm{r}} = P_{\mathrm{r}}^{\mathrm{i}}$.

Reaction mixture. The piston flow model was used for the reaction mixture. The component balance was written in the form

$$\mathrm{d}n_{\mathrm{j}}/\mathrm{d}z = r_0\, r_{\mathrm{j}}\, S / F_{\mathrm{r}}\,, \qquad (4)$$

where S is the cross-section of the reactor tube in the coke-free state and r_0 an adjustable parameter which will be called the relative reactivity of the reaction mixture. It was introduced to reflect the changes in the void reaction volume, on one side, and the uncertainity in the kinetic model on the other.

In integration of the model equations, the following initial condition was used:

$$\text{if } z = 0 \text{ then } C_{\mathrm{j}} = C_{\mathrm{j}}^{\mathrm{i}}\,.$$

The heat balance of the reaction mixture was used in the form

$$\mathrm{d}T_r/\mathrm{d}z = \frac{\pi}{F_r c_{pr}} (0.25\, d_{t1}^2 r_0 r_h + d_{t2} q)\,, \tag{5}$$

where d_{t1} is the inner diameter of the tube and q the heat flux density related to the external tube diameter.

In integrations the following initial condition was applied:

$$\text{if } z = 0 \text{ then } T_r = T_r^i\,.$$

Radiation chamber. The radiation chamber is supposed to be ideally mixed. The heat balance of the radiation chamber can be written in the form

$$F_g c_{pg}^a T_g^a - F_g c_{pg}^e T_g^e = Q_g\,, \tag{6}$$

where T_g^a is the temperature of adiabatic combustion. Its value was calculated from the initial compositions and feed rates of the air and the fuel gas. Q_g is the overall heat flux from the radiation chamber into the reactor tube.

Heat is transferred from the heating gas to the extrernal surface of the reactor tube by radiation. The heat flux density related to the tube external surface was described by equation

$$q_{gt} = k_{gt}[(T_g^e)^4 - T_{gt}^4]\,, \tag{7}$$

where k_{gt} is the effective radiative heat transfer coefficient. k_{gt} is the second adjustable parameter, because the radiative surfaces may change their properties during the operating cycle.

The radiated heat is transferred through the reactor wall into the reaction mixture. The heat flux density through the reactor wall, related to the tube external surface, was described by equation

$$q_{tr} = U_{tr}(T_{gt} - T_r)\,. \tag{8}$$

If Eqs (*7*) and (*8*) are applied in the same point of the tube surface, the equality (*9*) is valid:

$$q_{gt} = q_{tr}\,. \tag{9}$$

Conversion coordinates. In on-line control of a steam cracking furnace, a simple quantity must be defined to characterize the exit composition of the reaction mixture. The degree of conversion, which is used in reaction engineering of simple reactions, is not suitable in describing the steam cracking from the following reasons: The degree of conversion is based on evaluating the unchanged portion of reactants. For this portion to evaluate, all the compounds in the feedstock must be balanced, which is difficult, time spending and unreliable from practical reasons.

The decomposition of the molecules of reactants represent only a minor part of the transformations, because steam cracking is a complicated system of multi-stage consecutive reactions. As a consequence, the exit degree of conversion of reactants exceeds 97% in industrial reactors. That means that the range of its variations is very narrow and that it is a highly nonlinear parameter to temperature and feed rate.

To solve the problem, another conversion coordinate has to be defined. Principally, any characteristics, the value of which changes monotonously with increasing deepness of cracking (monotonously along the reactor tube), can be chosen. Of course, practical reasons must be considered. The characteristics should be readily evaluated. Its value should be, if possible, approximately a linear function of the tube length coordinate for the characterization to be sensitive within the whole range of exit composition.

Four characteristics were considered: the yield of methane (mol/kg of feed), the yield of ethene (mol/kg of feed), the ethene : propene ratio (dimensionless), the methane : propene ratio. Examples of changes of these parameters along the reactor tube are shown in Fig. 1. The yield characteristics are difficult to evaluate, because the overall process mass balance must be accomplished to evaluate the yields. The ratio characteristics are based on relative values and can be evaluated from the analysis of the gaseous stream without balancing the system. Then, either of them can be used as the conversion coordinate.

Overall heat balance of the reaction mixture. When using a conversion coordinate, the composition of the reaction mixture becomes a function of the coordinate

$$C_j = C_j(X)\,. \qquad (10)$$

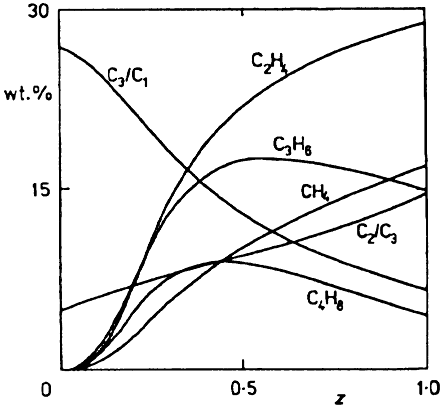


FIG. 1

Example of longitudinal product yields resulting from simulation with a naphtha blend. CH_4 methane, C_2H_4 ethylene, C_3H_6 propylene, C_4H_8 1-butene + 2-butene + isobutene, C_2/C_3 ethylene/propylene ratio, C_3/C_1 propylene/methane ratio, z dimensionless length. Reaction conditions: temperature interval 630 – 840 °C, total pressure interval 350 – 240 kPa, steam/oil ratio 0.7 kg kg^{-1}, naphtha density 706 kg m^{-3}

Examples of the effect of the coordinates on the products yields are shown in Figs 2 and 3.

Let's define the integral reaction heat as the heat which is consumed by all reactions in 1 kg of the reaction mixture when reaching the conversion coordinate X at a constant temperature. The integral reaction heat is a function of X (Eq. (*11*)), examples of these functions are shown in Fig. 4.

$$H_r = H_r(X) \qquad (11)$$

The value of H_r is slightly dependent on the reactor regime due to the effect of the reactor regime on the process selectivity. This fact causes some problems in the model identification. A corrective iteration loop must be added to compensate this effect.

The overall heat balance can be written in the form

$$Q_r = F_r c_{pr}^{e} T_r^{e} - F_r c_{pr}^{i} T_r^{i} + F_r H_r(X_e)\,, \qquad (12)$$

where Q_r is the overall heat flux into the reaction mixture.

RESULTS AND DISCUSSION

Measurable Quantities in Large-Scale Steam Cracking Reactors (Internal Information)

Generally, assessment of direct information on the reactor regime is an experimentally difficult task and information obtained is poor (see Table I). Most quantities can be

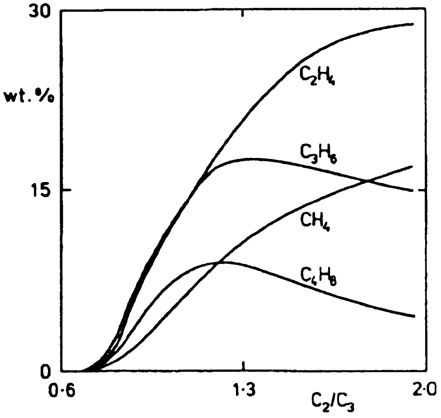


FIG. 2

Example of product yields dependence on ethylene/propylene ratio (in kg kg^{-1}). Symbols and regime characteristics are given in Fig. 1

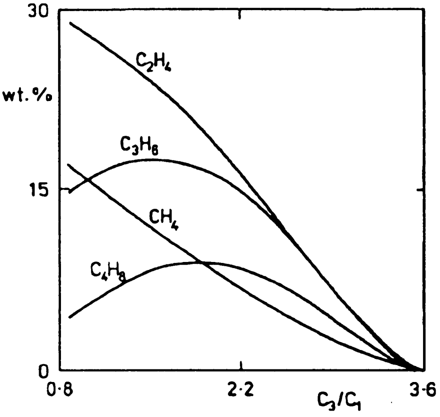


FIG. 3

Example of product yields dependence on propylene/methane ratio (in kg kg^{-1}). Symbols and regime characteristics are given in Fig. 1

measured exclusively at the inlet and exit of the reactor tube. For example, the longitudinal profiles of composition and reaction temperature cannot be obtained due to experimental problems. The only variable, which can be measured along the reactor tube is the tube skin temperature, T_{gt}. Unfortunately, its measurement is not reliable enough to permit any application of sophisticated methods to evaluate the longitudinal

TABLE I
Measurable quantities in industrial steam cracking reactors (direct information)

Symbol	Explanation	System
C_j^i	inlet composition	*reaction mixture*
C_j^e	exit composition	
P_r^i	inlet reaction pressure	
P_r^e	exit reaction pressure	
T_r^i	inlet reaction temperature	
T_r^e	exit reaction temperature	
F_r	feed rate	
C_g^i	inlet composition	*radiation chamber*
C_g^e	exit composition	
T_g^i	inlet temperature	
T_g^e	exit temperature	
F_g	feed rate	
T_g^a	temperature of diabatic combustion	
T_{gt}	tube skin temperature	*reactor tube*

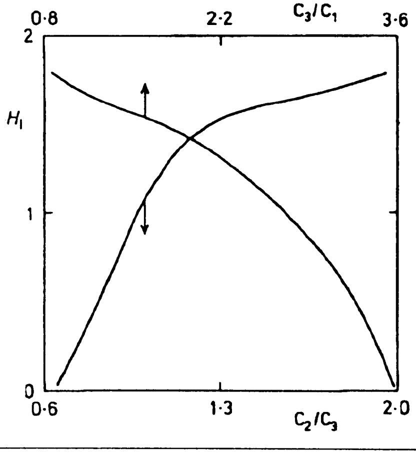


FIG. 4
Example of integral reaction heat H_l (MJ kg^{-1}) dependence on ethylene/propylene (C_2/C_3) and propylene/methane (C_3/C_1) ratios (in kg kg^{-1}). Regime characteristics are given in Fig. 1

profiles of the system properties developed to analyze regime catalytic tube reactors[2,3]. Neither a sophisticated statistical method can be used to treat the measured longitudinal tube skin temperature profile. In practical situations an intuitive method must be applied to obtain one reliable value of the tube skin temperature to be inserted into the process identification. The knowledge of at least one value of the tube skin temperature is essential for the model identification. Without its knowledge the relationship between the radiative heat transfer and the conductive and the convective heat transfer cannot be evaluated.

Redundancy of Information

Besides the tube skin temperature the overall heat flux from the radiation chamber into the reactor tube is the quantity necessary for identification of the model. As the heat transferred from the radiation chamber to the tube external surface, Q_g, equals the heat transferred from the external surface into the reaction mixture, Q_r, it can be evaluated from two independent sources: from the heat balance of the reaction mixture

$$Q_r = Q_r(F_r, T_r^i, T_r^e, X^e) \qquad (13)$$

and from the heat balance of the radiation chamber

$$Q_g = Q_g(F_g, T_g^e)\,. \qquad (14)$$

However, the heat balance of the radiation chamber is not reliable, because the flow pattern of the combustion gas is complex and the measurement of its temperature is difficult. Consequently, the heat balance of the reaction mixture is more accurate and more reliable than that of the radiation chamber.

TABLE II
Combinations of measured values enabling to evaluate the values of r_0, k_{gt} and U_{tr}

Radiation chamber		Reaction mixture				Tube	Free (dependent) variable
F_g	T_g^e		T_r^i	T_r^e	F_r	T_{gt}	X^e
F_g	T_g^e						
				T_r^i	F_r	T_{gt}	T_r^i
F_g	T_g^e	X^e	T_r^i		F_r	T_{gt}	T_r^e
F_g	T_g^e	X^e	T_r^i	T_r^e		T_{gt}	F_r
F_g		X^e	T_r^i	T_r^e	F_r	T_{gt}	T_r^e
	T_g^e	X^e	T_r^i	T_r^e	F_r	T_{gt}	F_g

In the model identification, a set of directly measured quantities enabling to evaluate the overall heat flux, Q_g, must be available. If both the heat balance of the reaction mixture and that of the radiation chamber are available, the comparison of their results can be used to check the consistency of experimental data. Then, only one of them can be selected as an input into the model identification. In the remaining heat balance, one quantity must stay free as an adjustable parameter to ensure the equality

$$Q_r = Q_g . \qquad (15)$$

All combinations of the directly measured quantities enabling the model identification are listed in Table II. In the heat balance of the reaction mixture, the feed rate, F_r, and the conversion coordinate, X^e, have the major effect, whereas the temperatures T_r^i and T_r^e cannot affect the heat balance significantly. This conclusion results from the fact, that the reaction heat forms the essential part of the heat consumed in the reactor tube. Consequently, if the heat balance of the reaction mixture is to be open, either the feed rate or the exit value of the conversion coordinate should be selected as the free variables. If either T_r^i or T_r^e were free, the sufficient variability of the heat balance Q_r would not be ensured. In practical controls, the heat balance of the reaction mixture will be used as the closed one, while that of the radiation chamber will be taken as a certain correction or check of heat balances. That means, that T_r^i, T_r^e, F_r and X^e will be measured as the basis to evaluate the overall heat flux Q_r.

As for the radiation chamber, two types of inputs can be accepted: T_g^e is the measured quantity and the feed rate of the heating gas is the dependent quantity, value of which is calculated from the heat balance of the radiation chamber, (Eq. (*6*)), by introducing the overall heat flux calculated from the heat balance of the reaction mixture (Eq. (*12*)). F_g is measured and T_g^e is free, its value being calculated from the heat balance of the radiation chamber (Eq. (*6*)).

Number of Iterated Unknown Quantities

There are three unknown parameters in the model which are to be evaluated in the model identification: k_{gt}, U_{tr}, r_0. The computing time to find their values depends on the number of parameters which must be found by empirical comparisons of the measured and the simulated regime characteristics. Computing of one state of the reactor may be time spending, especially, if a complex kinetic model of the steam cracking is incorporated in the model. Consequently, large number of necessary iterations may be a serious obstacle in using the model in the on-line control.

The number of iterated parameters may be either two or three, according to the way of introducing the tube skin temperature, T_{gt}. If the tube skin temperature is known in a point where the temperature in the radiation chamber is known and the reaction temperature is measured, only two parameters are to be iterated. Consequently, in this point the relationship between the radiative heat transfer coefficient, k_{gt}, and the overall heat transfer coefficient, U_{tr}, can be evaluated without iterations, using Eqs (*7*), (*8*) and (*9*). For example, if all the values are measured at the exit end of the tube the following expression is applied

$$k_{gt} = U_{tr} \frac{(T^{e}_{gt} - T_{r})}{[(T^{e}_{g})^{4} - (T^{e}_{gt})^{4}]} . \qquad (16)$$

Consequently, U_{tr} and k_{gt} become dependent one on another and only one of them can be selected as the iterated variable the other being dependent.

If the values of T_g, T_r and T_{gt} are measured in different points, k_{gt}, U_{tr} and r_0 must be iterated as independent variables. Then the number of iterated parameters will be three. In this research only the case with two iterated parameters was solved.

Iteration Methods

The aim of iterations can be formulated in the following way: a set of values of r_0 and U_{tr} is to be found for which the exit parameters T_r^e and X^e reach their measured values (k_{gt} can be directly calculated from Eq. (*16*)). When starting the research we hoped to solve the problem by applying general optimization techniques based on minimization of the penalty function (*17*).

$$Y = 1\,000\,(X^{e}_{sim} - X^{e}_{exp})^2 + (T^{e}_{r\,sim} - T^{e}_{r\,exp})^2 . \qquad (17)$$

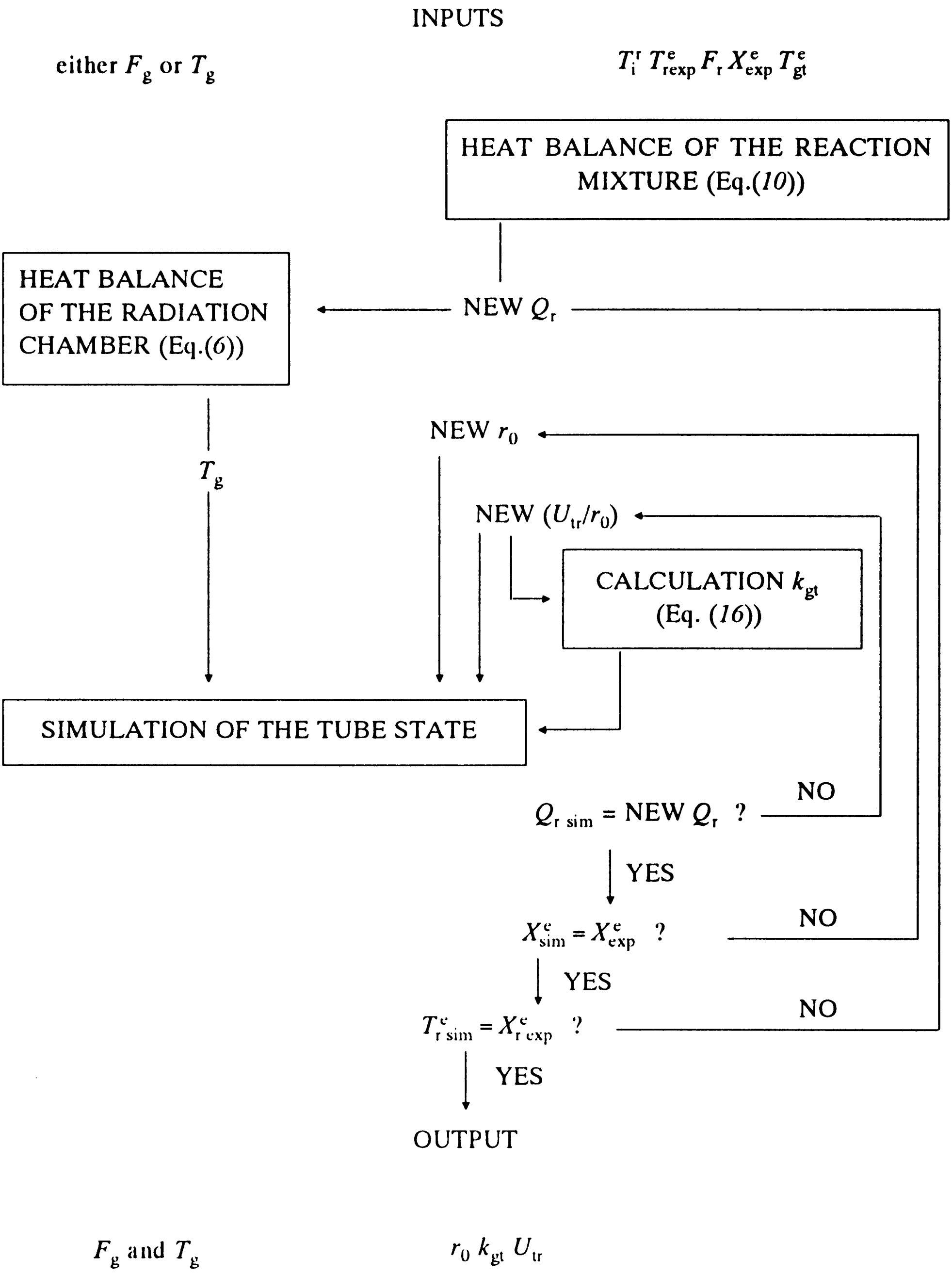
The application of standard optimization techniques (the simplex method, Monte Carlo search, the gradient method) proved to be ineffective and unreliable. The iterations were time consuming, more than 500 computations of the reactor state were necessary to reach a reasonable agreement between the simulated and experimental exit values. Moreover, the result was extremely sensitive to the location of the starting point. The reason for this behaviour is a strong interaction between the effects of the iterated parameters.

To develop an effective iteration method, two measures were taken: The manipulated parameters were transformed in such a way to reflect the inner couplings in the system. Instead of r_0 and U_{tr}, the parameters r_0 and U_{tr}/r_0 were iterated, because the heat input into the reaction mixture must increase with increasing reactivity of the mixture.

Control loops analogical to single-input single-output control loops in the control engineering were applied to control the movement of the tested state point in the phase plane. The structure of the control system is shown in Scheme 1.

The following control loops were introduced:

1. The rapid loop: the heat flux into the reactor tube is controlled by manipulating (U_{tr}/r_0) at unchanged value of r_0, until the heat flux into the reactor tube reaches the value calculated from Eq. (*10*) when introducing the measured values of X^e and T_r^e.


INPUTS
either F_g or T_g
T_i^r T_{rexp}^e F_r X_{exp}^e T_{gt}^e
HEAT BALANCE OF THE REACTION MIXTURE (Eq.(10))
HEAT BALANCE OF THE RADIATION CHAMBER (Eq.(6))
NEW Q_r
NEW r_0
T_g
NEW (U_{tr}/r_0)
CALCULATION k_{gt} (Eq. (16))
SIMULATION OF THE TUBE STATE
$Q_{r\,sim}$ = NEW Q_r ?
NO
YES
$X_{sim}^e = X_{exp}^e$?
NO
YES
$T_{r\,sim}^e = X_{r\,exp}^e$?
NO
YES
OUTPUT
F_g and T_g
r_0 k_{gt} U_{tr}

SCHEME 1

The new value of the parameter (U_{tr}/r_0) was calculated from an empirical equation

$$(U_{tr}/r_0)_{NEW} = (U_{tr}/r_0)_{OLD}\,(Q_{r\,exp}/Q_{r\,sim})^{a}\,, \tag{18}$$

where $Q_{r\,exp}$ is the heat flux into the tube calculated from Eq. (*10*) and $Q_{r\,sim}$ that resulting from simulation.

2\. The slow loop: after the agreement between the values of $Q_{r\,exp}$ and $Q_{r\,sim}$ is reached, the value of r_0 is corrected, at unchanged ratio (U_{tr}/r_0). An empirical control algorithm was applied to derive the new value of r_0,

$$(r_0)_{NEW} = (r_0)_{OLD}\,(X^{e}_{exp}/X^{e}_{sim})^{b}\,, \tag{19}$$

a and *b* in Eqs (*18*) and (*19*) are empirical parameters used in tuning the control loops. Their values were varied within interval 0.5 to 2 in such a way to avoid oscillations of the parameters during iterations.

3\. The corrective loop: this slowest loop had to be introduced to compensate the effect of the reactor regime on the overall heat flux into the reactor tube. The process selectivity being dependent on the reactor regime (on the longitudinal temperature and pressure profile), the value of Q_r calculated from Eq. (*10*) is not identical with that resulting from simulations after both condition (*15*) and the condition $X^{e}_{sim} = X^{e}_{exp}$ are fulfilled. The result is that the simulated exit temperature $T^{e}_{r\,sim}$ is not equal to the experimental value $T^{e}_{r\,exp}$. The new value of Q_r was calculated from the control equation:

$$Q_{r\,NEW} = Q_{r\,OLD} - (T^{e}_{r\,sim} - T^{e}_{r\,exp})\,F_r\,c^{e}_{pr}\,. \tag{20}$$

An amount of 10 to 30 iterations were necessary to achieve a reasonable agreement between the simulated and experimental exit values using these control loops. The method is not sensitive to the location of the starting point. The computing time on a PC computer with coprocessor is short enough for using identification in an on-line control system.

Pressure Drop

In developed turbulent flow, the friction coefficient can be considered as independent on the Reynolds number. The Eq. (*3*) can be transformed into the form

$$\mathrm{d}P_r/\mathrm{d}z = k_p\,F_r^2\,\frac{T_r}{M_m\,P_r}\,, \tag{21}$$

where M_m is the mean molecular weight of the reaction mixture (including the water steam) and k_p is a parameter involving the geometry of the reactor tube and its instantaneous state (thickness of the coke layer). Generally, both the inlet pressure, P_r^{i}, and the exit pressure, P_r^{e}, must be measured to evaluate the parameter k_p. Unfortunately, a direct measurement of the pressure at the inlet and exit from the radiation chamber is difficult. In most cases the pressure at the inlet into the convective section of the furnace and that at the exit from the cooling equipment can be measured. Consequently, the values of P_r^i and P_r^e should be considered more as estimates than as accurate values. Furthermore, the pressure drop is insensitive to temperature and the conversion coordinate, because these variables are not permitted to vary within a broad range.

Taking all these facts into account, the parameter k_p can be evaluated in a separated iteration loop based on integration of the equations describing the state of the reaction mixture at a fixed typical longitudinal temperature profile and a typical exit conversion coordinate. A pair of values of P_r^i and P_r^e must be introduced as input. This control loop is used to obtain the value of P_r^i necessary as input to evaluation of r_0, k_{gt} and U_{tr}.

SYMBOLS

a	empirical coefficient, Eq. (*18*), dimensionless
b	empirical coefficient, Eq. (*19*), dimensionless
C_j	vector of concentrations of compounds in the reaction mixture, mol kg^{-1}
c_{pg}	specific heat of the heating gas, J kg^{-1} K^{-1}
c_{pr}	specific heat of the reaction mixture, J kg^{-1} K^{-1}
d_{t1}	inner diameter of the reactor tube, m
d_{t2}	external diameter of the reactor tube, m
f_p	function describing the effects of composition, temperature, pressure and feed rate on pressure drop, Pa m^{-1}
F_g	feed rate of the heating gas, kg s^{-1}
F_r	feed rate of the reaction mixture, kg s^{-1}
H_l	reaction heat of reaction *l*, J mol^{-1}
H_r	overall reaction heat consumed to reach conversion coordinate *X*, J kg^{-1}
k_{gt}	effective radiative heat transfer coefficient radiation chamber–tube skin, W m^{-2} T^{-4}
n_j	concentration of component *j*, mol kg^{-1}
P_r	reaction pressure, Pa
q_{gt}	heat flux density, radiation chamber–tube skin, W m^{-2}
q_{tr}	heat flux density, tube skin–reaction mixture, W m^{-2}
Q_g	overall heat flux from the radiation chamber on the tube external surface, W
Q_r	overall heat flux transferred into the reaction mixture, W
r_h	rate of heat consumption by chemical reactions, W m^{-3}
r_j	rate of formation of component *j* by all reactions, mol m^{-3} s^{-1}
r_0	relative reactivity, dimensionless
r_l	rate of reaction *l*, mol m^{-3} s^{-1}
S	cross-section area of the reactor tube in coke free state, m^2
T_g	temperature of the heating gas in the radiation chamber, K
T_{gt}	temperature of the tube external surface, K
T_r	temperature of the reaction mixture, K
U_{tr}	overall heat transfer coefficient, tube skin–reaction mixture, K
X	conversion coordinate, dimensionless
z	length coordinate of the reactor tube, m

Subscripts

exp	measured value
sim	value obtained by simulation

Superscripts

a	adiabatic combustion of the fuel gas
e	exit of the reactor tube or radiation chamber
i	inlet of the reactor tube

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