# CONTRIBUTION TO THE RESEARCH AND DEVELOPMENT OF RADIATION CHAMBERS IN STEAM REFORMING. INFLUENCE OF SELECTED PARAMETERS ON MAIN CHARACTERISTIC QUANTITIES

Petr STEHLÍK
*Technical University, 616 69 Brno*

Received June 11, 1990
Accepted August 7, 1990

By means of a mathematical model simulating thermal chemical processes taking place in primary reformer radiation chamber, the influence of selected parameters on main characteristic quantities in steam reforming process was investigated. The parameters were divided into inlet parameters on flue gas side, inlet parameters on reaction mixture side and those of radiation chamber geometry. As main characteristic quantities outlet temperature of reaction mixture, maximum temperature of reaction tubes outer surface, outlet temperature of flue gases, absorbed heat, methane conversion into carbon dioxide and carbon monoxide as well as temperature distance from equilibrium were chosen.

The mathematical model of a steam reforming radiation chamber[1] is based on one of the theoretically most elaborated principles of modelling combustion spaces – on the zone method. This model has been developed and tested by being compared with the results of measurements carried out on an operational unit producing synthesized gas for a subsequent production of 1 000 tons of ammonia per day and later on also on units of 300 and 1 360 tons of ammonia per day. Attempts to visualize flue gas flow contributed to a relatively very good agreement of the main measured and calculated characteristics investigated[1]. Considerations dealing with a determination of reaction tubes life are also included in our previous paper[1].

It can be stated that it is no more possible to increase modelling reliability by applying a more complicated model. A source of inaccuracy and uncertainty of modelling are not, so to say, only simplifications incorporated in the calculation by modelling, but particularly a lack of data on the process itself.

The uncertainty when modelling steam reforming furnaces is associated with parameters whose value can be determined in a difficult way only, or with parameters whose value changes in the course of the operation. In order to be able to compare regimes of individual reactors or to confront the results of mathematical modelling with experiment, it is necessary to find out what the effect of these parameters is on the course of the process, on temperature distribution along reaction tube etc.

The mathematical model also enables the influence of the change in some parameters of radiation chamber geometry to be investigated, which facilitates designer's work.

## THEORETICAL

When investigating parametric sensitivity of the model it can be stated, to what extent selected parameters affect resultant values computed. As main characteristic process quantities whose course was investigated, the following ones were chosen: outlet temperature of reaction mixture ($t_{sm}$), maximum temperature of reaction tube outer surface ($t_{t,max}$), outlet temperature of flue gases ($t_{sp}$), absorbed heat ($\dot{Q}_{abs}$), conversion of methane into carbon dioxide and carbon monoxide ($x$), temperature distance from equilibrium ($\Delta T$).

Temperature distance from equilibrium[2] can be taken as one of the criteria evaluating regime of steam reforming. It is defined as a difference between outlet temperature of reaction mixture and the temperature at which outlet composition of reaction mixture would be an equilibrium one. It is an empirical criterium whose

TABLE I
Parameters investigated

| Parameter | | Unit | Value |
|---|---|---|---|
| One burner input | | $m_N^3\ h^{-1}$ | 165·474 |
| Emissivity of reaction tube surface | | — | 0·95 |
| Flame length | | m | 2·5 |
| Excess air | at inlet | — | 1·05 |
| | at outlet | — | 1·10 |
| Heat losses (% $\dot{Q}_{sp}$) | | — | 1·0 |
| Catalyst activity | | $mol\ kg^{-1}\ cat\ s^{-1}$ | 0·02 |
| Activation energy | | $J\ mol^{-1}$ | 87 100 |
| Correction factor of heat transfer coefficient | | — | 0·6 |
| Tube length | | m | 10·76 |
| Tube diameter | outer | mm | 145 |
| | inner | mm | 110 |
| Tube pitch | | mm | 354 |
| Distance of tube rows | | m | 2·5 |

main advantage lies in the fact that it contains quantities only which can be measured, i.e. outlet composition of reaction mixture and outlet temperature (equilibrium data being already available). Analysis performed[2] revealed that the so-called temperature distance from equilibrium was affected by all parameters of reactor regime in a relatively complicated way. It is therefore not correct to compare the numerical value of the above factor by means of a chart only stating that the reactor having a lower value is better but it is necessary to carry out a more detailed analysis since the influences of individual factors are mutually interconnected in a rather complicated way.

The influence of the parameter groups given below was investigated on the course of the main characteristic quantities referred to above: (i) influence of inlet parameters on flue gas side, (ii) influence of inlet parameters on reaction mixture side, (iii) influence of the change in some parameters of radiation chamber geometry. The parameters investigated can be seen in Table I. In simulation calculations always only the value of a selected parameter was changed, whereas the other data incorporated remained constant.

As a basic correlative variant that of the calculation of a radiation chamber unit producing 1 000 tons of $NH_3$ per day[1] was selected with inlet data obtained as based on operational measurements which were tested and compared with the results of measuring. The values of the parameters investigated in the above basic variant are reviewed in Table I.

When investigating parametric sensitivity, the deviation from the above values varied within real limits. The most instructive are graphical dependences (charts) from which it follows by how much percentage the value of the main characteristic quantity changes when the selected parameter is changed.

## RESULTS AND DISCUSSION

### INFLUENCE OF INLET PARAMETERS ON FLUE GAS SIDE

#### *Change in Burners Input (Fig. 1)*

The amount of fuel supplied to burners is an important factor by the change of which values of the main characteristic quantities in steam reforming can be affected. For instance a case can occur where in calculating heat balance based on values found, the amount of heat entering the process does not comply with that leaving the process[3]. Then a correction of fuel amount must take place which, however, does not considerably affect the values of main characteristic quantities. An example of applying graphical dependence (chart) of conversion increment on the change of fuel gas amount is given in another paper[4].

*Emissivity of Reaction Tube Surface (Fig. 2)*

One of the parameters whose value is not exactly known and changes during furnace operation is the emissivity of reaction tubes surface. To verify its influence on the values of the main characteristic quantities a value interval of 0·7 up to 1·0 was chosen. The measuring of tube surface temperatures revealed that the nominal value of emissivity was real in the basic variant (0·95).

*Profile of Fuel Burning and Burner Flame Length (Fig. 3)*

The profile of fuel burning characterizes the method of heat release by burning fuel gas and the flame length limits heat development area during fuel combustion. They are parameters depending on fuel composition, burner design, fuel gas and air flow.

By informative measurements carried out on an industrial unit in which the flue gas composition at radiation chamber ceiling was analyzed, it could be stated that

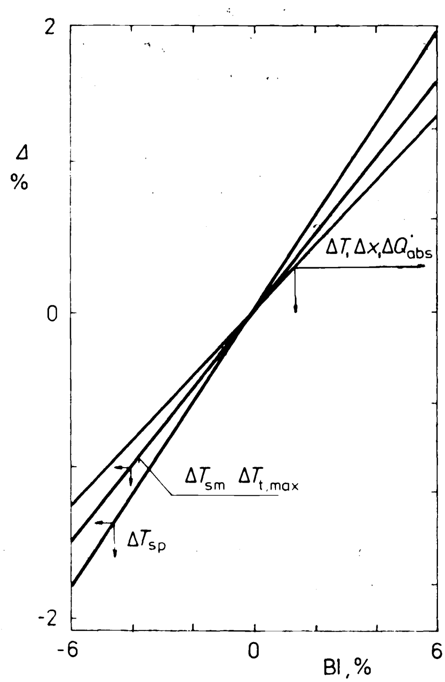


FIG. 1

Influence of the change in burner input; BI change of burner input, %

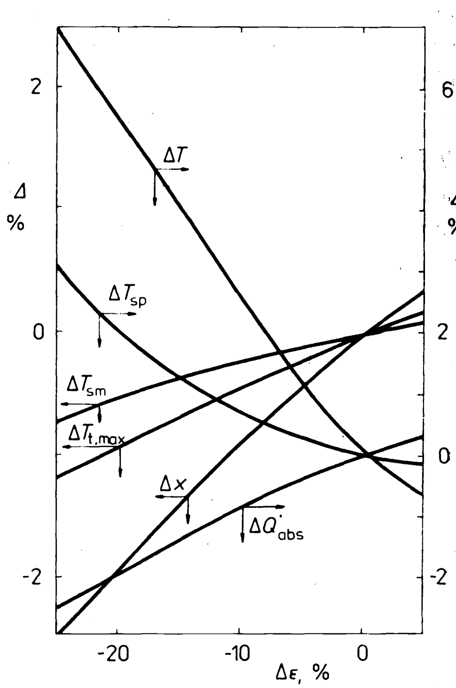


FIG. 2

Influence of reaction tube surface emissivity fuel burning took place approximately at the distance of 2·5 m from furnace ceiling. This value is included as flame length in the basic variant (see Table I). Fuel burning profile along flame length can be chosen – in mathematical modelling – from three possibilities (see Fig. 4) – i.e. as a parabolic asymmetric, *A*, Roesler's, *B*[5], and a uniform, *C*, profile.

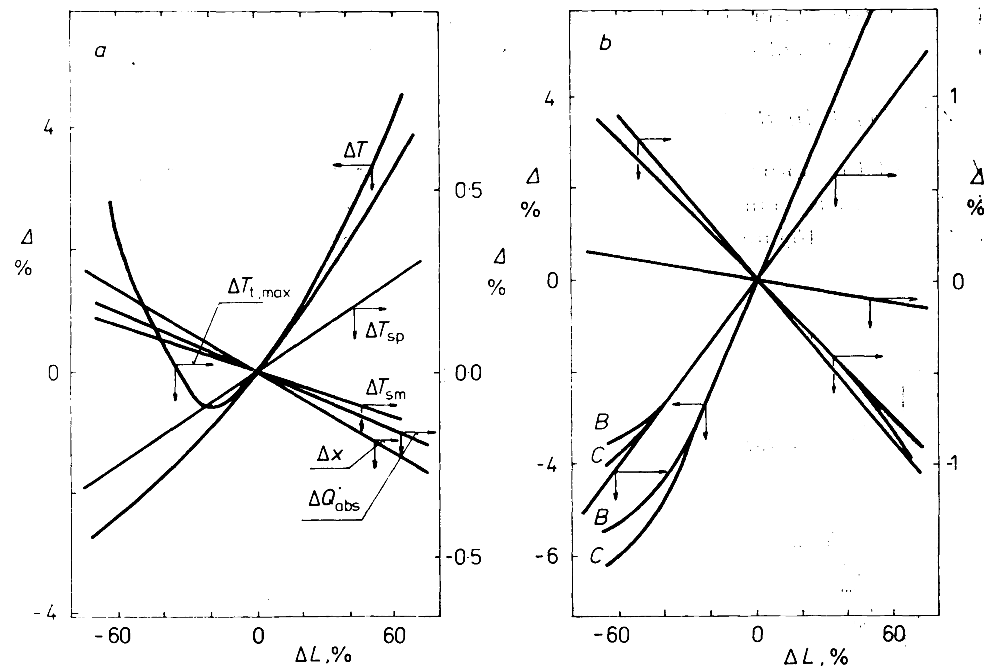


FIG. 3

Influence of fuel burning profile and burner flame length: *a A* parabolic asymmetric profile; *b B* Roesler's profile, *C* uniform profile (note: see Fig. 4)

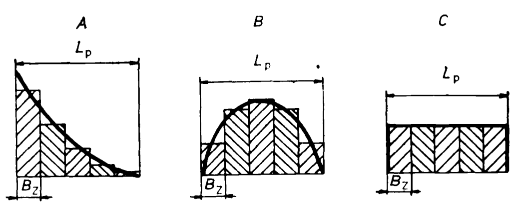


FIG. 4

Profiles of fuel burning: *A* parabolic asymmetric, *B* Roesler's parabolic symmetric, *C* uniform; $L_p$ flame length; $B_Z$ length of calculation zone

It can be stated that the choice of burning approximation does not play any decisive part, dependence curves for profiles $B$ and $C$ nearly coinciding.

*Mixing and Recirculation of Flue Gases*

The influence of mixing and a recirculation of flue gases has been dealt with in detail[3]. From the analysis it follows that the length of recirculation area exerts an important influence on the agreement of calculated courses of tube surface temperatures to the mean course found when choosing flue gas flow pattern, whereas a change in the maximum value of recirculation flow rate is of a minimum influence.

*Additional Air Suction* (Figs 5 and 6)

An effort to approach as much as possible actual operational conditions required to take into account the air additionally sucked from the environment by wall untightnesses. Figure 5 illustrates the influence of a change in inlet excess air with

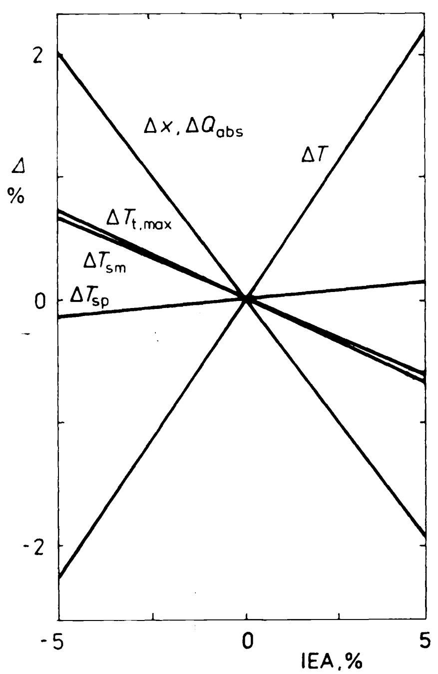


FIG. 5

Influence of inlet excess air; IEA change of inlet excess air, %. Note: amount of additionaly sucked air is constant

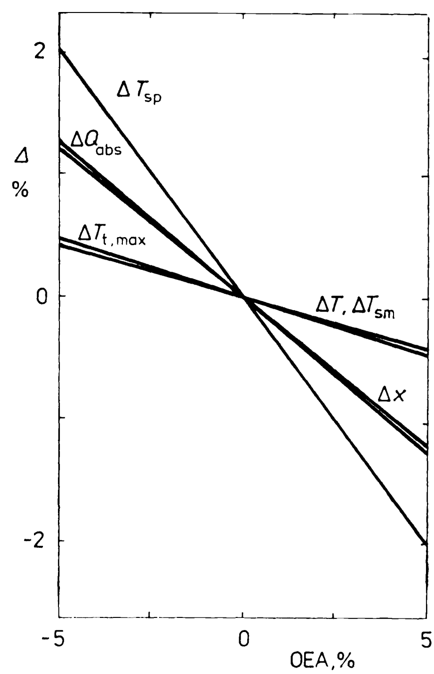


FIG. 6

Influence of outlet excess air; OEA change of outlet excess air, %. Note: inlet excess air is constant a constant amount of additionally sucked air and Fig. 6 shows/the influence of an increased amount of additionally sucked air (based on an increase of outlet excess air).

*Heat Losses* (Fig. 7)

Heat losses are included in the mathematical model as a certain portion of heat flow released during fuel gas combustion. By informative calculations it could be found that heat losses in case of the radiation chamber[1] were about 1% based on flow of heat released during combustion. These losses are relatively lower in big radiation chambers increasing with furnace size decrease.

## Influence of Inlet Parameters on Reaction Mixture Side

*Catalyst Activity* (Fig. 8)

The influence of catalyst activity change must be known owing to a gradual catalyst

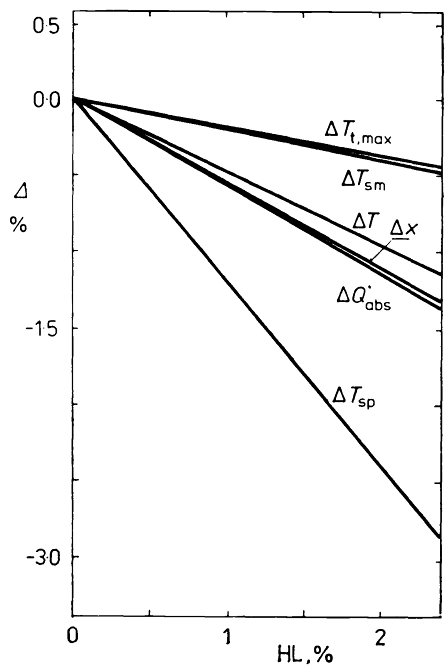


Fig. 7

Influence of heat loss amount; HL heat losses

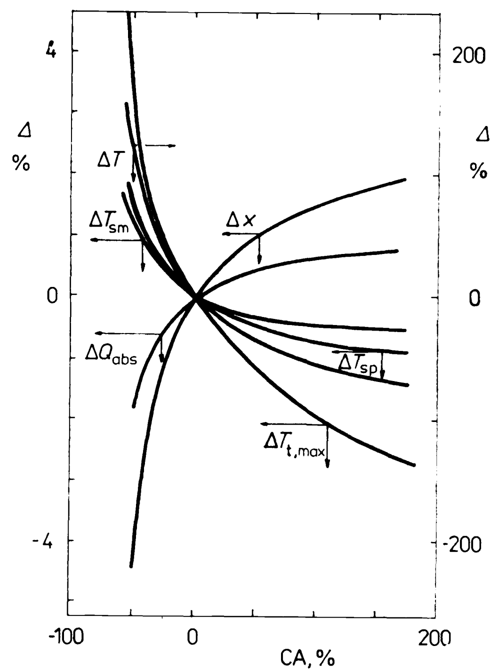


Fig. 8

Influence of catalyst activity; CA change of catalyst activity, %

deactivation during reactor operation. Reserves must be left in reactor output and in tube surface temperature so as to maintain required parameters even if catalyst activity drops.

The knowledge obtained when investigating the influence of activity change is in conformity to our conclusions[2]. An increase of catalyst activity improves heat transfer by radiation by increasing transfer motive force and decreases a possible overheating of reaction tube. The improvement of heat transfer by radiation enables the necessary amount of heat to be supplied to tubes, flue gas temperature being lower. A drop of reaction mixture outlet temperature enhances a reduction of temperature distance from equilibrium on whose value the activity of catalyst has its highest effect.

*Activation Energy* (Fig. 9)

From graphical dependences (charts) it follows that the change in activation energy value within the limits investigated has a minimum influence on the change in main characteristic quantities. With respect to the fact that the data on process kinetics in a specific catalyst are available in a rather difficult way, a conclusion can be drawn that the results of simulation calculations in steam reforming process cannot be affected if the initial value of activation energy is different from the exact value.

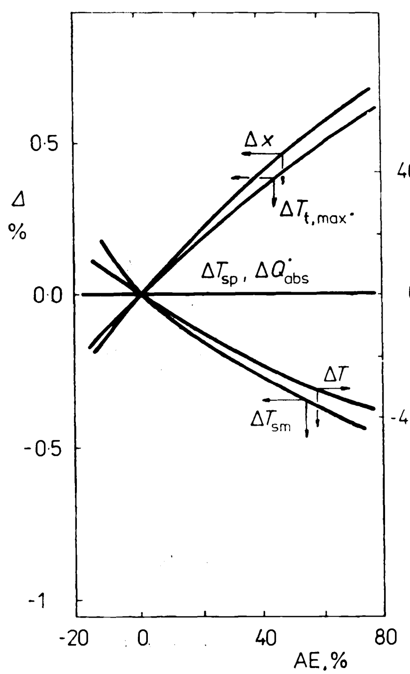


FIG. 9

Influence of activation energy; AE change of activation energy, %

*Heat Transfer Coefficient Value* (Fig. 10)

The total heat transfer coefficient value from reaction tube inner side to catalyst bed is a function of an apparent heat transfer coefficient at the wall and of an effective thermal conductivity of catalyst bed[6]. The data on the above coefficient obtained as based on correlation relations taken from literature are considerably uncertain. They may be uncertain due to different conditions (high flow velocity) and catalyst particle shape in an industrial reactor in comparison with laboratory instruments by which the values were measured serving as bases for the correlation relations in question.

With respect to the above uncertainties the mathematical model includes the so-called correction factor $f_k$ by which heat transfer coefficient from reaction tube inner wall to reaction mixture is multiplied. This correction factor is commonly used in steam reforming sphere and its value is considerably different based on various authors (see e.g. refs[7,8] where the value $f_k$ is 0·4 or ref.[9] where $f_k$ equals 1·33). The incorporation of $f_k$ resulted in obtaining a very good agreement of the values computed to those found in an industrial unit[1].

The change in the value of heat transfer coefficient distinctly affects tube surface temperature (Fig. 10). This temperature plays a primary part in tube life[1]. Correction

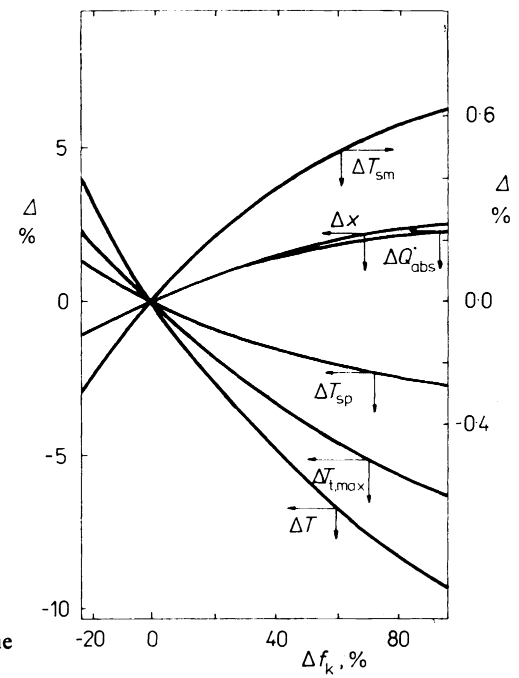


FIG. 10
Influence of heat transfer coefficient value

factor $f_k$ affects especially the absolute level foreaction tube surface temperature, whereas the shape of the temperature profile exerts a very little influence[3] similarly to the other main characteristic quantities. Due to the fact that the temperature of reaction tube outer surface is considered one of the main criteria when comparing values computed and found, the correction factor $f_k$ can be used for an "adaptation" of the mathematical model, i.e. for providing an agreement of both the calculations and the measurements. It is, however, necessary to mention that the recommended value of $f_k$ determined as based on a comparison of measured and computed values obtained in an industrial unit radiation chamber need not be in a good agreement to another industrial unit radiation chamber. Then it is also necessary to take into account an error in measuring tube surface temperatures, i.e. the likelihood of this value as a comparison criterium.

## Influence of a Change in Some Parameters of Radiation Chamber Geometry

### *Tube Length* (Fig. 11)

Heated tube length is a factor affecting considerably steam reforming conditions (see Fig. 11). In simulation calculations tube length was changed, tube total number being maintained, i.e. also catalyst total volume was changed. When shortening heated tube length, a rather marked increase of surface temperature could be stated, when extending it, decreasing surface temperature was found. This factor exerts a considerable influence on the change in reaction tube life.

The effect of tube length was also discussed in our paper[3]. It was found that with tube length shortening, the other conditions being maintained (total number of tubes or total catalyst volume) a progressive increase of requirements took place regarding the design (and production) of tube system due to high temperatures of reaction tubes. Tube extending, on the other hand, can result in possible material savings. For instance an extension of tubes from 10·7 m up to 12 m can save about 7·5% of material. From the point of view of fuel consumption in radiation chamber a drop of this consumption can be stated and at the same time an increase of chamber thermal efficiency takes place when extending heated tube length. Fuel savings must be, however, evaluated from the point of view of the whole technological approach.

### *Tube Diameter* (Fig. 12)

Similarly to testing tube length effect also reaction tube diameter was changed in this case, tube length being maintained. At the same time reaction tube wall thickness was changed as well (which is direct proportional to tube diameter) so as to maintain tube life required.

When changing tube wall thickness, also changes between heat exchange area and catalyst volume in reaction tube length element take place and at the same time the resistance to heat transfer from tube surface to catalyst bed interior is changed. An increase of tube wall thickness results in an increase of the maximum surface temperature. The designer must be aware of this fact since an effort of increasing the safety by using tube thicker wall is detrimental to its surface temperature.

*Tube Pitch*

The mathematical model also enables to find the influence of tube pitch change on the main characteristic quantities. From the simulation calculations it follows that the change of all quantities with the pitch change are not substantial. It is therefore obvious that the choice of reaction tube pitch of a specific diameter must be based on design viewpoints (location of inlet and outlet collectors, pigtails for reaction mixture supply, supply of fuel gas and combustion air to burners and the like).

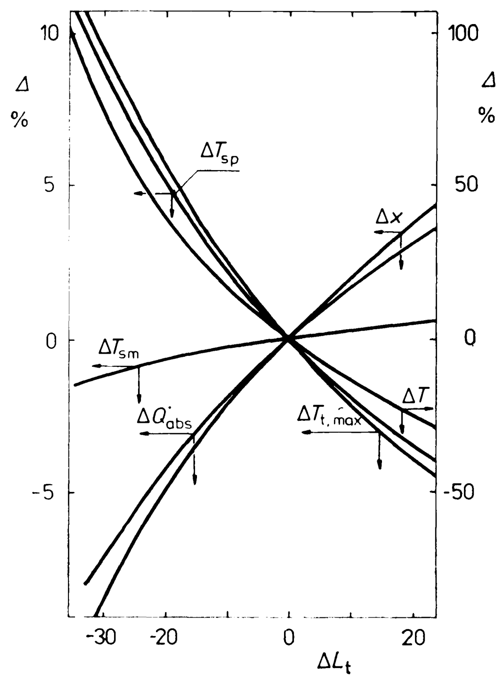


FIG. 11
Influence of tube length

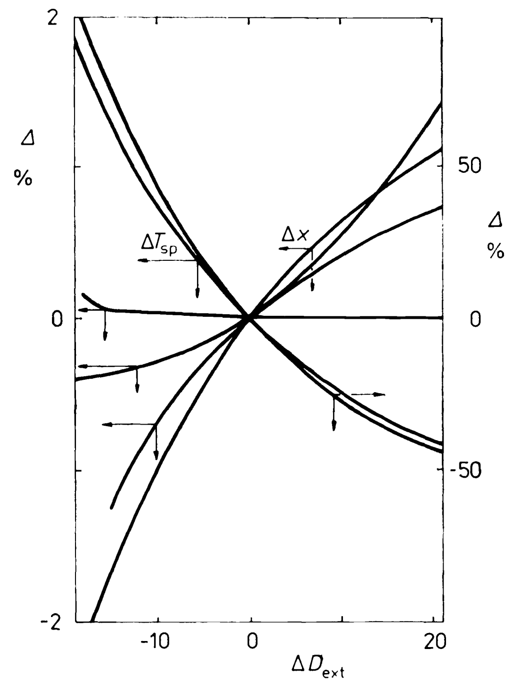


FIG. 12
Influence of tube diameter

*Distance of Reaction Tube Rows*

In simulation calculations taking into account the changes of tube rows distance in radiation chamber, tube distance from 1·75 up to 3·0 m was changed (in basic variant row distance being 2·5 m). It was found that the consequences of these changes were fully unimportant. Conclusions and recommendations for designers are therefore similar to the foregoing paragraph.

## EVALUATING THE INFLUENCE OF SELECTED PARAMETERS

An analysis of parametric sensitivity carried out in previous chapters reviews the influence of selected parameters on main characteristic quantities values. It enables a review to be obtained of the quantities which affect, in a considerable way, steam reforming process and which of them are of a less importance. This review is certainly not a complete one; there are selected parameters and chosen quantities involved whose course was investigated since they were considered the main ones.

The mathematical model, however, enables the designer to carry out a testing of other parameter influence in a similar way (e.g. ratio of water vapour to methane, inlet temperature and pressure of reaction mixture, amount of inlet reaction mixture etc.) and to investigate other quantities important for process evaluation (pressure drop, outlet concentration of reaction mixture individual components, heat flux and the like).

Some parameters have already been investigated in literature[2,10,11], which enables a comparison of the conclusions drawn with those of the present work to be carried out.

The influence of fuel burning rate has been dealt with in ref.[11], where a simplified mathematical model is applied to simulation, i.e. that a slow fuel burning (longer flame length) decreases reactor output as well as outlet conversion. Also the temperature of reaction mixture was lower.

The papers[2,11] referred, among other things, also to the recirculation (or recycling value) of combustion products. From the results of the simulation calculations it follows that all deviations from plug flow lead to a decrease in heat transfer efficiency. The most substantial is the change in tube temperature profile (see also ref.[1]). With the rising value of recirculation flow rate the outlet conversion and the temperature of reaction mixture drops. The authors draw identical conclusions, i.e. that the increase of recirculation flow rate exerts a minimum influence on the quantities investigated[11].

In papers[2,11] an analysis of the influence of catalyst activity on the change in reaction mixture temperatures, tube surface and combustion products as well as on conversion was carried out. By increasing catalyst activity it is possible to obtain a similar reaction velocity and thus also an identical heat consumption at a lower reaction temperature. When using a highly active catalyst, the reactor regime shifts towards transfer region[10], in which the amount of heat transferred by radiation is a limiting factor and a further increase of catalyst activity has only a small influence on the outlet quantities investigated. This tendency can also be seen in Fig. 8. It can be therefore stated that the rate of chemical reactions is determined by the velocity of heat transfer from combustion products onto tube surface and that the catalyst activity or concentration of reacting substances are not decisive for reaction rate, but transfer properties of the system and particularly combustion product temperature are of importance. Very significant is, however, catalyst durability, i.e. resistance to deactivation.

An analysis of the influence of heat transfer coefficient from reaction tube inner wall to catalyst bed on the course of temperatures[2] is of the same qualitative character, i.e. especially combustion product and tube surface temperature drop with the

TABLE II

Qualitative evaluation of the influence of parameters given with an increase of their values

| Parameter | $t_{sp}$ | $t_{t,max}$ | $t_{sm}$ | $\Delta T$ | $x$ | $\dot{Q}_{abs}$ |
|---|---|---|---|---|---|---|
| Change of burner input | + | + | + | + | + | + |
| Emissivity of reaction tube surface | − | + | + | − | − | + |
| Length of burner flame | + | + | (−) | + | − | − |
| Length of flue gas recirculation area | + | − | − | + | − | − |
| Inlet excess air[a] | (+) | − | − | + | − | − |
| Outlet excess air[b] | − | − | − | (−) | − | − |
| Heat losses | − | − | (−) | (−) | − | − |
| Catalyst activity | − | − | − | − | + | + |
| Activation energy | 0 | (+) | − | − | + | 0 |
| Heat transfer coefficient inside the tube | − | − | + | − | + | + |
| Reaction tube length | − | − | + | − | + | + |
| Reaction tube diameter | − | + | − | − | + | + |
| Reaction tube pitch | − | (−) | + | (−) | + | + |

$t_{sp}$ Outlet flue gas temperature, $t_{t,max}$ maximum temperature of reaction tube outer surface, $t_{sm}$ outlet temperature of reaction mixture, $\Delta T$ temperature distance from equilibrium, $x$ conversion of methane into carbon dioxide and carbon monoxide, $\dot{Q}_{abs}$ absorbed heat, + increase, − decrease, (+) slight increase, (−) slight decrease, 0 nearly without any change; [a] amount of additionally sucked air is constant; [b] inlet excess air is constant.

increase of heat transfer coefficient value. This knowledge also follows from the equations expressing heat transfer by radiation from combustion products onto tube outer surface as well as heat transfer from reaction tube surface into reaction mixture.

From graphical dependences dealt with in paper[11] it follows that with the increasing length of reaction tube, the temperature of reaction mixture increases, combustion product temperature drops and conversion increases, which is in agreement with the conclusions of the present and the previous paper[3].

It is necessary to note that the analysis of parametric sensitivity dealt with in papers[2,10,11] was carried out based on a simulation by means of a simplified mathematical model. The results obtained served above all for an analysis of physical and chemical phenomena taking place in reactor. The analysis of the influence of parameters in the present paper is based on the results of a simulation by means of a mathematical model applying zone method and tested by measurements on an industrial unit[1]. The results obtained should facilitate reforming furnace designers' work. The conclusions drawn from parametric sensitivity investigations based on simulations of either model can, however, be compared on a qualitative level.

Table II lists a qualitative evaluation of the effect of all parameters investigated on the selected main characteristic quantities in steam reforming. It can be seen whether the quantity investigated increases or decreases with the increase of the parameter value in question.

TABLE III
Extreme values of uncertain parameters for simulation calculations

| Uncertain parameter | Unit | Value of uncertain parameter for | | | |
|---|---|---|---|---|---|
| | | $t_{t,max}$ | | $x$ | |
| | | min. | max. | min. | max. |
| Emissivity of reaction tube surface | — | 0·7 | 1·0 | 0·7 | 1·0 |
| Flame length | m | 1·0 | 4·0 | 4·0 | 1·0 |
| Profile of fuel burning | — | *A* | *B*, *C* | *B*, *C* | *A* |
| Catalyst activity | mol $kg_{cat}^{-1}$ $s^{-1}$ | 0·05 | 0·01 | 0·01 | 0·05 |
| Activation energy | kJ $mol^{-1}$ | 80 | 150 | 80 | 150 |
| Correction factor of heat transfer coefficient inside | — | 1·2 | 0·5 | 0·5 | 1·2 |

By combining extreme values of various parameters based on the ranges in which their effect was investigated, an accumulation of value increments or losses can take place in some characteristic quantities. If one wants for instance to find extreme values of tube surface temperatures and that of conversion, one proceeds in the following way:

*a*) uncertain parameters are chosen taking into consideration constant operational conditions and a constant radiation chamber geometry,

*b*) based on Table II one finds out which extreme interval values of the parameters investigated cause an increase or decrease of the maximum temperature of tube surface and of conversion and one tabulates (Table III) data for simulation calculations,

*c*) after carrying out simulation calculations by means of the mathematical model, the following values are obtained:

$$(t_{t,max})_{min} = 842°C \quad x_{min} = 0.611$$

$$(t_{t,max})_{max} = 976°C \quad x_{max} = 0.712$$

They are resultant values being given by such a combination of uncertain parameter values causing extreme values of the main characteristic quantities obtained within the range of the parameter values investigated. It is necessary to note that they are actually extreme cases involved; the designer, however, must take the above factors into account.

## CONCLUSION

The mathematical model simulating thermal chemical processes in a radiation chamber based on an application of the zone method and tested by measurements carried out on an industrial unit, enables the influence of selected parameters to be investigated in a relatively complex way on the course of the main characteristic quantities in steam reforming.

The above knowledge can considerably facilitate designer's work helping him to project effectively a primary reformer radiation chamber.

## REFERENCES

1. Stehlík P., Šika J., Bébar L., Raus L.: Collect. Czech. Chem. Commun. *54*, 2357 (1989).
2. Valášková Z., Horák J.: Chem. Prum. *37*, 454 (1987).
3. Stehlík P.: *Thesis*. VUT (Technical University), Brno 1989.
4. Stehlík P.: Collect. Czech. Chem. Commun. *56*, 847 (1991).
5. Roesler F. C.: Chem. Eng. Sci. *22*, 1325 (1967).
6. Horák J., Prágrová M., Bébar L.: Chem. Prum. *35*, 231 (1985).

7. Singh Ch. P. P., Saraf D. W.: Ind. Eng. Chem., Process Des. Rev. *18*, 1 (1979).
8. Murty C. V. S., Krishna Murthy M. V.: Ind. Eng. Chem. Res. *27*, 1832 (1988).
9. Miyasugi T., Kosaka S., Mukai K., Suzuki A.: J. Jpn. Petrol. Inst. *25*, 260 (1982).
10. Horák J., Valášková Z.: Collect. Czech. Chem. Commun. *52*, 929 (1987).
11. Horák J., Valášková Z.: Chem. Prum. *37*, 227 (1987).

Translated by M. Vlachová.