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INFLUENCE OF STEAM REFORMING CATALYST GEOMETRY ON THE PERFORMANCE OF TUBULAR REFORMER – SIMULATION CALCULATIONS

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A proper selection of steam reforming catalyst geometry has a direct effect on the efficiency and economy of hydrogen production from natural gas and is a very important technological and engineering issue in terms of process optimisation. This paper determines the influence of widely used seven-hole grain diameter (ranging from 11 to 21 mm), h/d (height/diameter) ratio of catalyst grain and S_h/S_t (hole surface/total cylinder surface in cross-section) ratio (ranging from 0.13 to 0.37) on the gas load of catalyst bed, gas flow resistance, maximum wall temperature and the risk of catalyst coking. Calculations were based on the one-dimensional pseudo-homogeneous model of a steam reforming tubular reactor, with catalyst parameters derived from our investigations. The process analysis shows that it is advantageous, along the whole reformer tube length, to apply catalyst forms of $h/d = 1$ ratio, relatively large dimensions, possibly high bed porosity and $S_h/S_t \approx 0.30\text{-}0.37$ ratio. It enables a considerable process intensification and the processing of more natural gas at the same flow resistance, despite lower bed activity, without catalyst coking risk. Alternatively, plant pressure drop can be reduced maintaining the same gas load, which translates directly into diminishing the operating costs as a result of lowering power consumption for gas compression.

Keywords: tubular steam reforming, nickel catalyst geometry, process simulation, catalyst coking, process intensification

1. INTRODUCTION

Catalytic processes of hydrocarbon steam reforming belong to the group of the most important methods of synthesis gas and hydrogen preparation, which are widely used for the production of various chemicals of great economic importance (Holladay et al., 2009). The process has many possible variations. The one, which is the most popular in industrial practice (especially in medium scale plants), is reforming in a multitubular reactor, taking place in the temperature range of 400-900°C, at the pressure of up to 4 MPa. Heat necessary for highly endothermal reactions (1 and 2), generated by direct combustion of a fuel gas in burners mounted in the reformer furnace chamber, is supplied by externally heated tube walls.

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$$C_nH_m + nH_2O \rightarrow nCO + (n + 0.5m)H_2 \qquad \Delta H^0 > 0 \qquad (1)$$

$$CH_4 + H_2O \leftrightarrow CO + 3H_2 \qquad \Delta H^0 = +206\ \text{kJ/mol} \qquad (2)$$

$$CO + H_2O \leftrightarrow CO_2 + H_2 \qquad \Delta H^0 = -41\ \text{kJ/mol} \qquad (3)$$

The natural gas steam reforming proceeds in the presence of a catalyst. Nickel catalysts impregnated on the low surface of porous high alumina supports (with small amounts of MgO, CaO, and sometimes alkalies) are used in industry. Supports, and thus the final catalysts, are shaped into forms of developed geometric surface.

The catalyst bed is located in tubes of 100-125 mm internal diameter and 10-15 m long. It is favourable, due to thermodynamic considerations, to carry out the reforming process at the highest possible temperature and low pressure. However, in industrial practice, the temperature is limited by the strength of the reforming tube material whereas the reforming process, despite the thermodynamics and as a result of economic considerations, is conducted in high pressure conditions. It is advantageous that the plant gas pressure drop is possibly the lowest. The possibility of reducing the reformer pressure drop, in the range of a particular gas load, translates directly into decreasing the operating costs as a result of cutting back on gas compression energy consumption. Alternatively, it enables plant efficiency increase and to process larger amounts of gas, without the necessity of introducing changes into the existing gas compression loops.

Steam reforming catalysts should have the following features: (a) good mechanical strength, constant in time, (b) high resistance to dilatation forces, thermal shocks and steam action, (c) high and constant activity of a catalyst geometric surface unit, (d) grain size and shape providing high geometric surface of a bed volume unit and low flow resistance values of the process gas, (e) high coefficient of heat transfer to the reaction mixture, (f) high coking resistance, and (g) low production costs (Borowiecki and Gołębiowski, 2005; Ferreira-Aparicio et al., 2005; Peña et al., 1996; Wu et al., 2007).

Meeting all the requirements by one catalyst type is difficult, so producers offer various catalysts for specific operating conditions. Sometimes a catalyst shaped into small forms (in order to increase its activity) with potassium addition (to increase coking resistance) is used in the top (inlet) tube part, and in the shape of large forms (to decrease flow resistance) is applied in the bottom tube part (Shumake and Coleman, 2007).

Influence analysis of catalyst grain size and its geometry on the performance of a tubular reformer, in terms of process optimisation, is a very important technological and engineering issue. A proper selection of catalyst grain geometry brings many advantages, which have a direct effect on the efficiency and economy of hydrogen production from natural gas. Due to the fact that nickel catalysts in the form of cylinders with seven holes have found wide application among many shape types of industrial catalysts, this paper presents studies on the effect of dimensions of this catalyst type on the performance of a tubular reformer in natural gas steam reforming process. The influence of seven-hole grain diameter (d ranging from 11 to 21 mm), height to diameter ratio of catalyst grain (h/d) and the ratio of hole surface to the total cylinder surface in cross-section (S_h/S_t ranging from 0.13 to 0.37) on the gas load of a catalyst bed, gas flow resistance, maximum tube wall temperature and the risk of catalyst coking were determined. Simulation calculations were based on the one-dimensional pseudo-homogeneous model of a steam reforming reactor (Rostrup-Nielsen, 1984; Yu et al., 2006; Ziółkowski et al., 1980). The model adopts the catalytic filling parameters derived from our own investigations into catalysts, with the inclusion of their deactivation during long-lasting application in conditions of an industrial reactor.

2. EXPERIMENTAL

2.1. Catalysts

Nickel catalysts containing 17 wt.% NiO, prepared on low surface alumina supports of an identical chemical formula, in a form of cylinders with seven holes and flat bases were investigated. Support forms differed in geometry: cylinder diameter (*d*) and height (*h*), and also in the ratio of the hole surface area to the total cylinder surface in cross-section (S_h/S_t) – Fig. 1. Any change of this parameter has strong influence on the form strength – when it is increased, while maintaining the same cylinder porosity, the strength is reduced. This effect can be compensated by support sintering temperature. The temperature was adjusted in such a way that support strength properties (radial mechanical strength per a cylinder height unit), and thus those of final catalysts, were the same. Therefore, all investigated catalysts had the same chemical composition and mechanical strength, but different geometry and, as a result of dissimilar conditions of support sintering, a different porous structure.

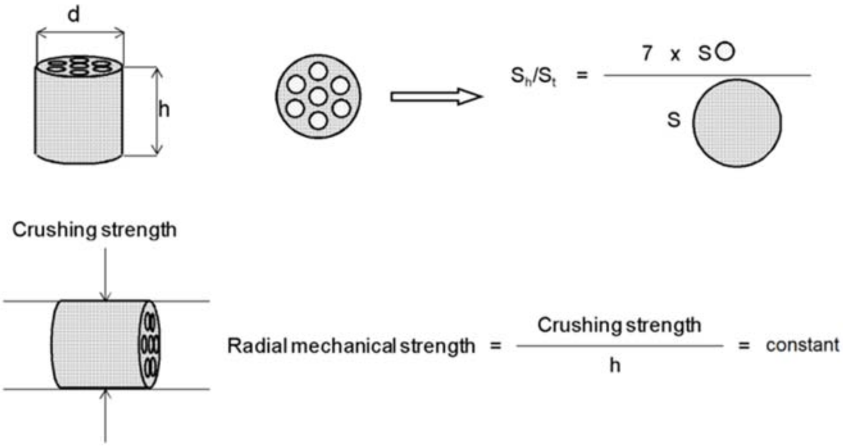

Fig. 1. Studied catalyst parameters influencing the performance of a tubular reformer

2.2. Methodology of investigations of parameters required for reformer simulation calculation

Catalyst bed parameters were calculated based on the determination of a number of catalyst grains, with defined and known dimensions, in a reformer tube. *Bed porosity* (ε) was calculated according to the following equation:

$$\varepsilon = 1 - N \cdot V_c \tag{4}$$

and *geometric surface area in a bed volume unit* (A_b) in accordance with the below equation:

$$A_b = N \cdot S_c \tag{5}$$

Dimensionless hydraulic friction factor (*f*) during fluid flow through the bed was determined on the basis of our own measurements of the flow resistance, taken for various air flow rates (Reynolds numbers in the range 3800 – 9000) in a tube with 116 mm internal diameter, filled up to the height of 4 m with the investigated catalyst. The air flow rate was measured with a calorimetric mass flow meter, and pressure drops in the catalyst bed were measured with a differential manometer.

The convective heat transfer coefficient from the hot internal side of the wall of the bed packed tubular reactor to the process gas contained therein (α) was calculated by Leva correlation (Leva, 1947) modified with a correction coefficient (c = 0.75), which was defined on the basis of measurements taken in our experimental plant for heat transfer determination in a wide range of gas flow rates for various catalyst grain dimensions (Ziółkowski et al., 1982a):

$$\alpha = c \cdot 0.813 \cdot e^{-6 \cdot \frac{d_V}{D_{in}}} \cdot \left(\frac{d_V \cdot G}{\mu}\right)^{0.90} \cdot \frac{\lambda_g}{D_{in}} \tag{6}$$

Suitability of the method proposed for determination of convective heat transfer coefficient was confirmed experimentally in real conditions of reactor operation in a catalytic methane steam reforming reaction.

The activity of a catalyst geometric surface unit in a methane steam reforming reaction was determined by a gradientless method in a tank reactor equipped with a stirrer (Gołębiowski and Stołecki, 1977). The measurements were taken in a diffusion regime, in operating conditions corresponding to those in an industrial reactor – covering the actual reaction rate for whole (uncrushed) catalyst grains, in the temperature range of 500-800°C, at 2.5 MPa pressure. Methane conversion rate (r_{CH4}) for successive measuring points was calculated on the basis of reactor mass balance, taking into account analysis results of reagent compositions and stream volumes. *Reaction rate constant,* changing with temperature exponentially according to Arrhenius equation, *related to the geometric surface unit of catalyst grains* (k_{CH4}), was accepted as a measure of catalytic activity and was calculated (assuming that it is a first-order reaction with respect to methane) from the following equation:

$$r_{CH_4} = k_{CH_4} \cdot p_{CH_4} \cdot \left(1 - \frac{p_{CO} \cdot p_{H_2}^3}{K_p^{CH_4} \cdot p_{CH_4} \cdot p_{H_2O}}\right) \tag{7}$$

where $k_{CH_4} = k \cdot e^{-\frac{E_a}{R \cdot T}}$

Activity changes during long-lasting application (k'_{CH4}) were evaluated on the basis of our own investigations of spent INS G-0117-7H commercial catalyst samples after operation in various conditions of tubular reformers (Franczyk et al., 2009):

$$k'_{CH_4} = 0.39 \cdot k_{CH_4} \tag{8}$$

3. REFORMER CALCULATIONS

A mathematical model of the process conducted in the reformer tube was based on a system of differential equations of mass, energy and momentum conservation, adequate to a one-dimensional pseudo-homogeneous system (Rostrup-Nielsen, 1984; Yu et al., 2006; Ziółkowski et al., 1980). This model assumes that concentration and temperature changes occur only along the tube axis and are caused by the proceeding chemical reactions and heat exchange that take place only through the tube wall. Its validity was confirmed by measurements in a semi-commercial plant (Ziółkowski et al., 1982b).

It was assumed in the model, that the following conversion reactions take place in the reactor: methane, which is the main component of natural gas (reaction 2), carbon monoxide (reaction 3) and, depending on gas composition, higher hydrocarbons (their stoichiometry can be written generally in one equation – reaction 1). The momentary adiabatic decomposition of higher hydrocarbons (C_3, C_{3+}), present in the processed natural gas, takes place in the front part of the bed, influencing the gas composition and state parameters (pressure, specific volume, temperature) at the inlet to the packing layer. CO shift conversion (reaction 3) is very fast and it proceeds practically in equilibrium in conditions of natural gas steam reforming process (relatively high temperature, steam excess). That is why every integration step was complemented with balance-equilibrium calculations in such a way so that to bring reaction mixture parameters to adiabatic equilibrium with respect to this reaction.

General mass conservation equation has the following form:

$$-G\frac{dC_n}{dz} = R_n \tag{9}$$

Diverse kinetic equations, formulated on the basis of our own studies on catalysts differing in porous structure and thus in the activity of a catalyst geometric surface unit (see section 2.2 - k'_{CH4}), were applied for the calculations of methane content change rates. The equations have such a form (R_{CH4}), which enables the calculation of methane conversion rates per a bed volume unit of the investigated catalysts differing in geometry and thus in geometric surface area in a bed volume unit (A_b):

$$R_{CH_4} = A_b \cdot k'_{CH_4} \cdot p_{CH_4} \cdot \left(1 - \frac{p_{CO} \cdot p_{H_2}^3}{K_p^{CH_4} \cdot p_{CH_4} \cdot p_{H_2O}}\right) \tag{10}$$

Ethane reforming rates (R_{C2H6}) for various catalysts were calculated, in relation to methane conversion rates, on the basis of literature data (Rostrup-Nielsen and Christiansen, 2011):

$$R_{C_2H_6} = R_{CH_4} \cdot F_{C_2H_6}\left(p_{CH_4}, p_{C_2H_6}, p_{CO}, p_{H_2}, p_{H_2O}, T\right) \tag{11}$$

Energy conservation equation can be written in the following way:

$$G \cdot c_p \cdot \frac{dT}{dz} = \frac{4 \cdot U}{D_{in}} \cdot (T_{ex} - T) - \sum_{n=1}^{2}(R_n \cdot \Delta H_n) \tag{12}$$

where $\frac{1}{U} = \frac{1}{\alpha} + \frac{x}{\lambda_w}$

Reaction heat values were calculated from the enthalpy change balance of products in relation to reactants, using a model of physico-chemical properties of a gaseous mixture under pressure presented by Dukowicz (1994).

Momentum conservation equation has the following form:

$$-\frac{dP}{dz} = f \cdot \frac{G^2 \cdot (1-\varepsilon)}{d_p \cdot \rho_g \cdot \varepsilon^3} \tag{13}$$

The above formulated model equations (9, 12, 13) form an ordinary differential equation system. The characteristics of the analysed reformer tube, parameters of the process gas contained therein, and of the catalyst filling determined on the basis of our own investigation (see section 2.2), were included in it. The system's independent variable (z) is the distance between the differential calculation slice of the filling and the cross-section, through which the reaction mixture flows onto the catalyst bed.

The model equation system is strongly non-linear and can be solved only by numerical integration. Runge-Kutta-Merson method with truncation error control and automatic adjustment of integration step, which provides high calculation efficiency with the required accuracy, was applied for numerical integration (Christiansen, 1970).

The aim of the model solution is the prediction and optimisation of industrial reactor performance.

The operation of a reformer tube of dimensions: external diameter - D_{ex} = 138.8 mm, internal diameter - D_{in} = 117.0 mm, tube length - H = 12 m, packed with the investigated catalyst, was analysed. The performance of the unit tubular reactor was determined from calculations: (a) for a given temperature profile of the external side of the wall along the tube length (tube temperature changes in a linear way from $T_{ex,1}$ = 700°C at the inlet to maximum temperature $T_{ex,\max}$ at a distance of 2.5 m from the inlet, and it was constant in the remaining part of the tube); (b) known gas parameters at the inlet: natural gas composition (gas without poisons), mol% of dry gas – CH_4 = 98.17, N_2 = 0.84, C_2H_6 = 0.73, C_3H_8 = 0.20, C_4H_{10} = 0.06; steam/carbon molar ratio (nH_2O/nC) – 3.7 mol/mol; pressure – 3.23 MPa; process gas inlet temperature – 480°C; (c) and on assumption, that the amount of heat supplied to a gas volume unit was the same for each of the analysed cases and it was 1887.86 kJ/Nm^3 (in order to obtain gas of parameters required for ammonia synthesis).

Calculation results were compared with data obtained for a commercial catalyst INS G-0117-7H of dimensions: $h = d = 16.5$ mm, 7 holes×3.4 mm ($S_h/S_t \approx 0.30$, $A_b = 408$ m^2/m^3, $\varepsilon = 0.577$), for which tube temperature changes from $T_{ex,1} = 700$°C to $T_{ex,\max} = 816$°C whereas pressure drop was 0.14627 MPa for the process parameters given above and initial total wet gas flow was 22.3 kmol/h (500 Nm^3/h).

4. RESULTS OF CALCULATIONS AND DISCUSSION

Fig. 2 reveals the influence of the S_h/S_t ratio on the relative activity of a geometric surface unit of the catalyst bed. As was mentioned earlier, if the hole diameter is increased, i.e. S_h/S_t ratio, and thus grain wall thickness is reduced, the support should be sintered at higher temperatures, in order to maintain the same strength properties. However, support sintering at higher temperatures lowers its porosity and specific surface area, and thus leads to the activity drop of the geometric surface unit of the catalyst bed. Resulting differences in the activities of catalysts with various S_h/S_t ratio, determined experimentally, were taken into account in further simulation calculations of the tubular reformer performance.

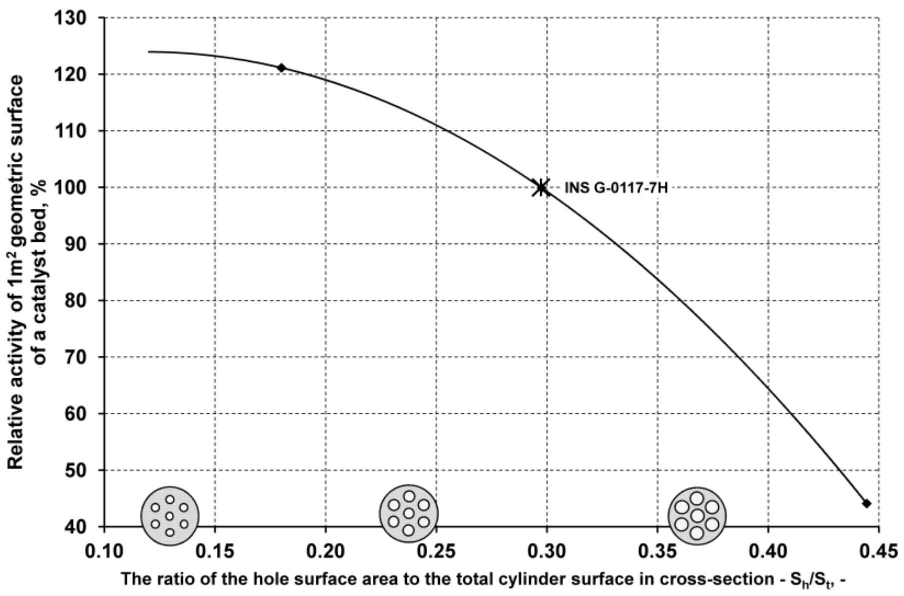

Fig. 2. The effect of the S_h/S_t ratio and the resulting catalyst porosity differences (resulting from different temperatures of support sintering, aimed at maintaining the same strength properties) on the relative activity of a catalyst bed geometric surface unit, in comparison with INS G-0117-7H commercial catalyst of dimensions: $h = d = 16.5$ mm, 7 holes×3.4 mm (activity of 1 m^2 of catalyst bed = 100%)

Fig. 3 shows the effect of grain diameter (for $S_h/S_t \approx 0.30$) on the relative gas load of a volume unit of the catalyst bed for various h/d ratios, at the same and constant values of flow resistance and maximum tube wall temperature. The effect was determined with the mathematical model of a natural gas steam reforming reactor. Results indicate, that the reduction of h/d ratio (i.e. catalyst grain height) is not advantageous. Differences in gas loads of the catalyst bed are significant for the selected h/d ratios. They are higher by about 20% and by 10% for cylinder diameters of 11 mm and 21 mm, respectively.

In Fig. 4 the effect of grain diameter ($h/d = 1$) on the relative gas load of a catalyst bed volume unit for various S_h/S_t ratios, maintaining the same catalyst strength properties and the same key parameters of the tubular reformer performance, i.e. constant values of pressure drop and maximum wall temperature, is presented. Calculations indicate, that it is advantageous to use catalysts of a higher grain size and an enlarged hole diameter. It is desirable for the hole diameter (in the investigated support formula) to be adjusted in such a way, that the S_h/S_t ratio is between 0.30 and 0.37.

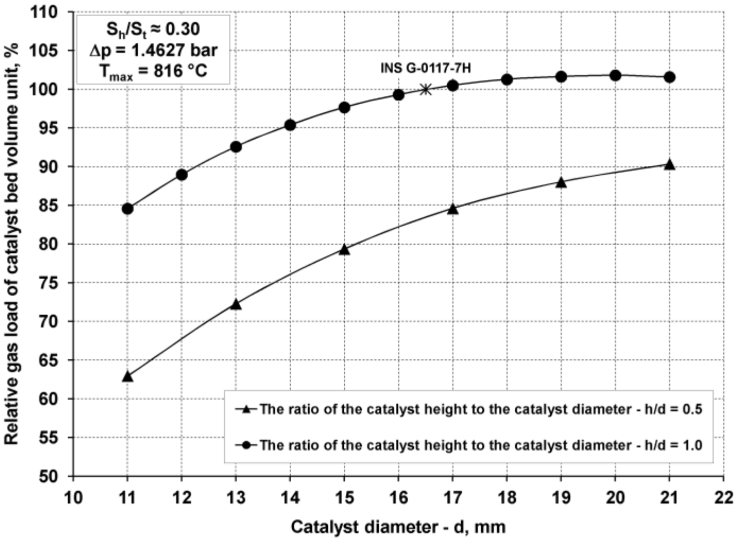

Fig. 3. The effect of grain diameter on the relative gas load of catalyst bed volume unit for various h/d ratios, in comparison with INS G-0117-7H commercial catalyst of dimensions: $h = d = 16.5$ mm, 7 holes×3.4 mm (gas load of catalyst bed volume unit = 100%)

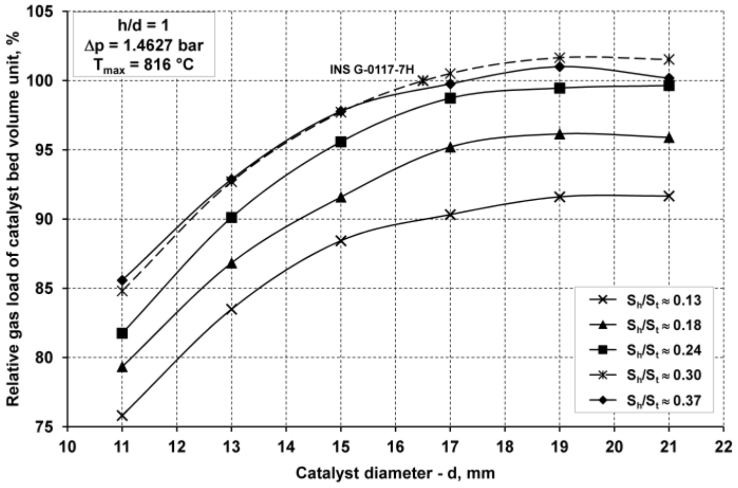

Fig. 4. The effect of grain diameter (h/d = 1) on the relative gas load of catalyst bed volume unit for various ratios of the hole surface area to the total cylinder surface in cross-section (S_h/S_t), in comparison with INS G-0117-7H commercial catalyst of dimensions: $h = d = 16.5$ mm, 7 holes×3.4 mm (gas load of catalyst bed volume unit = 100%)

For example, the use of INS G-0117-7H commercial catalyst grains of diameter = 16.5 mm and S_h/S_t ratio ≈ 0.30, instead of forms of diameter = 11 mm and S_h/S_t ratio ≈ 0.13, facilitates a considerable process intensification and processing of about 32% more natural gas, in spite of almost 1.6 times lower activity of a volume unit of INS G-0117-7H catalyst bed. Low catalyst activity is the result of the application of larger catalyst forms (and thus the catalyst geometric surface in a bed volume unit lower by about 22%) with a higher hole diameter (and thus lower by about 19% activity of a catalyst geometric surface unit, as a result of its worse textural properties – Fig. 2).

The seemingly paradoxical conclusion that reactor gas load can be increased while maintaining the same boundary conditions (i.e. pressure drop and maximum temperature of the tube wall), despite activity reduction of a catalyst bed volume unit, results from a specific character of the reforming process, where heat transfer phenomena play the main role. Thus, the application of a fine grain catalyst in the top part of the reformer tube, despite its high activity in the reactor volume unit, is not recommendable, since it limits the possible amounts of the processed natural gas.

A further increase of the grain size (up to 21 mm) and of the bed porosity (to ε = 0.618) by enlarging the hole diameter (to $S_h/S_t \approx 0.37$), in relation to the INS G-0117-7H catalyst, gave no evident results within the range of studied parameters. It results from too high activity decrease of the catalyst bed volume unit (by additional 36% in comparison with the INS G-0117-7H catalyst). The advantages of the possible application of catalysts with larger dimensions and bed porosity could be fully taken of and provide additional technological profits, if supports of a new upgraded formula with better correlation of strength parameters to their textural parameters were used. An alternative solution is conducting a reforming process at a higher temperature of the catalyst bed, which would compensate lower catalyst activity. At present, it is possible without the risk of reactor service life reduction, because of substantial progress in reforming tube metallurgy, which has taken place in previous years. Much better and much more readily available raw materials for reformer tubes facilitate higher operation temperatures, even over 1000°C (Schmidt + Clemens advertising materials, 2014).

Fig. 5 shows the influence of the S_h/S_t ratio (for a catalyst of dimensions: d = 21 mm, h/d = 1) on the relative plant gas load and maximum wall temperature, at standard pressure drop (Δp). The analysis of data indicates that application of a catalyst with $S_h/S_t \approx 0.30$ enables to increase the plant load by over 10% at the maximum wall temperature growth by only 10°C. When a catalyst of S_h/S_t ratio ≈ 0.37 is applied, the plant load can be increased even by over 20%, unfortunately, at the cost of increasing the maximum wall temperature by about 20°C, in comparison with INS G-0117-7H catalyst (dimensions: $h = d$ = 16.5 mm, 7 holes×3.4 mm).

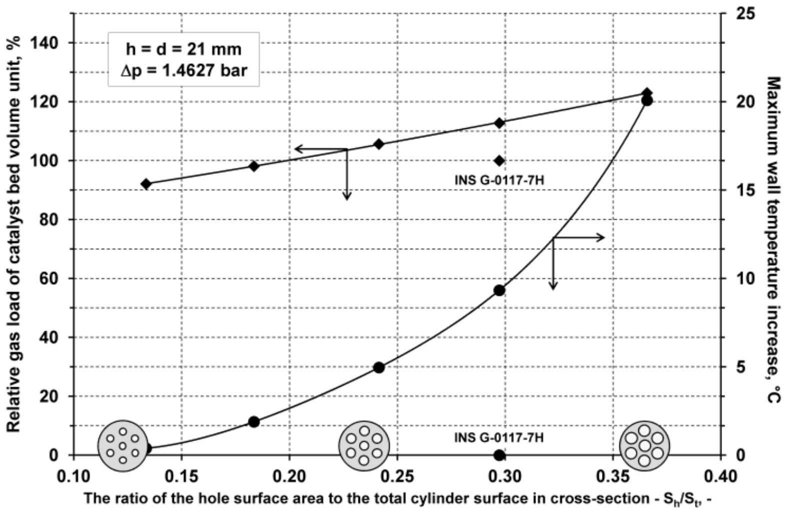

Fig. 5. The effect of the S_h/S_t ratio (for a catalyst of dimensions: d = 21 mm, h/d = 1) on the relative gas load and maximum wall temperature, in comparison with INS G-0117-7H commercial catalyst of dimensions: $h = d$ = 16.5 mm, 7 holes×3.4 mm (gas load of catalyst bed volume unit = 100%, maximum wall temperature = 816°C)

The influence of the S_h/S_t ratio (for a catalyst of dimensions: d = 21 mm, h/d = 1) on the relative flow resistance values and maximum wall temperature, at a standard gas load, is plotted in Fig. 6. The application of a catalyst with $S_h/S_t \approx 0.30$ can reduce the gas flow resistance by about 20% at the maximum wall temperature growth by less than 5°C. When a catalyst with S_h/S_t ratio ≈ 0.37 is used, the gas flow resistance can be diminished even by about 35%, but at the cost of increasing the maximum wall temperature by about 10°C.

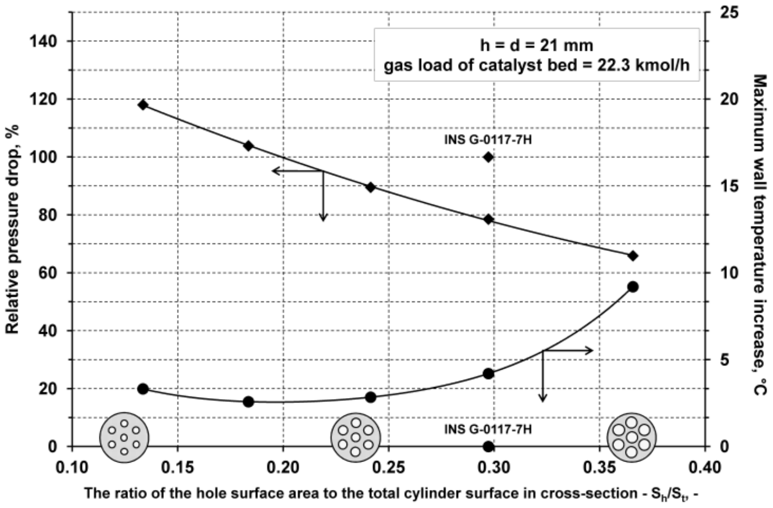

Fig. 6. The effect of the S_h/S_t ratio (for a catalyst of dimensions: $d = 21$ mm, $h/d = 1$) on the relative flow resistance values and maximum wall temperature, in comparison with INS G-0117-7H commercial catalyst of dimensions: $h = d = 16.5$ mm, 7 holes×3.4 mm (pressure drop = 100%, maximum wall temperature = 816°C)

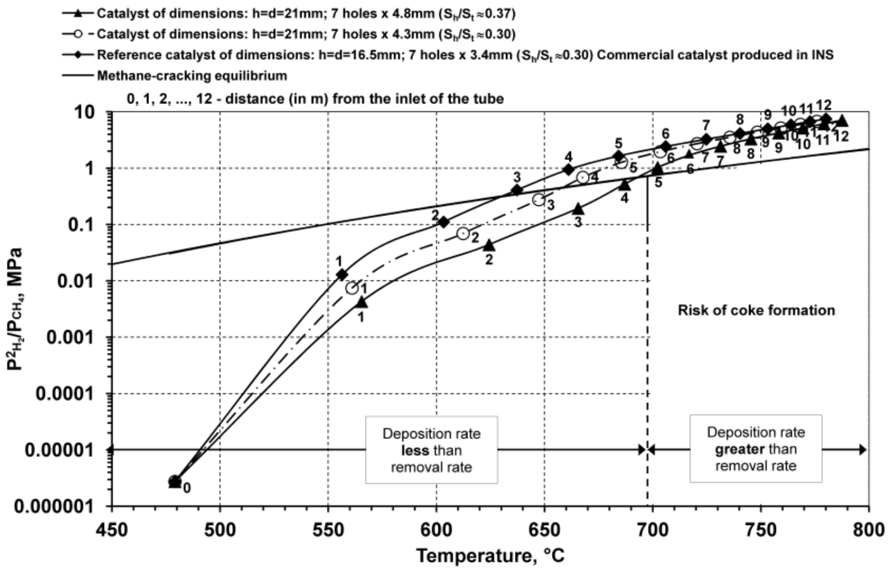

Fig. 7. Increased risk of coke formation on catalysts of large grain and hole dimension.
p_{H2} – partial pressure of H_2, MPa; p_{CH4} – partial pressure of CH_4, MPa

Fig. 7 depicts a methane decomposition reaction equilibrium curve ($CH_4 \leftrightarrow C + 2H_2$) and gas parameter alternations (in temperature and p^2_{H2}/p_{CH4} ratio composition) along the reformer tube filled with the investigated catalyst, illustrating an increased carbon deposition risk on the catalyst, in relation to INS G-0117-7H commercial catalyst, as a result of large catalyst forms application ($d = 21$ mm, $h/d = 1$) with large holes ($S_h/S_t \approx 0.30$ and 0.37). Reactions leading to carbon deposition are kinetically limited in the range of lower temperatures, and thermodynamically limited at higher temperatures. There is a risk of carbon formation in tubular reforming conditions when the process gas with a high hydrocarbon concentration (low degree of conversion) is subjected to elevated temperatures. When the natural gas is used as the raw material, the above mentioned situation can be observed very rarely and is typically caused by catalyst deactivation. Long-term analyses of Kellog–type reformer operations and results of investigations of six-year-old catalysts, taken from plants of this sort, led to a conclusion, that 700°C can be assumed as the critical temperature for catalyst coking processes within the range of the studied formula (Gołębiowski et al., 2009). Below that temperature coking reactions tend to be negligible due to kinetic conditions, and there is a risk of them occurring above the temperature of 700°C. An alteration in the catalyst form geometry as a result of increasing the ratio of S_h/S_t, as presented in Fig. 7, is related to a higher risk of such a situation occurring, and thus catalyst coking, which happens due to low activity of such catalysts.

The results of calculations indicate, however, that there is a sufficient safety margin to eliminate coke formation in the range of the investigated parameters. The safety margin can be additionally increased by the modification of support composition, or by potassium introduction (Michel, 2007).

5. CONCLUSIONS

The results of the engineering process analysis show that, in tubular reforming along the whole tube length, it is advantageous to apply catalyst forms of $h/d = 1$ ratio, of relatively large dimensions (the ratio of the tube diameter to the catalyst diameter cannot be less than 5) and of possibly high bed porosity. The hole diameter should be adjusted in such a way that the S_h/S_t ratio is between 0.30 and 0.37.

The increase of bed porosity (by about 10 vol.%) by enlarging hole diameters (increasing the S_h/S_t ratio from 0.13 to 0.30) and the application of higher dimension forms (forms with diameters of 16.5 mm instead of 11 mm) allow a considerable intensification of the steam reforming unit and processing of higher amounts of natural gas (by about 32%), despite lower catalyst activity in a bed volume unit (1.6 times), at the same maximum wall temperature and pressure drop. The seemingly paradoxical conclusion that reactor gas load can be increased while maintaining the same boundary conditions, despite catalyst activity decrease, results from reforming process specifics, in which heat transport processes play the main role. Alternatively, such a solution facilitates a reduction of flow resistance in reforming plants at the same gas load. Thanks to all that, the operating costs can be diminished as a result of limited power consumption for gas compression, otherwise reaching an amount twice as high as the cost of a catalyst purchase.

The reactor gas load can be increased by additional 20% at the same flow resistance values, as a result of increasing the grain size from 16.5 to 21 mm and from 0.30 to 0.37 S_h/S_t ratio or, alternatively, plant pressure drop can be reduced by about 35% maintaining the same catalyst bed gas load, conducting the process at higher tube temperature (by about 20°C and 10°C, respectively). It can be accomplished without the risk of catalyst deactivation by coke formation, despite a considerably lower catalyst activity.

The increase of tube wall temperature (to the maximum of 836°C), compensating low catalyst activity (the effect of support sintering at elevated temperatures in order to maintain high strength properties), does not deteriorate the tube service life, particularly when heat-resistant materials (operating at temperatures in excess of 1000°C) are used. The application of durable, however, more active catalysts, could eliminate the acceptable but yet disadvantageous increase of tube temperatures.

The results of the engineering analysis of a reforming process have become a clear indication to improve the catalyst supports formula, providing a better correlation of support strength parameters to their textural parameters and allowing the potential of higher dimensions and higher bed porosity catalysts to be fully used.

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SYMBOLS

A_b	geometric surface area in a bed volume unit, $m^2 \cdot m^{-3}$
α	convective heat transfer coefficient from tube wall internal side to the process gas, $W \cdot m^{-2} \cdot K^{-1}$
C_n	concentration of n-th order hydrocarbon ($n = 1, 2$), $mol \cdot kg^{-1}$
c	correction coefficient for Leva correlation, -
c_p	specific heat of gas at constant pressure, $J \cdot kg^{-1} \cdot K^{-1}$
D_{ex}	tube external diameter, m
D_{in}	tube internal diameter, m
d	cylinder diameter, mm
$d_p = 6V_c/S_c$	equivalent catalyst grain diameter (surface basis), m
$d_V = (6V_c/\pi)^{1/3}$	equivalent catalyst grain diameter (volume basis), m
ΔH_n	heat of n-th order hydrocarbon conversion reaction ($n = 1, 2$), $J \cdot mol^{-1}$
E_a	activation energy of catalytic reaction, $J \cdot mol^{-1}$
ε	bed porosity, -
$F_{C2H6}(p_i, T)$	function approximating values of the quotient of ethane conversion rate to methane conversion rate in the range of process parameters (p_i and T), -
f	hydraulic friction factor, -
G	mass flux, $kg \cdot m^{-2} \cdot s^{-1}$
H	reformer tube length, m
h	cylinder height, mm
K_p^{CH4}	equilibrium constant of methane steam conversion reaction, Pa^2
k	pre-exponential factor, $mol \cdot m^{-2} \cdot Pa^{-1} \cdot s^{-1}$
k_{CH4}	reaction rate constant related to a geometric surface unit of catalyst grains, $mol \cdot m^{-2} \cdot Pa^{-1} \cdot s^{-1}$
k'_{CH4}	reaction rate constant after 3-year operation, $mol \cdot m^{-2} \cdot Pa^{-1} \cdot s^{-1}$
λ_g	gas thermal conductivity, $W \cdot m^{-1} \cdot K^{-1}$
λ_w	tube wall thermal conductivity, $W \cdot m^{-1} \cdot K^{-1}$
μ	gas dynamic viscosity, $kg \cdot m^{-1} \cdot s^{-1}$
N	experimentally found number of catalyst grains for 1 m^3 of a reformer tube, m^{-3}
P	pressure, Pa
p_i	partial pressure of the i component ($i = CH_4, C_2H_6, CO, H_2, H_2O$), Pa
ρ_g	gas density, $kg \cdot m^{-3}$
R	universal gas constant, $J \cdot mol^{-1} \cdot K^{-1}$
R_{CH4}	methane conversion rate per a bed volume unit, $mol \cdot s^{-1} \cdot m^{-3}$
R_{C2H6}	ethane conversion rate per a bed volume unit, $mol \cdot s^{-1} \cdot m^{-3}$
R_n	conversion rate of n-th order hydrocarbon ($n = 1, 2$) per catalytic bed volume unit, $mol \cdot s^{-1} \cdot m^{-3}$
r_{CH4}	methane conversion rate per a catalyst geometric surface unit, $mol \cdot s^{-1} \cdot m^{-2}$
S_c	geometric surface area of a catalyst grain, m^2
S_h	hole surface area, mm^2
S_t	total cylinder surface in cross-section, mm^2
T	catalyst bed temperature (gas temperature), K
T_{ex}	temperature of tube wall external side, K
U	over-all heat transfer coefficient from tube wall external side to the process gas, $W \cdot m^{-2} \cdot K^{-1}$
V_c	volume of a catalyst grain, m^3
x	tube wall thickness, m
z	axial variable, m

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