Structured catalytic reactor for VOC combustion

Andrzej Kołodziej[1*], Joanna Łojewska[2], Tadeusz Kleszcz[1]

[1] *Institute of Chemical Engineering of the Polish Academy of Sciences, ul. Bałtycka 5, Pl 44-100 Gliwice, Poland, tel. +48 32 2310811, fax +48 32 2310318, e-mail: ask@iich.gliwice.pl*
[2] *Faculty of Chemistry, Jagiellonian University, Ingardena 3, 30060 Krakow, Poland, Fax: +48 12 6340515, e-mail: lojewska@chemia.uj.edu.pl*
[*] *Corresponding author.*

VOC emission has recently become a challenge for environmental protection. Catalytic combustion seems a promising method of VOC removal, however, there are still more specific demands concerning the process. The reactor design has to assure enhanced transfer properties accompanied by low flow resistance to reduce the pumping costs. Neither the packed beds nor the classic ceramic monoliths are able to fulfil the requirements.

To solve the problem we propose a wire gauze structure composed of several gauze sheets staked. A number of mass transfer and flow resistance experiments were performed for two gauze types and correlations were derived for the Sherwood number and the friction factor. The results were found to be in a reasonable agreement with the literature available.

The studied gauze structures were compared with a classic monolith for the assumed case study. The calculated length of the gauze structured reactor was significantly shorter, up to ten times, when compared with a classic ceramic monolith, but the pressure drop was higher.

Keywords: structured catalyst, gauze, mass transfer, diffusional limitation, performance efficiency.

REDUCTION OF VOC EMISSION BY CATALYTIC COMBUSTION

During the last two decades catalytic combustion spectacularly has succeeded in reducing the automotive emission of CO and NO_x. Nowadays, the emission of volatile organic compounds (VOC) to the atmosphere has become a vital environmental problem entailing large financial losses. For example, within the urban areas of the USA, benzene exceeded its allowable concentration in ambient air by 16 times while in the most occupied areas – by 1200 times, according to the standards given by the US Environmental Protection Agency[1]. There, a total yearly cost of VOC monitoring and controlling reaches 4 billion USD[2]. In Poland, the overall emission of VOC (excluding methane) exceeded 900 thousands tons in 2003[3]. As in other countries, the main sources of VOC are road transport, solvent use, oil industry and agriculture.

Catalytic combustion, still the most promising way to reduce the emission of many air pollutants, is in fact an extremely demanding process for both the catalyst and converter constructions. Its wide-spread use can be demonstrated by automotive catalytic afterburners based on ceramic monoliths – structured supports for three-way metallic catalyst (Pt-Pd-Rh) for CO and NO_x elimination.

However, there are still more demands concerning the VOC removal from exhaust gases in other than road transport areas. Usually VOC are highly diluted (up to ppm concentration), much more than vehicle pollutants. The end-pipe gas stream is usually large and the flow resistance should be as low as possible due to significant contribution of pumping costs. Furthermore, gas temperature is often too low to initiate catalytic combustion without additional heating. This last problem, however, exceeds the scope of this study.

Under the conditions described above catalytic combustion runs in diffusional regime, where combustion rate is limited by the mass transfer between the catalyst surface and a flowing gas mixture. The range of the reaction control can be spanned by increasing the mass transfer coefficients. However, in practice, the simplest solution, i.e. increasing gas velocity (by either reducing the reactor diameter or recirculating the gas mixture), is economically inefficient due to high pumping costs.

From the chemical point of view, the VOC problem differs significantly from that of CO/NO_x removal. One of the differences is the formation of toxic side-products such as dioxins and furans; and another – is catalyst deactivation due to coke formation and sintering.

Thus, to satisfy the specific demands of VOC combustion, a catalyst design in a molecular scale (or nanoscale) should be combined with a reactor structure design and optimisation. Therefore we decided to design an efficient microstructured catalytic converter based on the cobalt spinel catalyst.

The study consists of three parts: (i) designing the reactor microstructure, (ii) studying mass transfer coefficients and flow resistances: mathematical modelling and experimental investigation; (iii) developing appropriate performance efficiency criteria (PEC) for evaluating the structures; (iv) characterisation of cobalt catalyst deposited on metal surfaces by physicochemical methods and reactive tests. The last point (iv) is widely presented in our accompanying paper[4].

REACTOR MICTOSTRUCTURE DESIGN

Classic monolithic reactors, usually ceramic ones, assure low flow resistance in long strait parallel channels typically 0.8 to 4 mm in diameter[5]. However, the fluid flow in a small and long channel is undoubtedly laminar and well-developed along almost the whole channel length. Molecular diffusion is therefore a predominant mass transport mechanism, and local mass transfer coefficient approaches, for a major part of the channel, an asymptotic value. The latter depends only on the channel dimensions

and the cross-sectional shape and it is not influenced by the velocity of the reactants flowing through it. This phenomenon gives rise to low mass transfer coefficients, brings in an undesirable increase in the reactor length, and finally, a significant pressure drop. To overcome the above transport limitations we have proposed two alternative structures: a short-channel structure and a wire gauze structure. The first type of the structures is to be published in another paper. In this study we have mainly focussed on the wire gauze structures. To place our results in a broader context, in the next paragraphs, we consequently compare the gauze structures to 200 cpsi (channels per square inch) monoliths. The geometric parameters of the structures considered in this study are summarized in Table 1. Between the adjacent gauzes a 1.9 mm separating gap (equal to the seal thickness) was applied. Therefore the specific surface area referred to the volume of the gauze sheet (without the separation gap) a_{gauze} is significantly higher than apack which is referred to the entire volume of the packing, including the separation gaps.

The wire gauze structures presented in Figures 1 and 2 are built of wire gauze sheets. A single woven gauze sheet is depicted in Fig. 1A. Gauze sheets are stacked perpendicularly to the flow direction forming a gauze package. The design is similar to that used in reactors for ammonia oxidation. Possible arrangements, exemplified in Fig. 2, are staked as single sheets (2A), as zigzag (2B) and finally coaxially as cylindrical gauzes (2C). As regards 2C arrangement these are made as several gauze „tubes" or helically coiled single gauze sheets, with the radial flow of reactants. The successive gauzes can stick together or they can be separated by a certain distance, usually comparable to their thickness. The last way should be recommended to limit such phenomena as channelling or bypassing, as the separation gap equalizes the pressure, and in consequence the velocity profile, over the whole reactor dimension. Other configurations are also possible such as, for example, the corrugated gauze sheets staked, gauze sheets oblique to the flow direction, etc.

A number of studies have been published dealing with catalytic gauze reactors for ammonia oxidation. The studies, however, are usually not very recent, and they are based on the platinum woven gauzes applied to the ammonia oxidation, or very close to them. Combustion of hydrocarbons on catalysts of this kind has been studied e.g. by Satterfield and Cortez[6]. At present, more sophisticated catalytic gauzes are being developed, as the ones offered by Katator AB and studied by Ahlström-Silversand and Odenbrand[7]. Although gauze catalytic packings were used for years in nitric acid plants, only most recently have they appeared in other catalytic processes, mainly in catalytic combustion. The examples of advanced commercial structures of the same kind are e.g. solutions of Katator[7] or Microlith® described in[8]. So far, woven gauzes have been used mainly as the structured catalysts. Nowadays, knitted gauzes are still becoming more interesting for various catalytic processes[9], also for catalytic ammonia oxidation[10]. Gauzes or perforated plates of another construction are intensely studied, like the cut and slotted gauze sheets[11].

The designed structures have proved to be less sensitive to clogging by coke agglomerates. In a classic monolith,

coke being formed in a channel, can block it entirely and thus eliminate the channel from the process. Such coke agglomerates are difficult to burn even at elevated temperature as oxygen molecules migrating through long channels have to cover a long distance to reach them. Unlike in monoliths, in gauze structures (Fig. 1B) oxygen containing gas phase can get to the agglomerate from almost all directions. Suppose the deposit were not burnt and stayed on the gauze, only a small part of it (few meshes) becomes dead because the fluid is still able to bypass it.
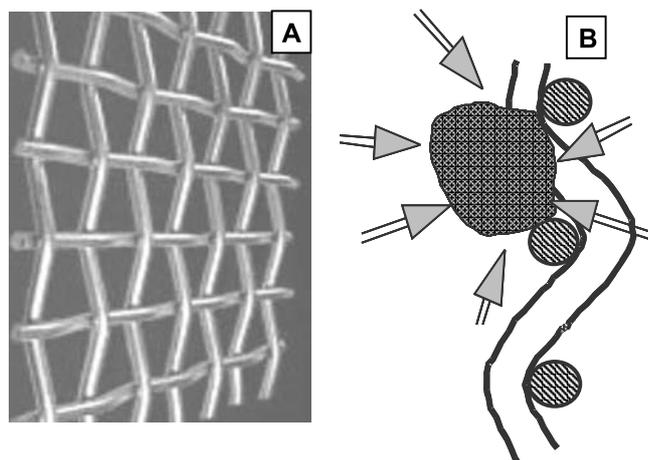

Figure 1. The woven wire gauze (A) and oxygen access (indicated by arrows) during the combustion of the carbonaceous deposit (B)
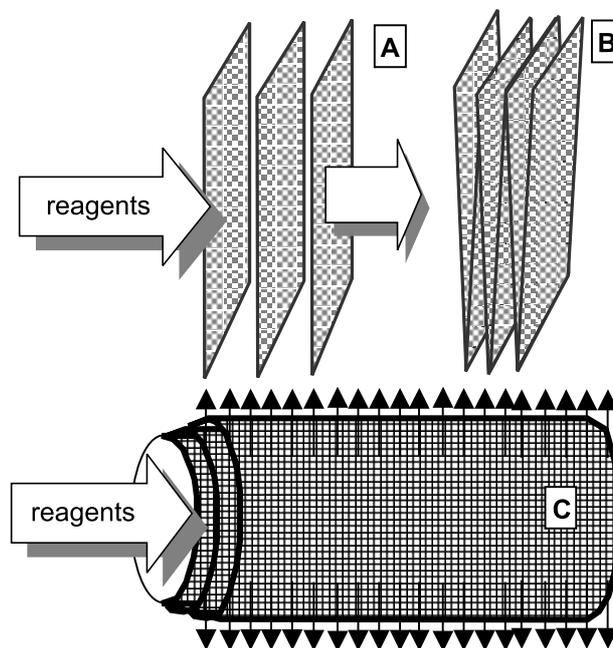

Figure 2. Possible arrangements of wire gauzes: flat gauze sheets staked (A), zigzag configuration (B), cylindrical coaxial gauzes with the radial flow of reactants (C)

MASS TRANSFER

According to Satterfield and Cortez[6], the basic model for the fluid flow through the gauzes is the flow past an infinite circular cylinder. Ahlström-Silversand and Odenbrand[7] agree with this assumption which, in turn, implies such boundary layer phenomena as static shed vortices, oscillating wake and von Karman vortex street[12].

Table 1. The geometrical parameters of the woven wire gauzes used in the study

Gauze type	Meshes per 1 inch	Meches per 1m	Wire diameter, $d \cdot 10^3$ [m]	a_{gauze}^* [1/m]	$a_{pack.}^*$ [1/m]	ε [m^3/m^3]	$d_h=4r_h=$ $4\varepsilon/a$ [m]
1	61.72	2429.82	0.16	8186	1180	0.673	$3.286 \cdot 10^{-4}$
2	30.48	1200.00	0.30	4005	961	0.700	$6.988 \cdot 10^{-4}$

* a_{gauze} refers to the volume of the gauze sheet, a_{pack} to the entire volume of the packing, including the separation gaps.

The main practical conclusion of 6 is, in fact, the use of a wire diameter (of which the gauze is manufactured) as the transversal dimension in criterial numbers of Reynolds, Nusselt or Sherwood. Moreover, the studies[6] and[7] confirmed the appropriateness of the Colburn analogy for the case of the staked wire gauzes. However, as regards wire gauze structures, the literature concerning mass and heat transfer is rather scarce and the results fairly out-dated.

A number of transfer experiments were performed for the gauze structures mentioned in Table 1. The number of gauzes staked together was from two up to fourteen. The experiments were carried out in a test reactor of a rectangular cross section, 45x30 mm, which was filled with stacked gauzes. The air flow through the reactor was measured using the flow-meters. The inlet and outlet air temperature was controlled by thermocouples. Electric current (up to 70 A, carefully stabilised) heated the gauze sheets, attaining reasonable heating power, and an appropriate temperature gradient between the structure and the flowing gas. The structure temperature was measured with small thermocouples attached to the gauzes and thoroughly electrically insulated although still assuring very good heat conduction. All the devices were connected to the computer data acquisition system. During the experiments, the typical temperature range of the gas was 30 - 100°C; of the structure elements 60 – 150°C. The temperature difference between the gas and the structure varied within the range 15 – 30K. The gas Reynolds numbers based on the wire diameter varied within the range from 1.0 to 100. Basing on the measured electric parameters (voltage and current, and thus, the heating power) as well as the gas and gauze temperatures, the heat transfer coefficient, the Nusselt number and the heat Colburn factor, j_H were calculated. Next, according to the Colburn analogy, the heat Colburn factor, j_H, and the mass Colburn factor, j_M, were assumed to be equal. This made the calculation of the Sherwood number and finally the mass transfer coefficients, possible.

The experimental results are presented in Fig. 3 in terms of the Sherwood vs. Reynolds number. Literature experimental correlations available[6, 7] and the theoretical solution of Lange et al.[13] for the infinite cylinder are shown for comparison. The particular configurations of the structure (i.e. the number of the gauzes staked) for both gauze types are given in the figure legend. As it can be seen, there is no noticeable influence of the number of the gauzes stacked and the curves for both gauze types lie very close one to another when the wire diameter is used as the transversal dimension. Therefore, a common correlation equation is proposed:

$$Sh = 0.334 Re_d^{0.722} Sc^{1/3} \qquad (1)$$

The correlation is based on 660 experimental points. Mean deviation amounts to 9%. The scatter of the data points with respect to the above correlation is presented in Fig. 4. For lower Reynolds range, the scatter attains
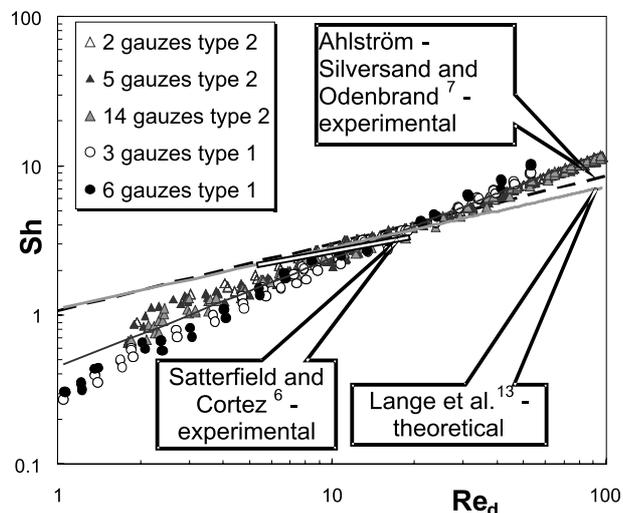

Figure 3. The experimental mass transfer results in terms of the Sherwood vs. Reynolds number. Literature experimental correlations available (refs. [6] and [7]) and a theoretical solution of Lange et al. [13] for the infinite cylinder are plotted for comparison
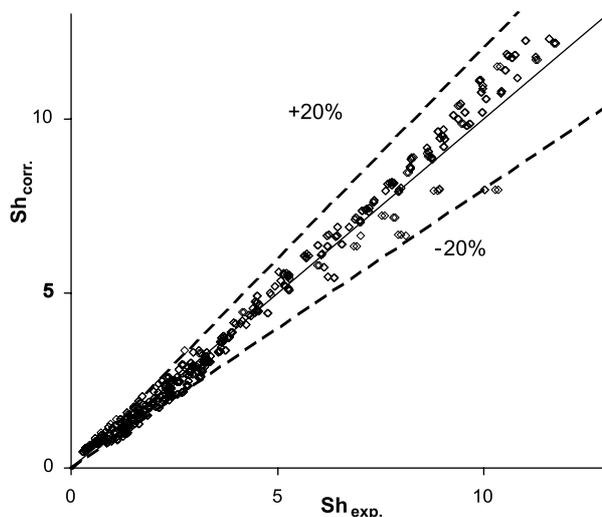

Figure 4. Scatter of the experimental mass transfer results

25% while for the upper one (Re>20) the scatter is less than 20%.

The correlations of Satterfield-Cortez[6] and Ahlström-Silversand and Odenbrand[7] as well as the theoretical results of Lange et al.[13] for an infinite cylinder display a very good agreement for low Reynolds values (Re<10). For higher Reynolds number (Re>20) the results slightly differ one from another. For a medium Reynolds numbers range, 8<Re<20, all literature data are very close to the experiments carried out in the present paper. For the limiting Reynolds values the differences are more substantial, up to 50%, especially for the lowest Re. It can be a result of different experimental techniques applied in references[6] and[7] (catalytic combustion in the range controlled by mass transfer) and in the present study (heat transfer technique).

For the low Reynolds range, the heat losses attained up to 25% of electric power supplied to the gauzes, which does not seem to be a reason for the observed deviations. Possible deviation sources can be attributed to significant differences in the gauze parameters. For example, the gauzes used in[6] show considerably higher void fraction and twice lower wire diameter than the gauze structure used by us (Table 1). Moreover, the transfer values measured in[6] and[7] could also be too high because of a significant contribution of homogeneous combustion of hydrocarbons to the overall combustion, that occurs at high temperatures in mass transfer controlling regime, especially at low gas velocities (long residence times).

FLOW RESISTANCE

The pressure drop experiments were performed using the same reactor and gauze configurations (1 up to 12 gauzes staked) for the whole attainable flow range. The Recknagel micromanometer was used to measure the pressure differences „before"and „after" the structure gauze packing. The pressure drop was assumed to be described using Darcy-Weisbach type equation defining the Fanning friction factor f:

$$\frac{\Delta P}{L} = 2f\,\frac{\rho w_0^2}{\varepsilon^2 d_h} = f\,\frac{\rho w_0^2}{2}\,\frac{a}{\varepsilon^3} \qquad (2)$$

The experimental results are presented in Fig. 5 in terms of the Fanning friction factor vs. the Reynolds number. In the figure, the ranges of the occurrence of characteristic flow patterns accordingly to the boundary layer theory[12, 13] are marked. The number of gauzes staked didn't noticeably influence the pressure drop. The results are very close to each other for all the gauze packings studied and they are correlated together as follows:

$$f = \frac{13.192}{Re_d} + 0.864 \qquad (3)$$

The correlation is based on 280 experimental points and the scatter amounts 15%. The comparison with the literature is not shown as the only one, and in fact, comprehensive study of Armour and Cannon[14] used a rather strange method of correlation and the results displayed
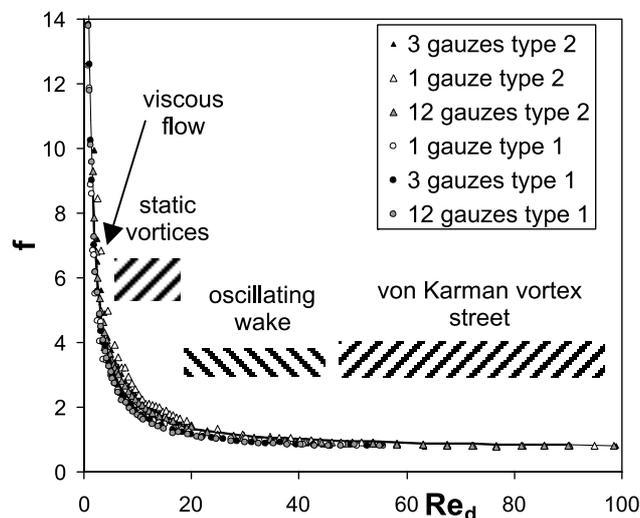

Figure 5. The fanning friction factor for the gauze structures studied vs. the Reynolds number. The flow patterns ranges are shown occurring for the flow past circular cylinder according to refs.[12, 13]

significant deviations form these of the present study, especially for low Reynolds values. Surprisingly enough the modelling of flow resistance for gauzes is still not satisfactorily solved. For example, there is a certain inconsistency in equations (2) and (3). The hydraulic diameter appearing in eq. (2) is defined as $d_h=4\varepsilon/a$ while the wire diameter d is used in the Re_d definition. An approach to this problem which would receive a wide-spread acceptance in the literature is still lacking.

REACTOR MODELLING AND COMPARISON

Nowadays, state of the art of the modelling of chemical reactors is a plug-dispersion model assuming heat and mass transfer between the solid catalyst and the flowing reactants. A similar approach is recommended, beside others, by Ahlström-Silversand and Odenbrand[7]. However, there is a pervasive lack of the axial dispersion data for gauze packings similar to those used in[7] or in the present study. The reasoning of the cited authors[7] was indirect; they used the axial dispersion values published by Levenspiel[15] in the diagrams and in this way they concluded that the dispersion was too low to influence the process noticeably. Thus, what they used, in fact, was a plug flow model, whose idea we decided to follow. Additionally, during the VOC combustion the amount of the evolved heat is very low due to a high dilution level which means that heat transfer problems can be securely neglected. Therefore we used a simple plug flow model assuming the mass transfer to the packing surface is balanced by the catalytic combustion. The model is described in details in[16]. Mass transfer coefficients and pressure drop were calculated according to the correlation derived in this study.

As a reference to the structured gauze reactor, we assumed a classic ceramic monolith of 200 cpsi, which is a commonly accepted solution for the catalytic combustion. The modelling is based on the work of Cybulski and Moulijn[17]. For the modelling of both monolith and gauze reactors we applied kinetics of our cobalt oxide catalyst promoted with palladium. The catalyst and kinetic experiments are described in reference[18]. To show some trends, we extremely extrapolated the range of kinetic equation derived in[18] being aware that this is made only for the sake of demonstration. To compare the gauze structures and the monolith during the catalytic combustion of VOC we assumed the following case study. The values used for modelling were as follows: the initial VOC concentration 100 ppm, final concentration 1 ppm, gas superficial velocity $w_0=5$m/s. The resulting reactor length and the pressure drop vs. the process temperature are shown in Figure 6. Here, the reactor length was calculated assuming no gaps between the gauze sheets. To take the separation gaps into account, it is necessary to divide the length L (Fig. 6) by a ratio (a_{gauze}/a_{pack}) (Tab.1). Moreover, a part of the modelling was carried out for the case of the mass transfer limitation (or extremely fast kinetics)[16]. The results are shown in Table 2 and they can be regarded as asymptotes for T→∞ in Fig. 6. It should be stressed that both the reactor length and the pressure drop depend on the gauze parameters and the process kinetics. For the transfer limitation, kinetics obviously does not influence the length and the flow resistance of the reactor.

Table 2. The comparison of the gauze structures used for the catalytic combustion of VOC. The initial concentration 100 ppm, final concentration 1 ppm, gas superficial velocity $w_0 = 5$ m/s, standard pressure, temperature 200°C. The case of diffusional limitation is assumed (extremely fast kinetics)

Structure	Reactor length L, mm	$k_c a$ [1/s]	Pressure drop ΔP, Pa
Monolith 200cpsi	446	51.6	1052
Gauze type 1	55.6*/8.0**	414*/2875**	2454
Gauze type 2*	83.6*/20.1**	275*/1148**	2296

* including the separation gaps (a_{pack}); ** without the separation gaps ($_{apack}$)

Figure 6. A comparison of the reactor length and the pressure drop for the classic 200 cpsi monoliths and two gauze structures. For the gauzes a case without a separation gap is assumed
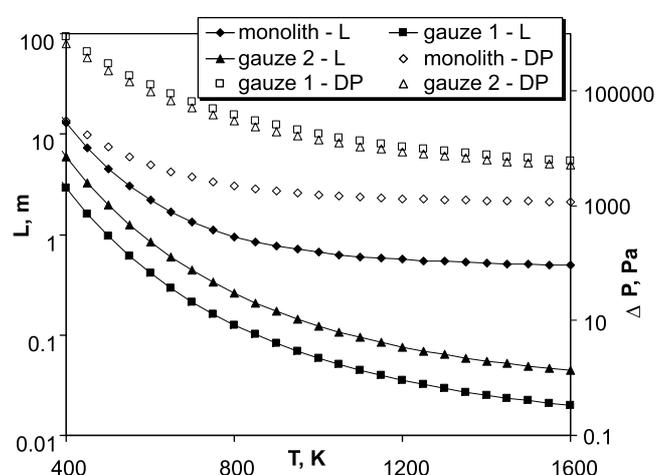
CONCLUSIONS

The structured reactor considered in this study can be regarded as an interesting alternative for the temporarily applied reactors for its extraordinary mass and heat transfer parameters.

• The mass transfer properties for the gauze structures are highly increased compared to the classic monoliths. Volumetric mass transfer coefficients are over 50 times higher than that of the classic monolith (Table 2, ref.[16]).

• The experimental values of transfer coefficients obtained for the stacked gauzes are in keeping with the literature data[6] and[7] for the moderate Reynolds numbers.

• The derived length of the gauze reactor is 2 up to 25 times shorter than that of the monolith, depending on the process kinetics (assuming no gaps). For a case of mass transfer limitation, the gauze reactor is up to 55 times shorter than the monolith.

• The pressure drop of the gauze reactor is 5 up to 16 times higher than that of the monolith (depending on the kinetics). For a mass transfer limitation case it is 2.3 times higher.

NOMENCLATURE

a   – specific surface area [m^{-1}]
d   – wire diameter [m]
d_h – hydraulic diameter, $= 4\varepsilon/a$ [m]
f   – Fanning friction factor
k_c – mass transfer coefficient, [m/s]
L   – reactor length [m]
Re   – Reynolds number
Sc   – Schmidt number
Sh   – Sherwood number
T   – temperature [K]
w_0 – superficial velocity [m/s]
ΔP – pressure drop [Pa]
ε – gauze void fraction
ρ – density [kg/m^3]

SUBSCRIPTS

corr   – calculated from a correlation
d   – based on wire diameter
exp   – experimental result
gauze – refers to the volume of single gauze sheet or gauzes stacked without separating the gaps
pack   – refers to gauze sheets stacked alternately with the separating gaps (gauze packing)

LITERATURE CITED

(1) Smuts M. B.: Hazardous air pollutants: inside and out, Public Health Report, Jan./Feb. **2001**, 58.

(2) Inst. Of Clean Companies Inc., Report abstract, Industrial News, Jan./Feb. **2002**, 6.

(3) Polish Air Emissions Database, Institute of Environmental Protection, available from: <http://emissions.ios.edu.pl/>

(4) Williams J. L.: Catal. Today 69 (**2001**) 3.

(5) Łojewska J., Kołodziej A., Żak J.: Cobalt oxide catalyst on metallic structured reactor filling for VOC combustion as an alternative to noble metal catalysts, submitted to Polish J. Chem. Technol.

(6) Satterfield C. N., Cortez D. H.: Ind. Eng. Chem. Fundam. **1970**, 9, 613.

(7) Ahlström-Silversand A. F., Odenbrand C. U. I.: Chem. Eng. J. **1999**, 73, 205.

(8) Lyubovsky M., Karim H., Menacherry P., Boorse S., LaPierre R., Pfefferle W. C., Roychoudhury S.: Catal. Today **2003**, 83, 183.

(9) Hills T., Kons G., Schwab E., Mueller-Everbusch M.: Knitted Metal Fabrics as Thin Layer Catalysts: Operational Experience in Steamcracker Gas Phase Hydrogenation, poster presented at ICOSCAR-2 conference, Delft, **2005** (not published).

(10) Personal communications from the Faculty of Textile Architecture of Lodz Univ. Technol. and Polish State Mint, **2005**.

(11) Personal communication from Katator AB, Sveden, **2005**.

(12) Schlichting H.: Boundary layey theory, 7th ed., McGraw-Hill, new York, **1979**.

(13) Lange C. F., Durst F., Breuer M.: Int. J. Heat Mass Transfer **1998**, 41, 3409.

(14) Armour J. C., Cannon J. N.: AIChE J. **1968**, 14, 415.

(15) Levenspiel O.: Chemical Reaction Engineering, Wiley, New York, **1972**.

(16) Kołodziej A., Łojewska J.: Catal. Today **2005**, 105, 378.

(17) Cybulski A., Moulijn J. A.: Catal. Rev.-Sci. Eng. **1994**, 36, 179.

(18) Łojewska J., Kołodziej A.: Catal. Today **2005**, 105, 655.