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Abstract

To carry out a comparative assessment of a recently proposed idea of using thermal flow-reversal reactors (TFRR) for mine ventilation air, the results for the catalytic flow-reversal reactor (CFRR) investigated within the European Project (2003) are briefly presented. Next, experimental investigations of thermal combustion are presented in this paper. These consisted of the kinetic study of homogeneous combustion in the pelletized bed and in the monolith. Kinetic equations for the two cases are derived and discussed. Experimental autothermal reverse-flow operation in a laboratory setup was performed. Due to the high heat capacity of the wall and insulation of the pelletized bed reactor, with considerable heat losses to the surroundings, autothermal operation was successful only in the monolithic reactor. It is finally concluded that the thermal combustion can be competitive compared with the catalytic oxidation.

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1. Introduction

Large amounts of methane are discharged into the atmosphere with mine ventilation air. A single ventilation shaft can emit over 500,000 m\textsuperscript{3}(STP)/h of ventilation air in which methane content can be as high as 1 vol% The abatement of this emission is therefore important from both economic and environmental point of view, as the gaseous fuel is inadvertently lost, simultaneously contributing to greenhouse effect. A number of studies have been carried out to utilize this methane via combustion and to recover the energy thus produced. Due to very low CH\textsubscript{4} concentrations the most promising solution seems to be autothermal combustion in reverse-flow reactors. The combustion converts CH\textsubscript{4} into CO\textsubscript{2}. Although this is also a greenhouse gas, its global warming potential (GWP, over a period of 100 years) is 21 times lower than that of methane. So far, most of the studies have focused on catalytic combustion in catalytic flow-reversal reactors (CFRRs) - cf., among others, the work done by CANMET in Canada (Sapoundjieva et al., 1999). Simulations and experimental studies performed within a European Project (2003) show that CFRRs are characterized by high operating temperatures (up to 800 °C for the 0.5% Pd/γ-Al\textsubscript{2}O\textsubscript{3} catalyst), leading to possible deactivation or even destruction of the relatively expensive catalyst. Thus, the study has revealed that the large-scale implementation of this technique may prove problematic in industrial applications.

Therefore, non-catalytic oxidation in thermal flow-reversal reactors (TFRRs) is now frequently regarded as an attractive alternative (cf. US EPA Reports, 2000, 2001). Such reactors have long been used, e.g. for the homogeneous (thermal) combustion of volatile organic compounds (VOCs). However, obvious differences exist between the combustion of VOCs and the oxidation of ventilation air methane in flow-reversal reactors. In the former case no heat is withdrawn from the system (sometimes the reactor has to be heated in order to sustain autothermicity), whereas during the combustion of lean methane–air...
mixture it is estimated that some 7 MWt can be produced per 100,000 m³(STP)/h of the gaseous feed. Thus, an installation connected to an average ventilation shaft can produce several dozen MWt/s. The thermal combustion in a TFRR should be carried out under conditions that do not promote excessive formation of NOₓ, i.e. at maximum temperatures in the reactor below 1300 °C. With the combustion of methane high temperatures are quite possible, thus it is important to estimate the extent of temperature rise under actual conditions. The use of a TFRR for the combustion of lean methane mixtures requires therefore detailed studies to determine the reasonable operating conditions. The paper presents the results of preliminary studies concerning this problem.

2. Catalytic flow-reversal reactor (CFRR)

The idea of using a CFRR was investigated in a European Project (2003) both experimentally and by computer simulations. More detailed results of this project can be found in earlier publications (e.g. Gosiewski, 2005; Gosiewski and Warmuzinski, 2007). In the present study these results were used only as a basis for comparison of the CFRR with the purely homogeneous combustion in the TFRR. The studies were performed for both 12% MnO₂/γ-Al₂O₃ and 0.5% Pd/γ-Al₂O₃. A mathematical model of the catalytic combustion of methane in a fixed-bed catalytic reactor has already been described by Gosiewski (2005). It is a one-dimensional, two-phase dynamic model for both heat and mass transfer. The model takes into account the effective thermal conductivity in the solid phase and dispersion in the gas phase. Both catalytic and homogeneous combustion are included in the model. In Table 1 the basic input parameters are listed together with their values used in computer simulations. The data given in the table are associated with a pilot-scale reactor, which was envisaged as the next step of the study. The simulation results can, however, be extended on the relevant industrial applications. The length of the inert section was determined to ensure temperatures well below the levels that might be detrimental to the catalyst. The catalysts themselves, alongside the relevant kinetic data were provided by the Boreskov Institute of Catalysis in Novosibirsk (European Project, 2003) as a reasonable compromise between the catalyst cost and activity. Further optimization of the catalyst may lead to slightly better parameters of the CFRR, although any significant qualitative improvement can hardly be expected.

The simulations reveal that if the technique of “hot gas withdrawal” is used, higher heat recoveries can be obtained. The technique of “hot gas withdrawal” (Fig. 1a) is based on feeding the boiler with a part of the hot gas withdrawn from the central part of the reactor, which is then discharged to the atmosphere. Both simulations and experimental studies carried out in BIC at Novosibirsk within a European Project (2003) show that up to about 30% of the gas can safely be withdrawn without any loss of autothermicity or stability of the process. The autothermicity of the flow reversal reactor with hot gas withdrawal depends directly on the amount of heat extracted. Thus, the higher the temperature in the middle section of the reactor, the lower the amount of gas which has to be withdrawn to produce the same amount of heat. As the TFRR temperatures are much higher than those in the CFRR, a comparable amount of the heat recovered can be obtained for less hot gas withdrawn from the reactor (cf. flow rate data in Tables 1 and 2). On the other hand, with too large withdrawal, the reactor may extinguish. In both cases the flow rates of the hot gas extracted from the reactor were adjusted in order to safeguard autothermicity with an appropriate safety margin.

The flux of the heat recovered as a function of concentration is presented in Fig. 1b. The relation between the maximum temperature and the heat recovery can be seen from the graphs shown in Fig. 2. The concentration of methane in ventilation air may reach 1%. However, with the use of the manganese catalyst the temperature of the catalytic bed may exceed 900 °C for CH₄ concentrations above 0.8%, even for a highly efficient removal of heat from the reactor. Thus, the relatively cheap Mn catalyst may undergo rapid destruction, and the MnO₂ catalyst should not be used as the excessive catalyst temperatures may sinter and damage the catalyst. Therefore, the higher heat recoveries (above 95%) indicated by the simulations for this type of catalyst may be impossible to attain in practice.

If the more expensive palladium catalyst is employed, the temperature can be kept at a level lower by about 100 °C. Unfortunately, the heat recovery also becomes considerably lower (see Gosiewski, 2005), and the cost of the Pd catalyst leads to an estimated payback period of almost seven years for an industrial plant. Su et al. (2005) present an economic analysis whereby the CFRR capital cost is much lower than that for the TFRR. It seems, however, that their analysis strongly underestimates the cost of the catalyst itself, since any less expensive catalyst (e.g. MnO or CuCr) is not appropriate for the temperatures prevailing in this case.

For the palladium catalyst the withdrawal of up to 30% of the gas leads to a heat recovery coefficient exceeding 70%, i.e.,

Table 1
Basic parameter values used in the simulations of CFRRs

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Gas flow rate</td>
<td>30,000 m³(STP)/h</td>
</tr>
<tr>
<td>Proportion of the hot gas withdrawn</td>
<td>(a) 29%</td>
</tr>
<tr>
<td></td>
<td>(b) 30%</td>
</tr>
<tr>
<td>Inlet temperature</td>
<td>293.15 K (20°C)</td>
</tr>
<tr>
<td>Methane concentration in ventilation air</td>
<td>0.2–1.0 vol%</td>
</tr>
<tr>
<td><strong>Height of the catalyst bed</strong></td>
<td></td>
</tr>
<tr>
<td>(a) Rings 10 × 10 × 5 mm (12% MnO₂/γ-Al₂O₃)</td>
<td>2 × 0.2 m</td>
</tr>
<tr>
<td>(b) Rings 15 × 15 × 9 mm (0.5% Pd/γ-Al₂O₃)</td>
<td>2 × 0.2 m</td>
</tr>
<tr>
<td><strong>Height of the inert bed</strong></td>
<td></td>
</tr>
<tr>
<td>(a) Ceramic rings 15 × 15 × 9 mm</td>
<td>2 × 0.2 m</td>
</tr>
<tr>
<td>(b) Ceramic rings 25 × 25 × 19 mm</td>
<td>2 × 0.2 m</td>
</tr>
<tr>
<td><strong>Superficial velocity in the reactor at standard temperature and pressure</strong></td>
<td>(a) 0.6 m/s</td>
</tr>
<tr>
<td></td>
<td>(b) 0.4 m/s</td>
</tr>
<tr>
<td><strong>Reactor diameter</strong></td>
<td></td>
</tr>
<tr>
<td></td>
<td>(a) 4.2 m</td>
</tr>
<tr>
<td></td>
<td>(b) 5.144 m</td>
</tr>
<tr>
<td><strong>Duration of the half-cycle of flow reversal</strong></td>
<td>(a) 120 s</td>
</tr>
<tr>
<td></td>
<td>(b) 300 s</td>
</tr>
</tbody>
</table>

(a) MnO₂ catalyst. (b) Pd catalyst.
Fig. 1. Schematic diagram of a reverse-flow reactor with the heat recovery by hot gas withdrawal from the central section of the reactor (a) and the flux of heat recovered as a function of the inlet methane concentration—simulation results for MnO$_2$ and Pd catalysts (b).

Table 2
Kinetic parameters of the equation for homogeneous combustion in the pelletized and monolith bed

<table>
<thead>
<tr>
<th></th>
<th>$k_o$ (mol$^{1-a}$ m$^{-3(1-a)}$ s$^{-1}$)</th>
<th>$E$ (kJ mol$^{-1}$)</th>
<th>$a$ (–)</th>
<th>Estimation quality</th>
<th>Mean abs. error</th>
<th>Correlation coefficient</th>
</tr>
</thead>
<tbody>
<tr>
<td>Peletized bed</td>
<td>$1.61 \times 10^7$</td>
<td>142.427</td>
<td>0.81</td>
<td></td>
<td>14.3%</td>
<td>98.2%</td>
</tr>
<tr>
<td>Monolith</td>
<td>$6.861 \times 10^6$</td>
<td>130.622</td>
<td>0.94</td>
<td></td>
<td>6.1%</td>
<td>99.4%</td>
</tr>
</tbody>
</table>

Fig. 2. Maximum catalyst temperature and heat recovery coefficient (i.e. ratio of the heat recovered to that produced by combustion) vs. inlet methane concentration for the two catalysts (simulation results).

7 MW$_i$ per 100,000 m$^3$ (STP)/h for the feed containing 1 vol% of methane. For an average value of the inlet methane concentration (0.3 vol%) the heat recovery for the Pd catalyst is negligible. If we assume, however, that the heat is produced using ventilation air with an average CH$_4$ content of 0.5 vol%, for an average output of a single shaft of about 700,000 m$^3$ (STP)/h it is possible to recover some 12 MW$_i$. For the hot gas withdrawal option the boiler (which is by far the most convenient type of exchanger) would operate at temperatures safeguarding vigorous heat transfer to the various elements of the system (superheaters, evaporators and water heaters). Production of electricity using the heat recovered also seems feasible. On
the other hand, even for the Pd catalyst the maximum temperature for higher concentration, however acceptable, seems to be too high to ensure the long life of the catalyst. The excessive temperature results mainly from a considerable share of homogeneous combustion in the gaseous phase, within both the catalytic bed and inert material whose sole purpose is the accumulation of heat. Thus, the question arises whether using catalytic combustion is at all necessary. An obvious advantage of the CFRR is the relatively low operating temperature, and therefore cheaper materials of construction. Safety margin for the temperature of NO\textsubscript{x} formation is also wider than for non-catalytic combustion. On the other hand, the cost of the expensive catalyst makes the total cost of the plant very high. It should also be taken into account that the catalyst will operate with wet and dusty gas, and thus the lifetime of the catalyst will probably be much shorter than in other applications.

3. Thermal flow-reversal reactor (TFRR)

Non-catalytic flow-reversal combustors (TFRR) (see e.g. US EPA Reports, 2000, 2001), due to the absence of expensive catalyst, offer clear advantage over CFRR although, as has been pointed out by King et al. (2001), the materials of construction will be more expensive. Another important advantage of the TFRR over CFRR is associated with its resistance to various impurities in the mine ventilation air.

An important upper limit of temperature is associated with the formation of NO\textsubscript{x}-these, however, do not appear in large quantities below 1300\degree C, at which temperatures the reactor will operate. Generally, the construction of the TFRR is similar to that of the CFRR (see Fig. 3), with the only difference being the absence of the catalytic part of the bed. Similar to the CFRR, heat recovery can be realised in two ways, either by central cooling (heat exchanger placed in the middle of the bed), or by hot gas withdrawal from the central section of the reactor. It can be expected that, similar to the CFRR (see e.g. Gosiewski, 2005), the hot gas withdrawal may be superior to the central cooling. Therefore, in the present study only this option was considered for the TFRR.

Mathematical simulations employing a model similar to that used for the CFRR can also yield operating parameters for the TFRR when the catalytic part of the bed is missing. In general, it is the same model as that described by Gosiewski (2005) for the CFRR.

The use of a TFRR for the combustion of lean methane mixtures requires therefore detailed studies to determine reasonable operating conditions. While for the CFRR thermal combustion occurs in parallel to catalytic oxidation and has only some share in overall conversion, for the TFRR the conversion and other quantities are much more dependent on kinetic parameters that describe thermal combustion. Therefore, if the simulation is to be used in process analysis, the reliability of kinetic equations for the homogeneous combustion becomes by far more important than for the CFRR. Unfortunately, kinetic data for such combustion, taken from various sources, differ significantly. Moreover, the combustion in the TFRR takes place in voids of the reactor bed. Consequently, it is sometimes assumed that even simple first order kinetic equation of the type

$$\rho_{\text{hom}} = k_0 \exp \left( \frac{-E}{RT} \right) \times C_{\text{CH}_4} \tag{1}$$

exhibits dependence of the experimentally obtained kinetic parameters ($k_0$ and $E$) on the geometry of the voids in the packed bed used in the experiments (e.g. diameter of the combustor, particle size for pelletized beds or geometry of the monolith). Such dependence was included in the kinetic equation developed by the Boreskov Institute of Catalysis SB RAS (BIC) for a European Project (2003). This, obviously, is difficult to interpret theoretically, although one of the possible explanations may be that non-catalytic surfaces can scavenge radicals or initiate radical reactions (the so-called heterogeneously ignited homogeneous gas phase reactions). On the other hand experimental kinetic studies of homogeneous combustion are much more difficult than for combustion on the catalyst. The main problem consists in the maintenance of isothermal conditions in an experimental setup. For catalytic experiments there is usually no problem with maintaining a constant temperature of a small amount of the catalyst. Also, due to the relatively large heat capacity of the sample the heat of reaction does not raise the temperature of the sample significantly. Homogeneous combustion occurs in the gaseous phase with small heat capacity, so when a gaseous fuel ignites, the temperature increase of the gas phase can become significant. Moreover, a very fast reaction leads to the formation of a combustion wave whose propagation and concentration of energy may follow various mechanisms (see e.g. Babkin et al., 2002) and depend on the geometry of the open space where the combustion occurs. Thus the determination of the “isothermal” temperature for reaction rate
calculations becomes doubtful. Additionally, the measurement of the temperature is unreliable as any thermocouple inserted either into the pelletized bed or inside the monolithic substrate displays a value, which may be highly inconsistent even with an average combustion temperature. The meaning of the term “average” is also vague. This explains why any experimentally determined kinetic equation for the homogeneous combustion can exhibit dependence on the geometry of a combustor and its packing. On the other hand, such a kinetic equation is indispensable for further scale-up and design of the TFRR, even if it does not have any general character or only approximately describes the process for a particular set of conditions.

Furthermore, CH₄ is not a single step reaction. Bendtsen et al. (1998) presented a reaction mechanism which they qualify as “simplified” and which contains 23 intermediate reactions. However, they quote publications that propose a much more complex theory of combustion, with significant amounts of CO that can appear at intermediate stages. To simplify the experiments a straightforward single-step reaction mechanism was assumed in the present study:

\[
\text{CH}_4 + 2\text{O}_2 \rightarrow \text{CO}_2 + 2\text{H}_2\text{O}.
\]  

(2)

Ignoring CO as an intermediate seems justified due to the large excess of oxygen. The kinetic studies were supplemented with a sensitive CO measurement after the combustion; this did not indicate any presence of carbon monoxide.

It cannot be expected, however, that the single step combustion model can yield a general kinetic equation. This is an obvious drawback of this fairly simple model which can otherwise be very useful in simulation studies. Despite this deficiency, attempts to describe methane oxidation in this way have had a long history (see e.g. Westbrook and Dryer, 1981); for a single-step mechanism the reaction rate of combustion is expressed as

\[
r_{\text{hom}} = k_0 \times T^n \times \exp \left( \frac{-E}{RT} \right) \times \left[ \text{Fuel} \right]^a \times \left[ \text{Oxidizer} \right]^b,
\]

(3)

where the temperature \( T \) is given in K. Term \( T^n \) appears according to Eyring’s transient state theory (see Glassstone et al., 1941).

In the present study large excess of oxygen should lead to exponent \( b = 0 \). Also, the fitting of the kinetic equation for the two cases investigated was not improved significantly for the non-zero temperature exponent, \( n \neq 0 \). It can thus be assumed that the reaction rate constant for the homogeneous combustion can be described using the Arrhenius formula:

\[
k(T) = k_0 \times \exp \left( \frac{-E}{RT} \right).
\]

(4)

Simulation results based on kinetic equations taken from various sources were analysed by Gosiewski et al. (2007), where both the rate parameters (activation energy \( E \) and pre-exponential factor \( k_0 \)) and the simulation results varied significantly depending on the kinetic equation used. On the other hand, such a single-step kinetic model can be useful if only experimental conditions for the homogeneous combustion are similar to those prevailing in the actual reactor.

4. Kinetic experiments for the TFRR

The experiments were aimed at the determination of a kinetic equation describing homogeneous combustion in the two experimental setups. Further, the possibility was investigated of the autothermal operation in these setups in the reverse-flow regime. Since it is difficult to determine a general kinetic equation describing the combustion rate for any reactor packing or for the open space (cf. the preceding section), the results obtained should be understood as experimental description of the combustion phenomena occurring in the reactor packing used in a particular experiment.

For the two cases studied (i.e. pelletized bed and monolith) the parameters for the following kinetic equation:

\[
r_{\text{hom}} = k_0 \times \exp \left( \frac{-E}{RT} \right) \times (C_{\text{CH}_4})^a
\]

(5)

were estimated.

In order to avoid a large change in methane concentration and temperature in the combustion zone, the kinetic experiments were limited only to such conditions in which the conversion was low. Moreover, to obtain an Arrhenius plot for the two cases analysed either temperature or CH₄ concentration was taken as an average value in the combustion zone. The results of the kinetic experiments are summarized in Table 2.

It has to be stressed that the values of \( k_0 \) and \( E \) can only be regarded as apparent quantities, since rigorous rules governing the determination of kinetic parameters were not strictly observed in the present experiments.

4.1. Kinetic experiments for the homogeneous combustion in the pelletized bed

The experiments were done in an 18 mm ID tube, packed with 3 mm spheres and placed in an oven. The length of the bed was 20 cm in kinetic experiments, and 30 cm in flow-reversal experiments. The kinetic studies were carried out for CH₄ concentrations between 0.5 and 2 vol% and for temperatures at which the conversion of methane did not exceed 15%. Flow rate through the bed was 0.68 m³ h⁻¹. The Arrhenius plot summarizing these studies is shown in Fig. 4a. Based on this plot and for the kinetic equation of the form (5) the following parameter values were estimated:

\[
k_0 = 1.61 \times 10^7 \text{ mol}^{0.19} \text{ m}^{-0.57} \text{ s}^{-1}, \quad E = 142.427 \text{ kJ mol}^{-1}, \quad a = 0.81.
\]

For these parameters a mean absolute error (calculated vs. measured reaction rate) of 14.3% was obtained, with a correlation coefficient of 98.2%.

4.2. Kinetic experiments for the homogeneous combustion in the monolith

Kinetic experiments were carried out in a 39 mm ID, 1 m long ceramic tube, packed in the middle section with four monolith segments, each 10 cm long. Thus, the total length of the
Fig. 4. Experimental Arrhenius plots for the homogeneous combustion in the pelletized bed (a) and in the monolith (b).

Fig. 5. An example of the observed temperature profiles along the monolith for the constant preset temperature of the oven and various methane concentrations during kinetic experiments.

monolith was 40 cm. The kinetic experiments were carried out at a constant gas flowrate of 0.5 m$^3$ h$^{-1}$. The tube was placed in a temperature-controlled oven (BI Barnstead Thermolyne 21100 Tube Furnace), also 40 cm long. The thermal capacity of the insulation was much smaller than in the pelletized bed case described in the previous section.

The determination of the “combustion temperature” was done in the following way. Since the total length of the monolith was larger than that of the “hot zone” (where the combustion occurs), for each experiment carried out at the same preset temperature a temperature profile along the monolith was measured. In the initial series of experiments the ignition temperature of the combustion was determined as the highest monolith temperature for which (independently on the inlet methane concentration) the combustion did not start (i.e. methane conversion was equal to zero). This temperature, $T_{\text{ign}}$, is shown in Fig. 5 as a broken line. As can be seen from Fig. 5, the temperature profiles are practically independent of methane concentration. It is even difficult to differentiate between the individual profiles for different concentrations. The ignition temperature line makes it possible to determine the length of the “combustion zone” $L_{\text{comb}}$ in the monolith, i.e. a part of the monolith where the combustion can appear. For the case shown in Fig. 5 this zone was estimated roughly as $L_{\text{comb}} \approx 20$ cm. Obviously, the higher the preset temperature in the oven, the longer the “combustion zone”. As the temperature of the homogeneous combustion an average temperature $T_{\text{average}}$ in the combustion zone was calculated, and this value was taken as a basis for the determination of a single point in the Arrhenius plot shown in Fig. 4b.

The kinetic studies for the monolith were carried out for CH$_4$ concentrations between 0.5 and 1.7 vol% and temperatures at which the conversion of methane did not exceed 25%. Flowrate through monolith was 0.5 m$^3$ h$^{-1}$. When the temperature exceeds about 750°C total combustion (100% CH$_4$ conversion) is possible. Thus, the kinetic experiments within the temperature range 565–620°C were carried out to safeguard a relatively low conversion.

The Arrhenius plot summarizing these studies is shown in Fig. 4b. Based on this plot and for the kinetic equation of the form (5) the following parameter values were estimated:

$$k_0 = 6.861 \times 10^6 \text{ mol}^{0.06} \text{ m}^{-0.18} \text{ s}^{-1},$$
$$E = 130.622 \text{ kJ mol}^{-1}, \quad a = 0.94.$$

For these parameters a mean absolute error of 6.1% was obtained with a correlation coefficient of 99.4%. Thus, for the monolith the fitting of the kinetic equation was better than for the pelletized bed.

4.3. Comparison of the combustion rates in the pelletized bed and monolith

Dependence of the combustion rate on temperature for an inlet methane concentration of 0.5 vol% for the pelletized bed and the monolith according to Eq. (5), with the parameters given in Table 2, is shown in Fig. 6. The same function is presented using the linear (a) and logarithmic (b) $r_{\text{hom}}$ scale. The linear scale better visualizes the differences in the reaction rates calculated from various equations for higher temperatures, while the logarithmic scale better illustrates the differences for lower temperatures.

The plots reveal, that for higher temperatures the combustion rate is higher in the pelletized bed, while for lower temperatures
5. Flow-reversal experiments

It is not easy to obtain reliable information about the possibility of the autothermal operation of reverse-flow reactors under laboratory conditions, characterized by considerable heat losses to the surroundings. It can be expected, however, that it is possible to estimate at least roughly, the maximum temperature, which may appear in the TFRR. On the other hand, due to large heat losses in laboratory installations, the experiments will not yield the lowest inlet methane concentration for which autothermal operation would be possible in large scale applications.

It is generally possible to obtain pseudo-adiabatic behaviour in a reverse-flow reactor, although this requires a special setup. Such a setup was successfully used in a reverse-flow reactor by Fissore et al. (2005) and earlier for a counter-current reactor by Gosiewski et al. (1996). The problem is, however, that in the two foregoing pseudo-adiabatic systems the reactors were operated at temperatures below 600°C, while in the TFRR the temperatures well above 1000°C may be expected. Practical experience shows that the higher the temperature in the reactor, the more difficult it is to maintain stability of the temperature control system. Due to these problems this method was not used in the present study.

The temperatures in the reverse-flow reactor fluctuate in every cycle of reversal. Thus, during the experiments both minimum $T_{\text{min}}$ and maximum $T_{\text{max}}$ temperatures were recorded.

5.1. Reverse-flow experiments in the TFRR with the pelletized bed

The reverse-flow experiments for the case with the pelletized bed were carried out for a half-cycle of 15 s and for the reactor initially heated to about 900°C. During the reverse-flow operation it was necessary to supply heat into the system to compensate for the heat losses to the surroundings. In Fig. 7 the temperature transients are shown at the end of the bed for the inlet CH$_4$ concentration varied during a single experimental series (which took 200 full cycles). The graph shows the temperature transients both at the beginning and at the end of the half-cycle, as well as the inlet CH$_4$ concentrations and methane conversions corresponding to subsequent parts of the individual experimental series.

Since the heat capacity of the oven was much larger than the capacity of the bed itself, the experiment does not reflect the actual operating conditions of the TFRR. The heat capacity of the oven equalizes temperature, so the influence of the heat generated inside the bed on the temperature is strongly affected by the temperature of the body. It can, however, be concluded that at temperatures of about 1000°C it is possible to attain high conversions of methane during its homogeneous combustion. Unfortunately, due to considerable heat losses it
was impossible to obtain the autothermal operation in the experimental installation with pelletized bed reactor, and it was impossible to avoid compensatory heating during the individual series of experiments.

5.2. Reverse-flow experiments in the TFRR with the monolith

The experience gained during experiments with the pelletized bed led to a laboratory setup for the reverse-flow combustion in the monolith. The setup was better insulated in order to minimize the influence of the surroundings on the process inside the reactor itself. The main modifications include:

- the use of a well insulated oven, with insulation of much lower heat capacity than in the previous case;
- an increased amount of heat generated in the combustion zone by an increase in the diameter of the reactor (monolith) and the use of higher flowrates through the reactor.

These changes led to the fully autothermal operation in the flow-reversal regime, although for a rather high methane concentration of about 1.8 vol%. The temperature transients for this autothermal run (without any additional heating) and for a 30 s half-cycle are shown in Fig. 8.

For reproducible flow-reversal experiments with an inlet concentration of about 1.8 vol% a stable cyclic steady state was observed, with a methane conversion of 100%. For lower methane concentrations a very slow temperature drift was observed (although still at 100% conversion), and the reactor extinguished altogether with very rapid drop in conversion (to zero) and temperature for an inlet concentration of about 1.6 CH₄ vol% after 5 h.

During the experiments in the autothermal reverse-flow regime (without any additional heating), thermal efficiency of the reactor was estimated in the cyclic steady state. The term “thermal efficiency” $\alpha$ has the same meaning of that given by Tavazzi et al. (2006):

$$\alpha = \frac{\Delta T_{\text{exp}}}{\Delta T_{\text{adiab}}}$$  \hspace{1cm} (6)

where

$$\Delta T_{\text{exp}} = (T_{\text{outlet}}^{\text{av}} - T_{\text{inlet}}).$$  \hspace{1cm} (7)

The value $T_{\text{outlet}}^{\text{av}}$ is the reactor outlet temperature averaged over the full reversal cycle, while $T_{\text{inlet}}$ is the inlet temperature, usually kept constant during the experiments, and $\Delta T_{\text{adiab}}$ represents the calculated temperature rise of an adiabatic reactor for parameters associated with a given experiment.

For experiments carried out for a methane concentration of 1.8 vol% the estimated thermal efficiency $\alpha$ was about 38%. This means that in such experiments over 60% of the heat generated by combustion is inevitably lost. Obviously, in larger scale reactors thermal efficiency can be much better, and thus the reactor will work autothermally for much lower inlet methane concentrations.

During stable, reverse-flow cyclic steady-state operation an interesting observation was made. The cyclic steady-state temperature profile along the monolith is shown in Fig. 9. It is clearly visible from plots in Fig. 9 that in the cyclic steady state the temperature profiles in the reactor are asymmetric. This is an experimental proof of the theoretical findings of Rehacek et al. (1992) concerning intensive heat losses through the wall. They suggested that “gradually heat begins to accumulate at one side of the reactor and the profiles appear to approach the unsymmetrical stationary ones”. The same was observed in simulations presented by Gosiewski and Warmuzinski (2002, 2007), where for intensive central cooling similar asymmetric profiles were obtained.

6. Simulation studies

In order to evaluate the operating parameters for a larger scale reactor simulations were performed employing the experimental kinetic data. The calculations were done for a TFRR with a 40 s half-cycle, a 1 m long pelletized bed and at a feed flow rate of 30,000 m³(STP)/h i.e. for the parameters similar

![Temperature profile graph](image-url)
to those which characterised the catalytic reverse-flow reactor analyzed by Gosiewski (2005). Basic parameters used in simulations are given in Table 3. They correspond to a pilot-scale reactor which was analysed in the CFRR simulation study within a European Project (2003). For the present TFRR simulations a similar scale of the combustor was assumed. The model was generally the same as for the CFRR (see Section 2) but with an assumption that the length of the catalyst section is equal to zero.

The simulations show that for an inlet concentration of 0.63 vol% the maximum temperature slightly exceeds 1100 °C, whereas the conversion of methane approaches 100%. The simulated temperature profiles in the reactor are shown in Fig. 10.

The efficiency of heat recovery for the case simulated was estimated to exceed 48%. The heat recovery can thus be expected to be higher than for the CFRR with the palladium catalyst (cf. the plot in Fig. 2b).

However, as shown by Gosiewski et al. (2006, 2007), simulation results depend on a kinetic equation used. Unfortunately, kinetic equations available in the literature for the homogeneous oxidation described by the global reaction (2) exhibit excessive differences in both pre-exponential factor $k_0$ and activation energy $E$. Thus, if the parameters depend on the combustor packing one should use an equation estimated for conditions similar to those existing in the reactor simulated. On the other hand, the simulations carried out for various kinetic equations reveal that either the maximum temperature (always below 1200 °C) or the overall conversion (approaching 100%) in such a reactor is acceptable from the practical standpoint. Since the operating temperature range of the TFRR is of great importance in process design, one should rely upon experiments on a reasonable scale rather than on purely numerical simulations, although they can always be helpful in process development.

7. Summary and conclusions

The preliminary study of the homogeneous, thermal combustion of lean methane mixtures shows that the TFRR technology can be fully competitive to catalytic combustion in the CFRR. It can be expected that complete thermal combustion will be obtained at reasonable operating temperatures. Complete combustion can be expected above 750 °C, but heat accumulation in the reverse-flow reactor leads to a much higher maximum temperature. However, for optimized process parameters the maximum temperature for the combustion of coal mine ventilation air will not exceed 1200 °C (i.e. about 400 °C higher than for the CFRR with the Pd catalyst). Such a temperature is still acceptable from the standpoint of the formation of NOx.

Wrong way behaviour in the TFRR is generally more likely than in the CFRR due to the stronger temperature dependency of the homogeneous reactions. This could be a disadvantage of the TFRR vs CFRR. On the other hand, it is also important to equip the two types of reactor with a control system able to protect them either against extinguishing when CH4 concentration is very low or against too high a temperature when the

Table 3
Basic parameter values used in the calculations of the TFRR

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Gas flowrate</td>
<td>30,000 m$^3$(STP)/h</td>
</tr>
<tr>
<td>Proportion of the hot gas withdrawn</td>
<td>7%</td>
</tr>
<tr>
<td>Inlet temperature</td>
<td>293.15 K (20 °C)</td>
</tr>
<tr>
<td>Methane concentration in ventilation air</td>
<td>0.63 vol%</td>
</tr>
<tr>
<td>Height of the inert bed (ceramic)</td>
<td>2 x 0.5 m</td>
</tr>
<tr>
<td>Raschig rings 25 x 25 x 19 mm</td>
<td></td>
</tr>
<tr>
<td>Superficial velocity in the reactor (STP)</td>
<td>0.3 m/s</td>
</tr>
<tr>
<td>Reactor diameter</td>
<td>5.9 m</td>
</tr>
<tr>
<td>Duration of the half-cycle of flow reversal</td>
<td>40 s</td>
</tr>
</tbody>
</table>

Fig. 10. Simulated temperature profiles in the pelletized-bed TFRR in a cyclic steady state for an inlet methane concentration of 0.63 vol%.
concentration is high. At present, it is too early for us to suggest any detailed solutions. The present study is to be continued for larger gas flow rates (200–400 m³/h (STP)). Research will first be carried out in our large-scale laboratory, and then this TFRR will be fed with real ventilation air withdrawn from a coal-mine ventilation shaft.

The choice between the CFRR and TFRR needs a reliable cost analysis. It can be expected that further studies on a larger scale will make it possible to carry out more reliable cost estimations. The basic question is whether the cost of more expensive materials of construction for the TFRR does not exceed the cost of the expensive catalyst in the CFRR. On the other hand, the analysis should take into account the fact that due to higher temperatures of the hot gas withdrawn from the TFRR the efficiency of heat recovery should also be higher.

The kinetic results obtained in the present study for only two cases (spheres and monolith) do not make it possible to draw any general conclusions. Although in packed beds or monoliths the combustion rates will probably differ, the difference will not be large. Kinetic equations can be used in simulations with caution, due to practical impossibility of maintaining isothermal combustion in kinetic experiments. Thus, it seems reasonable to determine the actual, experimental kinetics for each type of the reactor packing and conditions of the combustion.

### Notation

- **a**: exponent for fuel (methane) concentration in the kinetic equation
- **b**: exponent for oxidizer (oxygen) concentration in the kinetic equation
- **C_CH₄**: methane concentration, mol m⁻³
- **E**: activation energy, kJ mol⁻¹
- **k₀**: pre-exponential factor in the rate equation mol⁻¹m⁻³s⁻¹
- **k(T)**: reaction rate constant, mol⁻¹m⁻³s⁻¹
- **L_comb**: length of combustion zone, cm
- **n**: exponent for temperature in the kinetic equation
- **r_hom**: rate of thermal combustion of methane, mol m⁻³s⁻¹
- **R**: gas constant, kJ mol⁻¹K⁻¹
- **t**: time, s
- **t_c**: half-cycle time, s
- **T**: temperature, K or °C
- **T_average**: average temperature in the “combustion zone”
- **T_outlet**: outlet temperature averaged over a full reversal cycle, °C
- **T_ign**: ignition temperature, °C
- **T_inlet**: inlet temperature °C

### Greek letters

- **α**: thermal efficiency defined by formula (6)
- **ΔT_ad**: adiabatic temperature rise in the reactor, °C
- **ΔT_exp**: experimental temperature rise in the reactor, °C

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### References


