

1           **Combustion of coal mine ventilation air methane in a**  
2           **regenerative combustor with integrated adsorption: reactor**  
3           **design and optimization**

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9  
10 **Abstract**

11 Coal mine ventilation air methane is an important environmental concern due to its  
12 contribution to global warming. Catalytic combustion in reverse flow reactors is an efficient  
13 treatment technique, but high emission moistures lead to catalyst inhibition. To overcome this  
14 issue a novel reverse flow reactor with integrated water adsorption has been proposed.

15 In this work, the design of a reverse flow reactor adequate to treat a typical real coal  
16 ventilation stream, 45 m<sup>3</sup>/s with 0.30% (mol) methane and 5% (mol) water, has been studied.

17 The performance of the reactor design has been simulated using a 1D heterogeneous dynamic  
18 model, previously validated with experimental results. Particular attention has been paid to  
19 reactor stability when water and methane feed concentration change upon time. Real coal  
20 mine ventilation air data have been used to produce realistic simulations. The optimization of  
21 the operating conditions (surface velocity and switching time) has been carried out based on  
22 the total cost of the reactor (considering fixed capital and 10-year variable cost).

23  
24 **Keywords:** regenerative catalytic oxidizer; hybrid reactor; methane combustion; water  
25 inhibition; reverse flow reactor; dynamic modelling.

# 1. Introduction

In the last decades, environmental issues related to global warming have gained importance. Methane is considered a major contributor to global warming (second in importance, after carbon dioxide), with global atmospheric concentrations raising from a pre-industrial value of about 0.7 up to 1.8 ppm in 2014 [1]. The main anthropogenic sources of methane are coal mines, landfills, natural gas distribution systems, sewage systems, etc. [2]. It is well known that the global warming potential of methane is 25 times greater than that of carbon dioxide, and for this reason the combustion of methane to carbon dioxide before releasing to the atmosphere is environmentally beneficial, as it reduces greatly the net warming potential of the emissions [3].

Coal mining has an important negative impact in relation to greenhouse emissions, because important amounts of methane (concentration 0.1 to 1%) are released to the atmosphere during coal extraction [4]. Thus, ventilation air methane represents the main contribution (approximately 78%) to the carbon footprint of the coal mining activity [5].

Catalytic combustion is a very interesting alternative for the treatment of these emissions [6], because of its low energy consumption (especially if compared with thermal oxidation) and the negligible formation of noxious by-products, such as thermal NO<sub>x</sub> [7]. An appropriate option for the treatment of coal mine ventilation air methane is the use of regenerative catalytic oxidation (RCO) in a reverse flow reactor [8].

Reverse flow reactors (RFR) consist of a catalytic fixed bed reactor in which the feed flow direction is periodically reversed [9]. By selecting the appropriate switching time ( $t_{sw}$ ), defined as the time elapsed between two consecutive flow reversals, a great amount of the heat released in the reaction can be stored inside the reactor in consecutive cycles, and therefore autothermal operation (e.g. without the addition of external heat or fuel) can be possible even

1 for very low concentration of hydrocarbons (1500 ppm methane) [10]. For higher hydrocarbon  
2 concentration, the energy released by the reaction can be also recovered [11].

3 The RFR potential advantages are a consequence of its forced unsteady state operation [12].  
4 However, this can also be a drawback from the stability point of view, i.e. maintaining ignited  
5 operation under disturbances in flow rate or concentration. For example, if the feed is too  
6 lean, there is a risk of extinction, because the amount of heat released by the reaction is very  
7 low; in these situations the RFR heat regeneration capacity is crucial to maintain autothermal  
8 operation [13]. Under rich feed conditions, the heat released and accumulated in the reactor  
9 can result in too high bed temperatures, with the risk of causing catalyst thermal deactivation  
10 [14]. This issue has limited the industrial use of this type of reactors, and encouraged research  
11 in the development of suitable control systems [15].

12 The performance of the catalyst can be affected by the presence of other compounds,  
13 different from methane, in the ventilation air [16]. Water is usually present in high amounts  
14 (nearly at the saturation point), and it is well-known that water has a negative effect on the  
15 activity of supported precious metal catalysts [17]. Palladium catalysts on various supports, the  
16 most active for methane oxidation, have been studied by different authors with a general  
17 agreement in the existence of a reversible inhibitory effect of water [18]. This inhibition  
18 reduces the relative stability of the reverse flow reactor, and to overcome this, the reactor  
19 must be oversized, with the corresponding increase in purchase and operation costs.

20 One solution to avoid the decrease in catalyst activity caused by water is the use of a reverse  
21 flow reactor with integrated adsorption. Such a device, proposed by Bos et al. [19], consists of  
22 a reverse flow reactor in which the inert beds are replaced, at least partially, by an appropriate  
23 adsorbent material [20]. Thus, the water of the feed is retained in these adsorbent beds before  
24 reaching the central catalytic bed [21]. The adsorbent is regenerated in situ, because of the  
25 parabolic temperature profile that develops in reverse flow reactors, with high temperature in

1 the middle and low temperature at the sides. The temperature profile is not static, but moves  
2 in the direction of the flow, and produces a displacement of heat from the centre to the sides  
3 of the reactor. Thus, while feed water is being adsorbed at low temperature in the first  
4 adsorbent bed (in the corresponding direction of the flow), the water adsorbed in the previous  
5 cycle desorbs at a higher temperature from the adsorbent bed placed in the opposite side of  
6 the reactor.

7 The working principle of the reverse flow reactor with integrated adsorption was  
8 experimentally demonstrated in a previous work for methane oxidation in a bench-scale  
9 device [22]. In the same work, a mathematical model to simulate the behaviour of this reactor  
10 was proposed. This model accurately predicted the experimental results.

11 The aim of the present work is to apply all this knowledge on reverse flow reactors with  
12 integrated adsorption to the design and optimization of commercial scale devices for the  
13 treatment of methane emissions from coal mines. The scope of the work is summarized as  
14 follows. Firstly, emissions of methane from different coal mines are analysed to determine  
15 representative average methane and water concentrations. Then, a reverse flow reactor with  
16 integrated adsorption is specifically designed to deal with this emission. The performance of  
17 the proposed design is tested by means of simulations for different feed water concentrations.  
18 Then, the capacity of the reactor to deal with disturbances in the feed (e.g. methane  
19 concentration) is also evaluated. Finally the influence of operational conditions on the total  
20 cost is studied and the cost is optimised.

21

## 1 **2. Materials and methods**

### 2 **2.1. Reverse flow reactor model**

3 A mathematical model for reverse flow reactors should predict the dynamic evolution of  
4 concentration and temperature profiles. Phenomenological models based on mass and energy  
5 conservation equations have been found to simulate RFRs with good results [23]. In the  
6 context of a previous work, a 1D heterogeneous model was proposed and validated for the  
7 case of a reverse flow reactor with integrated adsorption [22]. Table 1 shows the set of partial  
8 differential equations corresponding to this model. These equations were obtained from  
9 conservation equations (mass and energy) applied separately to the gas and solid phases. Gas  
10 and solid mass balances are valid for both compounds, methane and water.

11 The mass and energy balances to the gas phase (equations of  $c_i$  and  $T_G$ ) accounts for the  
12 following terms (in the order of appearance in the equation): accumulation, convective flow,  
13 dispersion and mass or heat transfer from/to the solid phase. The gas phase non-catalytic  
14 combustion of methane is not included in the model, being negligible compared to catalytic  
15 combustion at the operating temperature of the reactor. The change in velocity due to density  
16 is accounted for by means of the continuity equation:  $v = v_0 \rho_{G0}/\rho_G$ , where  $\rho_G = pM/RT_G$ .  
17 Ideal gas law behaviour has been assumed.

18 The mass and energy balances to the solid phase (equations of  $n_i$  and  $T_S$ ) consider the  
19 accumulation in the solid, dispersion (only for the energy balance), mass or heat transfer  
20 from/to the gas phase and reaction terms.

21 The resolution of the partial differential equations of the model requires a given set of initial  
22 and boundary conditions, shown in Table 2. The switch of the feed flow direction is modelled  
23 by shifting the boundary conditions at both sides of the reactor. The model has been solved

1 using the 'method of lines' programmed as a MATLAB code. This method, proved to be  
2 accurate in previous works [24], consists of approximating the space derivatives in a mesh of  
3 400 nodes by finite differences obtained from Taylor polynomials. This number of nodes was  
4 found enough to provide a grid-independent solution. The resulting set of ordinary differential  
5 equations (with only one independent variable: time) is solved using a specific MATLAB  
6 function for stiff problems ("*ode15s*" function).

7 The physical, chemical and transport properties appearing in the equations of Table 1 must be  
8 specified to solve the model. Table 3 shows the geometrical and physical properties of the  
9 catalytic and adsorbent beds [22], while Table 4 summarizes the expressions used to calculate  
10 the chemical and transport properties. The catalytic bed considered is formed by blocks of a  
11 commercial monolith of 390 cpsi (cells per square inch) and square channels of  $10^{-3}$  m side.  
12 The channel walls are covered by a washcoating layer (volume fraction,  $f_w = 26\%$ ) of average  
13 thickness,  $L_w = 76 \times 10^{-6}$  m. The washcoating is porous (internal porosity,  $\epsilon_{int} = 0.16$ , and  
14 average pore size,  $d_{pore} = 12 \times 10^{-9}$  m) and is impregnated with the palladium active phase.  
15 Intrinsic reaction rate of methane oxidation was measured in the laboratory in a previous work  
16 and fitted to a Langmuir-Hinshelwood model capable of predicting catalyst inhibition caused  
17 by water (Table 4) [25]. Mass transfer inside the washcoating layer is taken into account by  
18 means of the internal effectiveness factor ( $\eta$ ) and Thiele modulus ( $\phi$ ), which is calculated from  
19 the above-mentioned textural properties of the washcoating. Gas to solid mass and heat  
20 transport and axial dispersion are estimated using correlations from the literature specific for  
21 monoliths at laminar conditions (Table 4) [26].

22 The adsorbent bed consists of a random particles,  $\gamma$ -alumina pellets of 4 mm diameter. The  
23 adequacy of this adsorbent material was assessed in a previous work [22]. Its adsorption  
24 capacity was experimentally measured and equilibrium data fitted to a Freundlich model  
25 (Table 4). This model is used to calculate the gas concentration of water in the solid-gas

1 interphase. Mass transfer, experimentally found to play an important role in the adsorption of  
2 water, was modelled using the linear driving force model. The global mass transfer coefficient  
3 ( $K_C$ ), which accounts for mass transfer external and internal to the particles, was measured  
4 experimentally and correlated with temperature (Table 4). Gas to solid heat transport and axial  
5 dispersion are estimated using correlations from the literature, specific for packed beds (Table  
6 4) [26].

7 The physical properties of the gas have been considered equivalent to those of air and  
8 calculated using temperature-dependent expressions from the literature [27].

9

10

### 11 **3. Results and discussion**

#### 12 **3.1. Coal mine ventilation air emissions**

13 In subterranean coal mining, methane must be diluted in the working area down to safety  
14 constraints. This is accomplished by the use of large axial fans that flows fresh air through the  
15 shaft, diluting the methane released during the mining activities. The lower explosive limit of  
16 methane in air is 5%, but methane concentration is usually reduced below 1%. The exhaust of  
17 the fans can contain other compounds, such as carbon dioxide, and trace amounts of hydrogen  
18 sulphide or sulphur dioxide. The amount emitted depends on the coal rank and depth of seam.  
19 For example, high-rank coals, such as anthracite, produce the highest methane emissions [2].

20 The composition of the ventilation air of different coal mines from Asturias (northwest Spain)  
21 has been measured experimentally, and the results are summarized in Table 5. No sulphur  
22 compounds were found in the exhaust [5]. The time-averaged methane concentration was  
23 found to range from 0.18 to 0.40%, depending on the mine site [5]. Methane concentration is  
24 not constant with time, and varies according to other factors, with atmospheric pressure being

1 the most important. Variations in methane concentration are illustrated in Figure 2 for mine  
2 site 1 and a monitoring period of 70 days, shown as an example. Methane concentration varies  
3 mostly within the range 0.25 % to 0.50 %, with average methane concentration 0.39 % (mol).  
4 Water concentration in the ventilation air was found to greatly depend of ambient conditions.  
5 For this reason, the range of variation for the different mine sites is reported in Table 5,  
6 instead of the time-averaged value. As a general trend for all mine sites, water concentration  
7 varies within the range 2 to 5 % (mol).

8

### 9 **3.2. Design of a reverse flow reactor**

10 A reverse flow reactor will be designed to treat the ventilation air of mine site 1 (Table 5),  
11 considered representative of the coal mines of the Asturian region (Spain). The design is based  
12 on a total gas flow of 45 m<sup>3</sup>/s at 1 atm and 25°C, with a nominal methane concentration of  
13 0.30% (mol). As shown in Figure 2, this nominal concentration value is close to the lower  
14 concentration limit (0.25%) reported for this mine site. For the so called “base design” of the  
15 reactor, the feed will be considered to be free of water, and the reactor designed consists of a  
16 central catalytic bed and two heat-regeneration beds. A sketch of the reactor is shown in  
17 Figure 1. The design of the reactor with integrated adsorption is addressed in Section 3.3.

18 The reverse flow reactor will be designed to maintain stable operation with high conversion  
19 (99.9%) for the nominal concentration of 0.30% (vol.) methane. However, methane  
20 concentration varies with time, so the dynamic response of the reactor to these variations will  
21 be also studied afterwards. The design of the reactor involves calculating the total reactor  
22 length and diameter, and the length of the different beds of the reactor.



1 The catalytic bed consists of palladium-based monolithic blocks with a cell density of 390 cpsi  
2 (cell per square inch). This type of bed has two important advantages for the present case: low  
3 pressure drop at high gas flow rates, and reduction of diffusional resistances for the catalytic  
4 reaction. The latter is particularly important for fast reactions and catalysts based on precious  
5 metals, as the present case, because the precious metal is deposited only in a thin porous  
6 washcoating layer, so the reactants diffusion path is lower when compared to particulate  
7 catalyst, and the active phase is more effectively used [26].

8 The heat-regeneration beds consist of  $\gamma$ -alumina pellets of  $4 \times 10^{-3}$  m (this material will act also  
9 as adsorbent in Section 3.3). Random particle beds have higher pressure drop than monolithic  
10 beds, but in our opinion the advantages when used in the reverse flow reactor with integrated  
11 adsorption are more important. Unlike the catalyst, there are not expensive active phase  
12 dispersed in the adsorbent particles, so when diffusional limitations are important, there is not  
13 expensive precious metal unused in the inside of the pellet. The adsorbent must present a high  
14 adsorption capacity to prevent premature saturation of the adsorbent bed, and this is  
15 obtained with random particle beds. Another important advantage of random particle beds is  
16 their higher thermal inertia, which results in more efficient heat storage between cycle, and  
17 hence reactor stability [28].

18 The geometrical and physical properties of catalytic and inert beds were measured  
19 experimentally or taken from the literature, as summarized in Table 3 and 4.

20 Switching time ( $t_{sw}$ ) is an important variable that affects the behaviour of the reactor. This  
21 parameter can be adjusted during operation to control the reactor (e.g. to avoid extinction or  
22 overheating). For the design of the reactor (reactor dimensions), an appropriate nominal  
23 switching time value is selected. When selecting switching time it should be considered that  
24 lower switching time decrease the required reactor size, but on the other hand, the  
25 contribution of the wash-out effect increases, and the lifespan of the valves and the flexibility

1 of the control system decrease. In the present work, and according to our experience, a value  
2 of  $t_{sw} = 240$  s is chosen, considered a good balance between these factors [29]. This value will  
3 be optimized in section 3.5 according to an economic optimization.

4 The procedure for the model-based design of reverse flow reactors has been discussed and  
5 validated elsewhere [30]. The steps of the procedure are summarised as follows. First, a  
6 superficial velocity value is selected; this is required because reactor length, diameter and  
7 superficial velocity are not independent (one must be set to calculate the others). The value of  
8 1 m/s was found to be appropriate in a previous work [30], but its influence will be studied in  
9 detail in section 3.5, in the scope of an economic optimization. Second, the reactor cross  
10 section diameter (circular section) or side (square section) is calculated for the actual gas flow  
11 rate (45 m<sup>3</sup>/s): in this case, 7.57 m and 6.71 m, respectively. Third, the reactor length required  
12 to achieve 99.9% conversion is determined using the reactor mathematical model  
13 (methodology section). This cannot be done directly because the reactor length is an implicit  
14 variable that must be supplied to solve the model. Hence, the reactor length is determined by  
15 trial and error, simulating the reactor up to the pseudo-steady state for different lengths, until  
16 the desired 99.9% conversion is achieved. At this stage, all the reactor bed is considered to be  
17 catalytic. Following this procedure, a reactor length of 1.52 m was determined.

18 Finally, the last design parameter of the reactor is the length of the catalytic bed (once  
19 determined, the length of the adsorbent beds can be easily calculated from the total bed  
20 length). In reverse flow reactors, all the catalyst at temperature below the ignition  
21 temperature of the hydrocarbon/air mixture should be replaced by cheaper inert material (in  
22 the present work by an adsorbent material) [10]. The ignition temperature of methane in our  
23 catalyst is around 350°C, so the boundaries of the catalytic bed are directly determined from  
24 the simulated temperature profile at the middle of a cycle. Hence, the required length for  
25 central catalytic bed is 0.49 m, corresponding to a fraction of catalytic bed of 32%; the length

1 of the adsorbent beds situated at both sides of the reactor is 0.52 m each. The reactor  
2 equipped with these inert beds has been simulated to check all the constraints used in the  
3 design are fulfilled. The results of the simulation are summarized in Figure 3.

4 The simulated temperature and methane concentration profiles of Figure 3 clearly show the  
5 displacement of heat and concentration fronts inside the reactor. The catalytic bed is  
6 maintained at high temperature during a cycle, which results in high methane conversion and  
7 prevents the extinction of the reactor. In the adsorbent beds, the difference between the  
8 temperature profile at the beginning and end of cycle is an indication of the amount of heat  
9 stored in the bed. As shown in Figure 3, this difference is large, which is due to the high energy  
10 efficiency of the designed reactor.

11

### 12 **3.3. Design of the integrated adsorption**

13 In the reactor designed in Section 3.2, the influence of the feed moisture on the combustion  
14 has not been taken into account, as water is supposed to be separated in the adsorbent beds  
15 before reaching the catalytic bed. The design of the integrated adsorption consists of  
16 calculating the minimum length of adsorbent required to accomplish this at the reverse flow  
17 reactor operating conditions (mainly temperature profile). This has been done by simulating  
18 the reverse flow reactor designed in the previous section, fed with a ventilation air containing  
19 the same methane 0.30% (mol), and in addition 5% (mol) water. This water concentration is  
20 the highest registered during the monitoring of the ventilation air.

21 The evolution of water concentration profiles in gas and solid at the pseudo-steady state are  
22 depicted in Figure 4. It can be observed that the adsorbent bed captures the water from the  
23 gas in a small part of the bed situated close to the reactor inlet. This part of the bed has the  
24 lower temperature, and hence the highest adsorption capacity. Regarding the water

1 concentration profiles in the solid, it should be noted that at the beginning of the cycle the bed  
2 contains some adsorbed water from previous cycles. Desorption takes place when the flow is  
3 reversed and the high temperature wave from the centre of the reactor moves to the  
4 adsorbent bed, but complete water desorption does not occur at these operating conditions.  
5 The effective capacity of the adsorbent is the difference between the solid concentration  
6 profiles at the end and beginning of cycle.

7 Figure 5 shows the evolution of water concentration in the gas effluent at pseudo-steady state  
8 conditions. At the beginning of a cycle, the concentration is the highest, because water is being  
9 desorbing from an adsorbent with high water concentration (from the previous cycle). The  
10 effluent concentration decreases upon time, and close to the end of the cycle a marked  
11 decreased is observed, indicating that the adsorbent bed is approaching depletion. Although  
12 water desorption has not been complete, the degree of regeneration of the adsorbent is high  
13 enough as to deplete water from the feed in the next cycle.

14 The performance of the integrated adsorption has also been evaluated for different water feed  
15 concentrations in the range 2-5% (mol). The gas and solid water concentration profiles of the  
16 inert beds at the end of a cycle are depicted in Figure 6. These are the profiles just before the  
17 flow is reversed, and hence correspond to the maximum displacement of water in the  
18 adsorbent bed. When water feed concentration increases from 2 to 5% (mol), the adsorption  
19 equilibrium concentration increases from 7.5 to 11.7 mol/kg, as shown in Figure 6b., and more  
20 water can be retained by the adsorbent. However, the higher water feed concentration  
21 produces a displacement of the concentration profiles, which is nearly proportional to the  
22 increase in feed concentration. The minimum lengths of adsorbent bed required to adsorb all  
23 the feed water are 0.060, 0.071, 0.081 and 0.097 m, respectively for 2, 3, 4 and 5% (mol),  
24 respectively. Figure 6 also shows the profiles in the second adsorbent bed (BED2), where in  
25 this cycle desorption is taking place. The solid profiles are particularly interesting, showing the

1 adsorbed water that does not desorb between cycles. The behaviour is inherent to every  
2 temperature-swing adsorption processes, and its consideration is very important in order to  
3 not underestimate the required amount of adsorbent.

4 It can be concluded that in the present reactor design and conditions, at least 0.1 m of  
5 adsorbent is required in each inert bed to separate the water from the ventilation air (2-5%). In  
6 the remaining inert bed (0.42 m each), the adsorbent can be replaced by a cheaper inert  
7 material with thermal properties more suited for regenerative devices. In this context, a  
8 material of high thermal inertia,  $\rho_S(1 - \epsilon_b)C_{PS}$ , is advised (at least more than  $700 \text{ kJ/m}^3_{\text{bed}} \text{ K}$ ).

9

#### 10 **3.4. Analysis of the reactor stability**

11 The reactor stability can be affected by changes in feed conditions, such as gas flow rate and  
12 methane and water concentration, or operational parameters, like switching time. In the  
13 previous section, it was demonstrated that the integrated adsorption system is capable of  
14 separating water within the concentration range typically found in coal mine ventilation air  
15 flows. The air flow rate is directly related to the power and performance of the fan that  
16 propels the air, and the fan is usually operated at constant nominal conditions. For this reason,  
17 no important fluctuations in the flow rate are expected. Hence, this section is devoted to  
18 analyse the capacity of the designed reverse flow reactor to cope with disturbances in  
19 methane feed concentration, which have been observed experimentally in real emissions, and  
20 are directly related to the reactor thermal behaviour and stability.

21 First, the influence of a step decrease in methane concentration has been considered.

22 Temperature and methane concentration profiles at the middle of cycle are depicted in Figure  
23 7. Initially, the reactor was simulated up to the pseudo-steady state at 0.30% vol. methane (the  
24 concentration used in the reactor design). Then, concentration was decreased to 0.27% for 16

1 min (4 cycles). This disturbance produces a clear decrease in the reactor temperature, related  
2 to the lower amount of heat released by the reaction. However, this decrease in temperature  
3 is not critical, and the reactor remains stable with high methane conversion, as observed in the  
4 concentration profile. Finally, the concentration was increased back to 0.30% methane. The  
5 reactor temperature exhibits a sudden increase to the initial temperature profile. This  
6 indicates that, within a certain margin, changes in concentration do not produce a permanent  
7 effect in the performance of the reactor, and the reactor does not extinguish.

8 The reactor performance was studied simulating its response to a real evolution of methane  
9 concentration in a coal mine ventilation air was. Figure 8 shows the evolution of methane  
10 concentration in the ventilation air, with an average value of 0.30% (vol.) methane and positive  
11 and negative variations within the range  $\pm 0.05\%$ . The corresponding reactor outlet methane  
12 concentration obtained by simulation is depicted in the same figure. It is clearly observed that  
13 the reactor is capable of operating at stable conditions with high conversion under these real  
14 feed disturbances. Temperature and methane concentration profiles are presented in Figure 9,  
15 where different situations, representative of high and low methane feed concentrations, are  
16 considered. Thus, it can be seen that the temperature profile moves in the vertical direction,  
17 with a maximum within the range 485-528°C. This temperature range is adequate, because it  
18 is below the catalyst overheating limit and above the reaction extinction limit.

19 It can be concluded that, in the conditions studied, representative of the treatment of real coal  
20 ventilation streams, the operation of the reverse flow reactor is efficient and stable, being able  
21 of responding to disturbances in methane feed concentration. It is advisable to design the  
22 reactor for the average methane concentration, and then test by means of simulations the  
23 capability of this design to maintain stable operation for typical concentration disturbances  
24 present in the emission.

1 When the magnitude of disturbances can produce reactor extinction or overheating, the use of  
2 a control system is recommended. In this case, the reactor can be designed to maintain stable  
3 operation for the lowest methane feed concentration. Then, the control system is designed to  
4 deal with high methane concentration disturbances, avoiding overheating. Many different  
5 control strategies have been proposed and tested for reverse flow reactors [31].

6

### 7 **3.5. Economic optimisation of the reverse flow reactor with integrated adsorption**

8 The cost is a very important factor to consider when a new reactor is going to be implemented.  
9 Given that, this reverse flow reactor with integrated adsorption is a new and innovative  
10 approach in this subject, the total cost will be optimised for the actual case from section 3.2,  
11 considering the operational conditions: switching time and gas velocity.

12 The methodology to optimise the cost is described afterwards. Firstly, a switching time and a  
13 gas velocity are chosen and the MATLAB code is used to calculate the length of the reactor and  
14 the catalytic fraction, as explained in section 3.2. Then, the cost of the reactor and also a fan  
15 required for the gas flow are calculated [32]. The fan power was calculated from an energy  
16 balance (Bernouilli equation) and considering a fan efficiency of 85%. The reactor cost was  
17 estimated considering it as a stainless steel framework. The prices for the catalyst, adsorbent  
18 and inert were provided by BASF. The Lang factorial method [32] was used to estimate the  
19 fixed capital cost of a project from the costs of the major equipment units. One of these  
20 factors estimates the cost of instrumentation, pipes and connections, while other considers  
21 the indirect costs such as contingencies, set-up and maintenance. The variable costs consist  
22 basically of the electricity consumed by the fan and the replacement of the catalyst, inert and  
23 adsorbent every five years. Deducting start-up and maintenance times, a basis of 320 days per

1 year can be used as a representative rate for a large company. The variable costs were  
2 calculate over a timeframe of 10 years.

3 The parametric analysis for the cost was carried out as follows:  $170 \leq t_{sw} \leq 390$  s and  $0.75 \leq$   
4  $v \leq 1.4$  m/s. From the practical point of view, the minimum values for the switching time and  
5 gas velocity are set to 170 s and 0.75 m/s, respectively. Figure 10 shows a contour chart where  
6 total cost in M€ has been plotted as a function of the switching time and the gas velocity. An  
7 optimal can be found for a switching time of 250 s and a gas velocity of 1.13 m/s.

8 The topology of the optimum should be taken into account to select the optimum operating  
9 conditions. Thus, the gas velocity should be fixed at  $v = 1.13$  m/s, because an optimum at this  
10 value is clearly observed. As the gas velocity decreases, the total cost exhibits an increase of  
11 50%; the same increase in the cost is observed on increasing the gas velocity to 1.26 m/s. On  
12 the contrary, the switching time produces a wider optimum at  $t_{sw} = 240$ -260 s, which means  
13 that within this range costs do not change dramatically. A recommend switching time value of  
14 240 s was found in literature [29], which is in agreement with the findings of the present  
15 economic optimization.

16 Considering an optimal case of  $v = 1.13$  m/s and  $t_{sw} = 250$  s, the reactor length would be 1.43  
17 m with a catalytic fraction of 29%. The total cost for this case would be 1.57 M€. However, if  
18 this case is re-designed without using integrated adsorption, the total cost would increase to  
19 1.77 M€. The main individual and total costs are summarized in Figure 11. When no adsorbent  
20 is used, reaction rate decreases and more catalyst is required to maintain the same  
21 conversion. Hence, the catalyst amount increases, but also the reactor framework size, as  
22 observed in Figure 11. This affects both fixed capital and 10-year variable costs. The later takes  
23 into account the replacement of the catalyst, which is an important contribution. These two  
24 costs, reactor framework and catalyst, are the two main costs of the reverse flow reactor  
25 project, and for this reason the use of adsorbent contributes to reduce the total cost in 14%.



1

## 2 **4. Conclusions**

3 The use regenerative catalytic oxidation in a novel reverse flow reactor with integrated  
4 adsorption is proposed to treat coal mine ventilation air methane emissions. The novelty of  
5 this reactor is the use of an adsorbent material to separate water from the ventilation air,  
6 where the concentration is as high as 2-5% (mol), and avoid the inhibition of the catalyst.

7 The reverse flow reactor has been designed for 45 m<sup>3</sup>/s (1 atm, 25°C) of ventilation air with  
8 0.30% (mol) of methane and 5% of water. The computer simulations have shown that the  
9 adsorbent is capable of self-regenerate in situ by means of the switch of the flow direction and  
10 the parabolic temperature profile. Thus, when one of the adsorbent beds is adsorbing the feed  
11 water, the other is being regenerated by the displacement of the high temperature of the  
12 middle of the reactor. This design has been tested against typical variations in the  
13 concentration of methane in the ventilation air of a real coal mine. The simulations shown that  
14 the reactor is affected, but does not extinguish.

15 The operating conditions of the reactor with integrated adsorption have been optimized by the  
16 minimization of the total cost (fixed capital and 10-year variable). A gas velocity of 1.13 m/s  
17 and a switching time of 240-260 s were found to be optimum.

18

## 19 **Acknowledgements**

20 This work was supported by the Research Fund for Coal and Steel of the European Union  
21 (contract UE-10-RFCS-CT-2010-00004), and by the Local Asturian Government (FC-15-  
22 GRUPIN14-078)

1

## 2 Nomenclature

3	$a$	surface to bed volume ratio ( $\text{m}^2/\text{m}^3_{\text{bed}}$ )
4	$c_i$	gas molar concentration ( $\text{mol}/\text{m}^3$ )
5	$C_P$	heat capacity ( $\text{J}/\text{kg K}$ )
6	$D_{im}$	molecular diffusion coefficient ( $\text{m}^2/\text{s}$ )
7	$D_{ax}$	axial dispersion coefficient ( $\text{m}^2/\text{s}$ )
8	$D_{ep}$	effective pore diffusion coefficient ( $\text{m}^2/\text{s}$ )
9	$D_h$	hydraulic diameter of the monolith (m)
10	$d_p$	particle diameter (m)
11	$f_w$	washcoating fraction (%)
12	$h$	gas to solid heat transfer coefficient ( $\text{W}/\text{m}^2 \text{K}$ )
13	$k$	thermal conductivity ( $\text{W}/\text{m K}$ )
14	$K_{eqi}$	water adsorption equilibrium constant ( $\text{mol}/\text{kg}_{\text{ads}})(\text{m}^3/\text{mol})^{0.5}$ )
15	$K_{inh}$	water inhibition constant ( $1/\text{Pa}$ )
16	$L_w$	washcoating size (m)
17	$K_C$	gas-solid mass transfer coefficient (m/s)
18	$k_w$	kinetic constant ( $\text{mol}/\text{kg}_{\text{cat}} \text{s Pa}$ )
19	$L_R$	reactor length (m)
20	$m$	Freundlich exponent
21	$n_i$	concentration in the solid ( $\text{mol}/\text{kg}$ )
22	Nu	Nusselt number ( $\text{Nu} = hD_h/k_G$ )
23	$p$	Pressure (Pa)
24	Pr	Prandtl number ( $\text{Pr} = C_{PG}\mu_G/k_G$ )
25	Re	Reynolds number ( $\text{Re} = D_h v \rho_G/\mu_G$ )

1	$r_i$	reaction rate (mol/kg s)
2	$R$	ideal gas constant (8.314 J/mol K)
3	$Sc$	Schmidt number ( $Sc = \mu_G/(\rho_G D_{im})$ )
4	$Sh$	Sherwood number ( $Sh = K_C D_h/D_{im}$ )
5	$t$	time (s)
6	$T$	temperature (K)
7	$T_{ph}$	pre-heating temperature (K)
8	$t_{sw}$	switching time (s)
9	$v$	gas (interstitial) velocity (m/s)
10	$y$	mole fraction (-)
11	$z$	spatial coordinate (m)
12		
13	<b>Greek symbols</b>	
14	$\epsilon_b$	bed porosity (-)
15	$\Delta H_i$	reaction enthalpy (-802.5 kJ/mol)
16	$\phi$	Thiele modulus (-)
17	$\kappa_{Gax}$	axial dispersion coefficient for the gas phase (W/m K)
18	$\eta$	internal effectiveness factor (-)
19	$\rho$	density (kg/m <sup>3</sup> )
20		
21	<b>Subscripts</b>	
22	0	inlet
23	cat	catalyst
24	G	gas
25	S	solid
26		

## 1 Caption to figures

2

3 Figure 1 Sketch of the reverse flow reactor with integrated adsorption.

4 Figure 2 Monitoring of methane concentration in the ventilation air of mine site 1.

5 Figure 3 Evolution of temperature (a) and methane concentration (b) profiles during a  
6 cycle at the pseudo-steady state: begin (—), middle (—) and end (—) of cycle. The  
7 arrow indicates the direction of the flow.

8 Figure 4 Evolution of water gas concentration (a) and water solid concentration (b) profiles  
9 during a cycle at the pseudo-steady state: begin (—), middle (—) and end (—) of  
10 cycle. Water feed mole fraction = 0.05. The arrow indicates the direction of the  
11 flow.

12 Figure 5 Evolution of water mole fraction in the effluent of the reactor.

13 Figure 6 Water gas concentration (a) and water solid concentration (b) profiles in the inert  
14 beds (BED1 and BED2) at the end of a cycle (the arrow indicates the direction of  
15 the flow). Feed water mole fraction: 0.02 (—), 0.03 (—), 0.04 (—) and 0.05 (—).

16 Figure 7 Capacity of the reverse flow reactor design to deal with disturbances in methane  
17 feed concentration. Temperature (a) and methane concentration (b) profiles  
18 (middle of cycle): pseudo-steady state at 0.30% methane (•••), after 16 min (4  
19 cycles) at 0.27% methane (—), and after other 16 min (4 cycles) another time at  
20 0.30% methane (—).

21 Figure 8 Performance of the reverse flow reactor with integrated adsorption for methane  
22 changes in a real ventilation air emission: evolution of inlet (—) and outlet (—)  
23 methane concentration. Switching time = 240 s.

24 Figure 9 Performance of the reverse flow reactor with integrated adsorption for methane  
25 changes in a real ventilation air emission: evolution of temperature (a) and

1 methane concentration (b) profiles (profiles corresponding to the middle of a  
2 cycle). Switching time = 240 s. Lines correspond to times (in min): 120 (—), 144  
3 (—), 168 (—), 192 (•••) and 216 (•••).

4 Figure 10 Optimisation of the total cost (M€) as a function of the switching time and the gas  
5 velocity for a reverse flow reactor with integrated adsorption.

6 Figure 11 Contribution of main individual costs and total costs (fixed capital and 10-yr  
7 variable) for reverse flow reactor with (■) and without (■) integrated adsorption.

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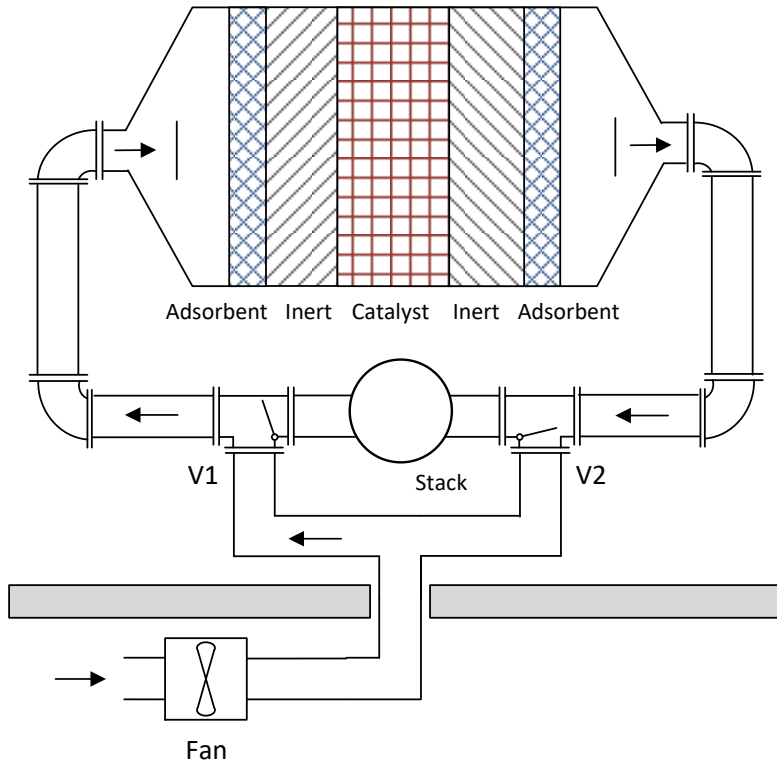
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2 Figure 1

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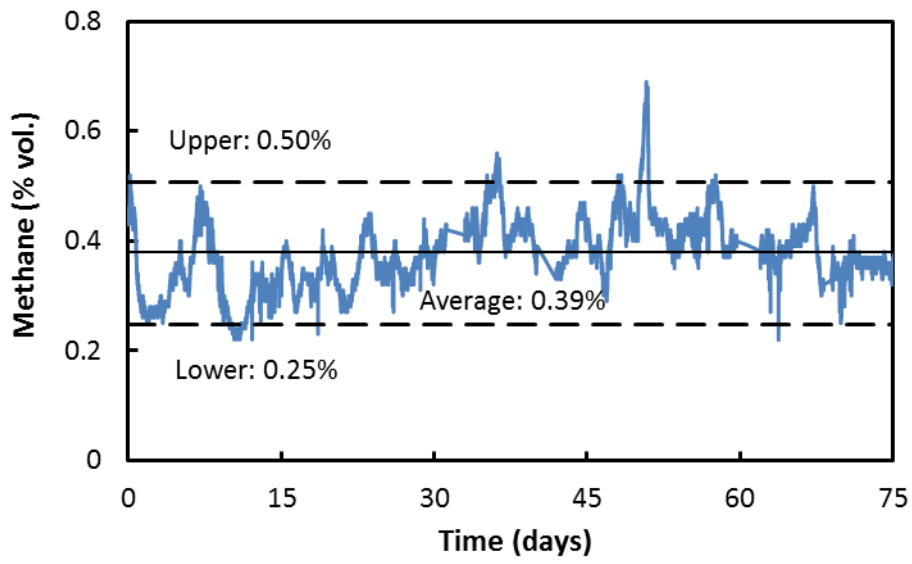
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2 Figure 2

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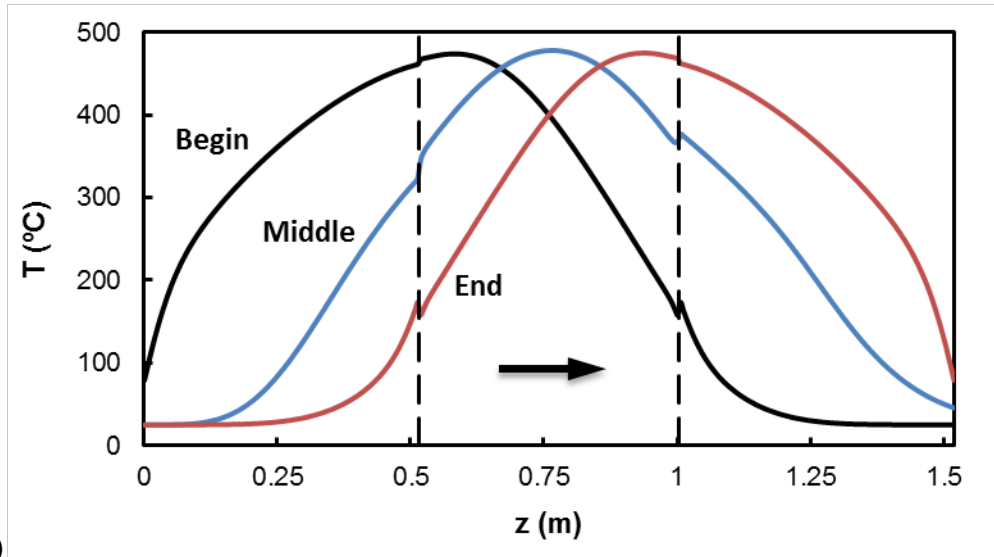
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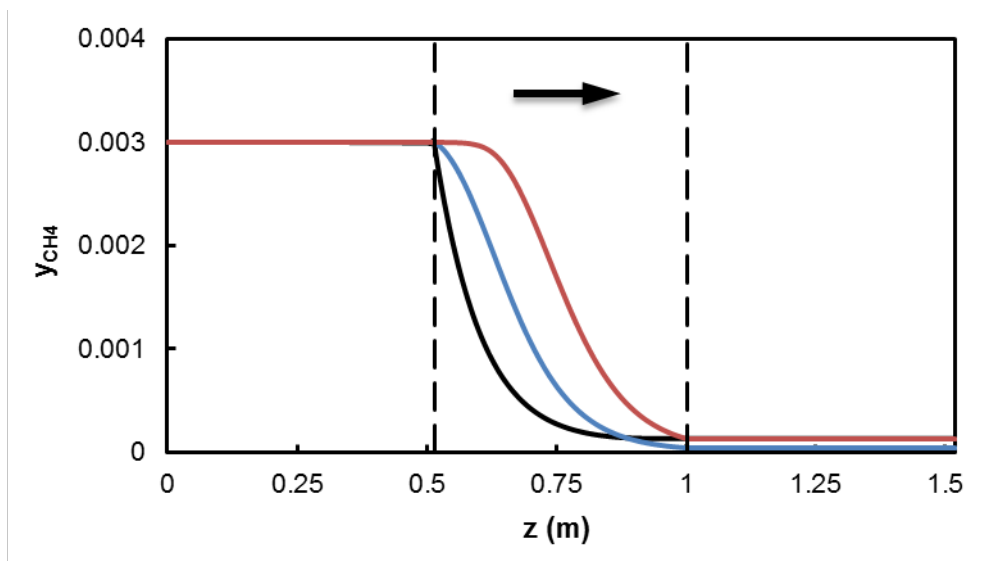
2 Figure 3

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(a)



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(b)

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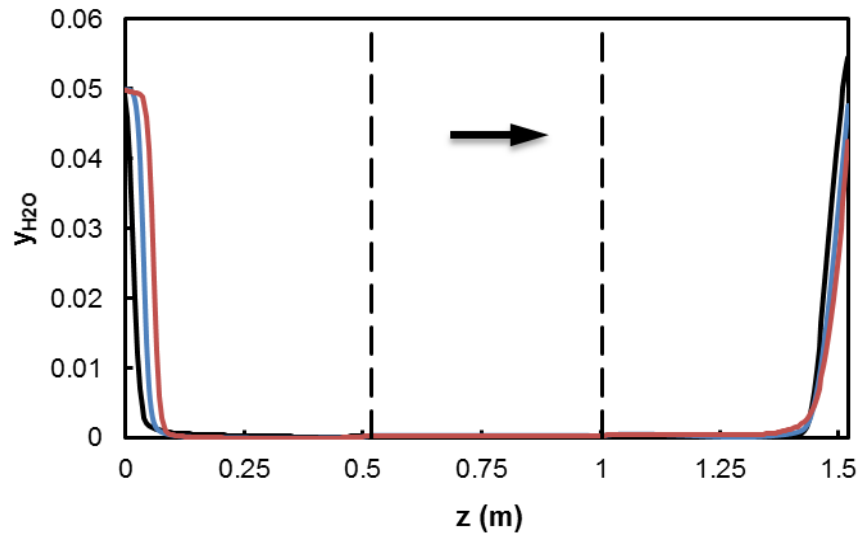


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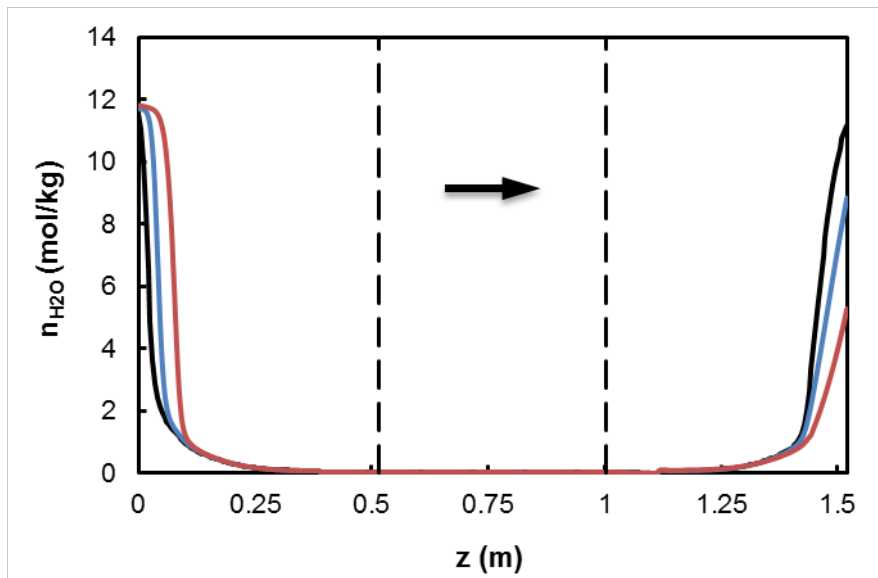
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3 Figure 4

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5 (a)



6 (b)

7

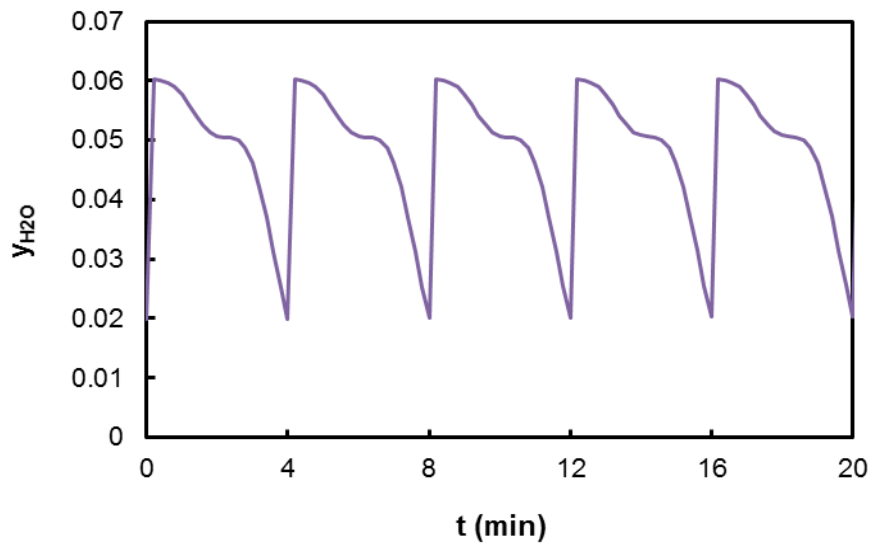
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2 Figure 5

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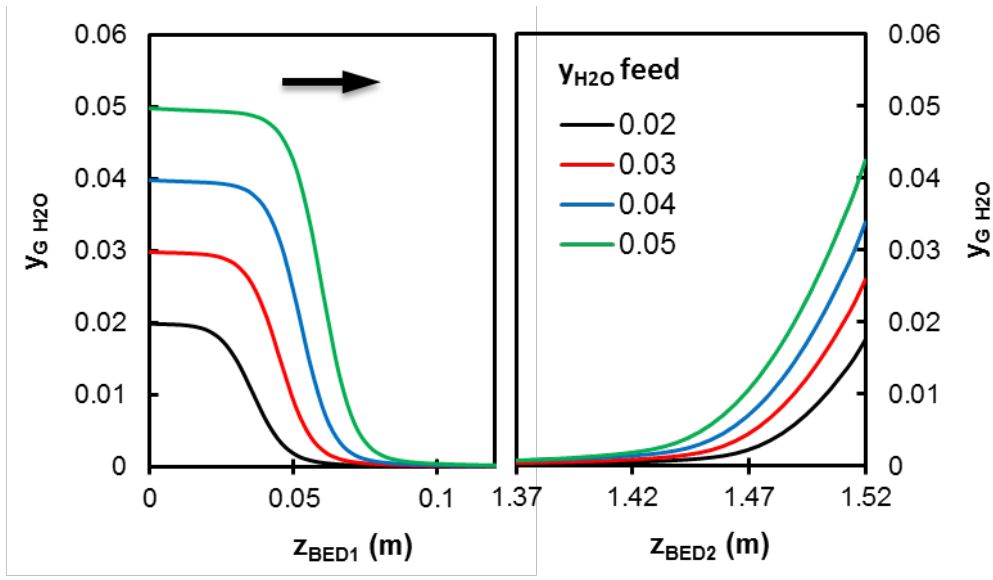
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2 Figure 6

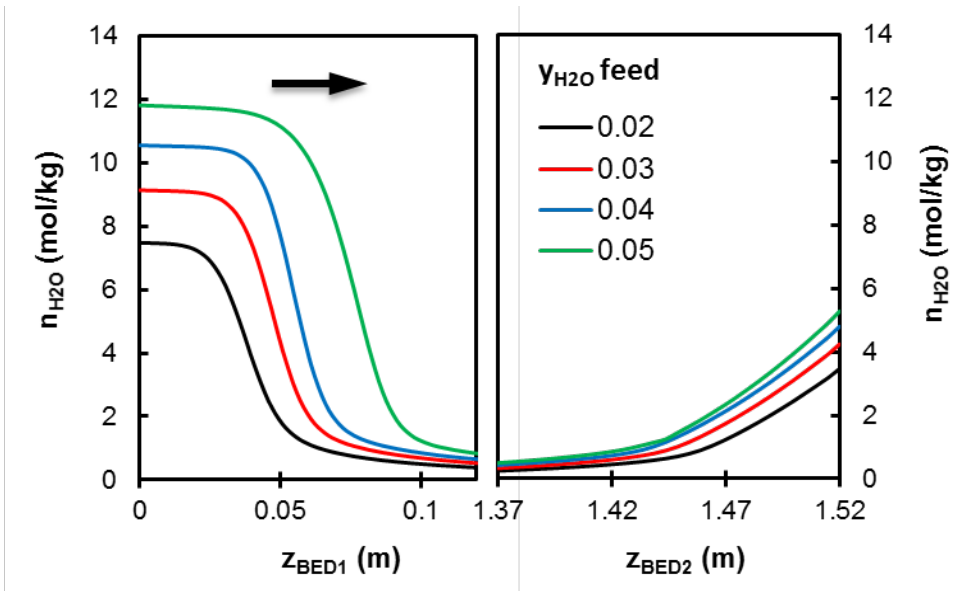
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5 (a)



6 (b)



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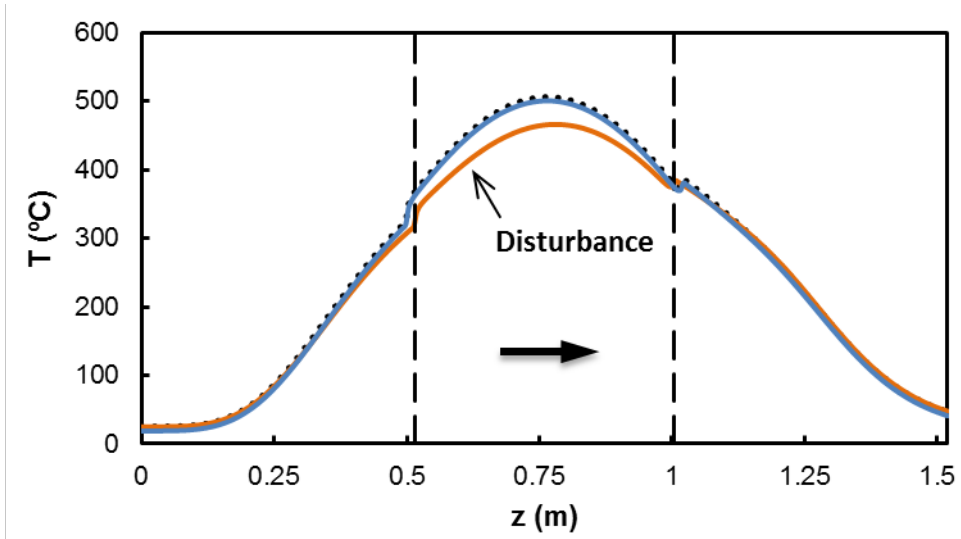
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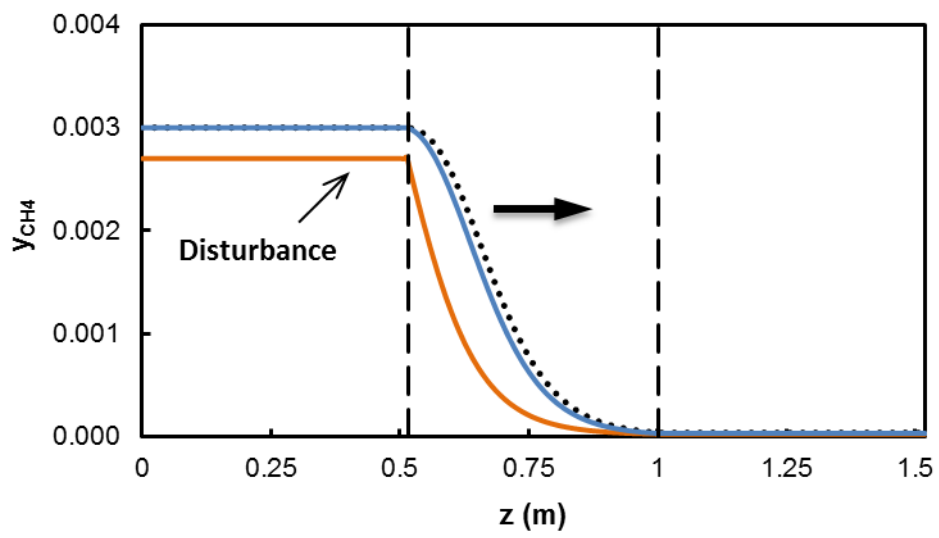
2 Figure 7

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(a)



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(b)

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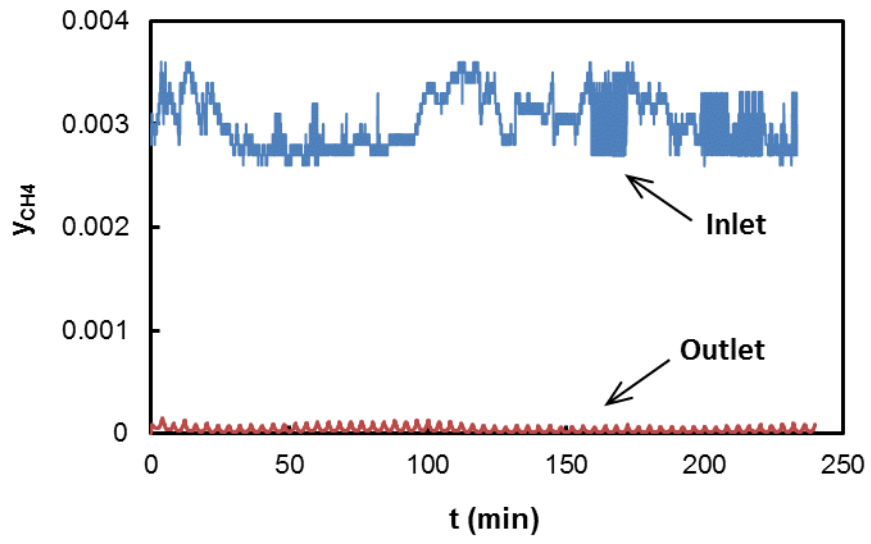
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2 Figure 8

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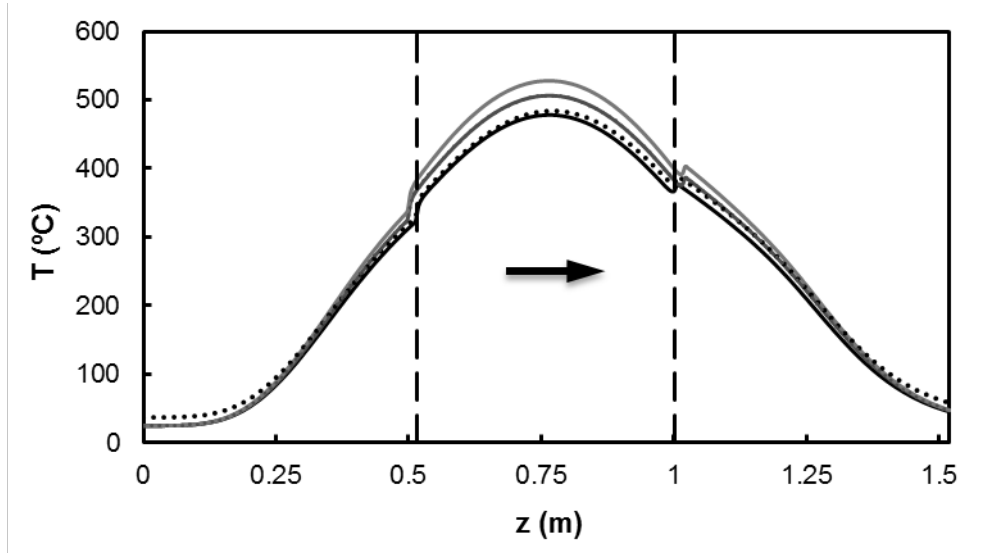
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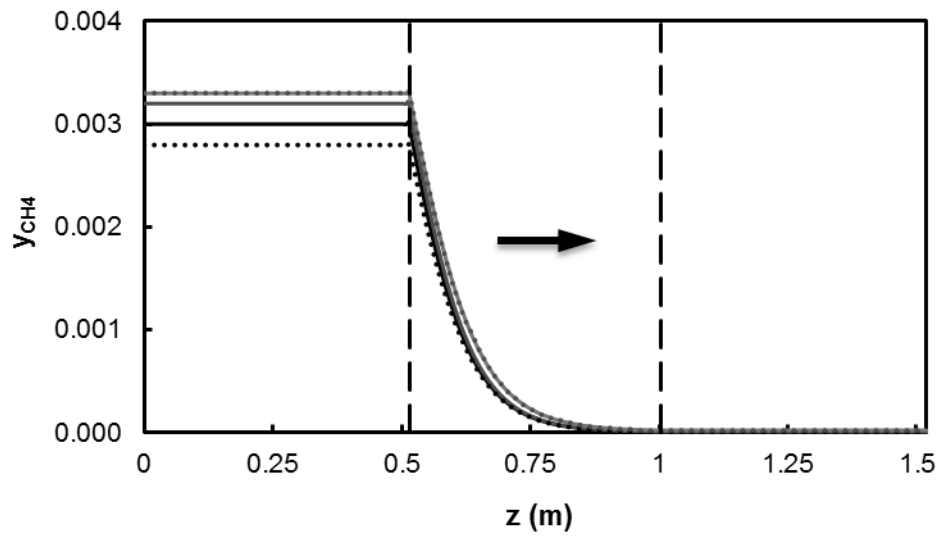
2 Figure 9

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(a)



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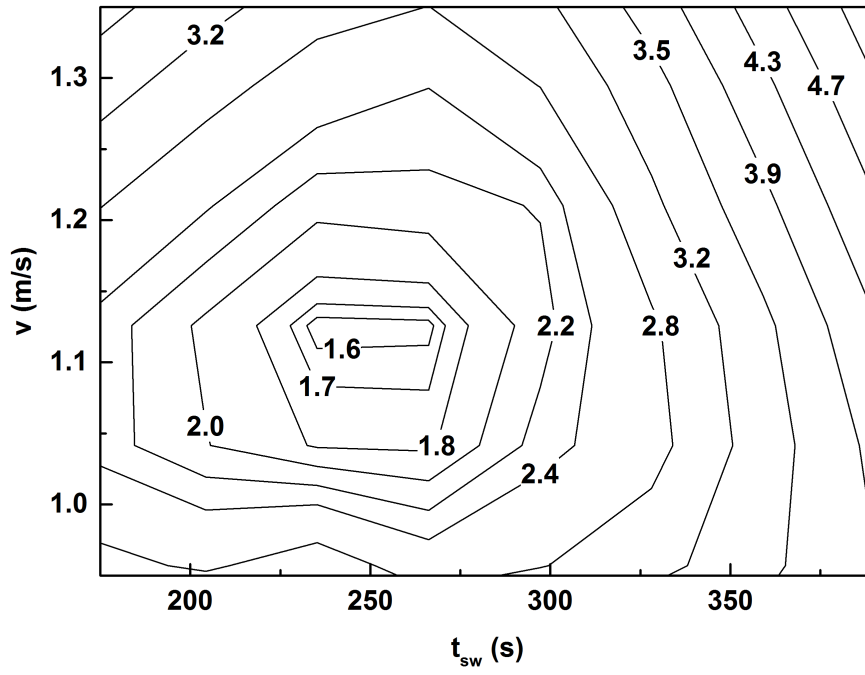
(b)

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1 Figure 10

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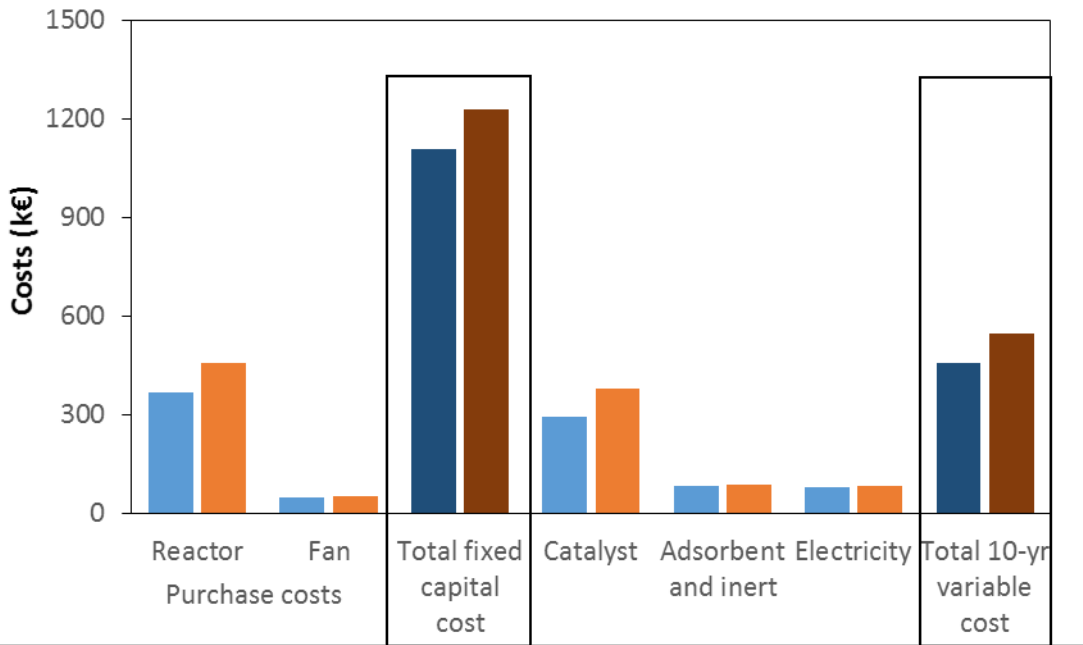


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1 Figure 11

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3



## 1 Tables

2

3 Table 1 Conservation equations for the reverse flow reactor with integrated adsorption:  
4 heterogeneous 1D dynamic model.

5

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Mass balances

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$$\frac{\partial c_i}{\partial t} = -v \frac{\partial c_i}{\partial z} + D_{ax} \frac{\partial^2 c_i}{\partial z^2} - \frac{aK_C}{\epsilon_b} (c_i - c_{Si})$$

$$\frac{\partial n_i}{\partial t} = \frac{aK_C}{\rho_S(1 - \epsilon_b)} (c_i - c_{Si}) + \eta r_i$$

---

Energy balances

---

$$\frac{\partial T_G}{\partial t} = -v \frac{\partial T_G}{\partial z} + \frac{\kappa_{Gax}}{\rho_G C_{PG}} \frac{\partial^2 T_G}{\partial z^2} + \frac{ah}{\rho_G C_{PG} \epsilon_b} (T_S - T_G)$$

$$\frac{\partial T_S}{\partial t} = \frac{k_S}{\rho_S C_{PS}} \frac{\partial^2 T_S}{\partial z^2} + \frac{ah}{\rho_S C_{PS} (1 - \epsilon_b)} (T_G - T_S) + \frac{\rho_{cat} \eta r_i \Delta H_i}{\rho_S C_{PS}}$$

---

6

$i = \text{CH}_4, \text{H}_2\text{O}$

7

1

2

3 Table 2 Initial and boundary conditions for the reverse flow reactor with integrated  
4 adsorption.

5

---

Initial conditions

---


$$c_i|_{t=0} = n_i|_{t=0} = 0$$

$$T_G|_{t=0} = T_S|_{t=0} = T_{ph}$$


---

Boundary conditions

---


$$(c_i)_{0^-} = (c_i)_{0^+} - \frac{D_{ax}}{v} \left( \frac{\partial c_i}{\partial z} \right)_{0^+}$$

$$(T_G)_{0^-} = (T_G)_{0^+} - \frac{\kappa_{Gax}}{v\rho_G C_{PG}} \left( \frac{\partial T_G}{\partial z} \right)_{0^+}$$

$$\left( \frac{\partial c_i}{\partial z} \right)_{z=L_R} = 0$$

$$\left( \frac{\partial T_S}{\partial z} \right)_{z=0^+} = 0$$

$$\left( \frac{\partial T_G}{\partial z} \right)_{z=L_R} = \left( \frac{\partial T_S}{\partial z} \right)_{z=L_R} = 0$$


---

6

7

8

1

2

3 Table 3 Geometric and physical properties of the catalytic and adsorbent beds [22].

4

<b>Bed properties</b>	<b>Catalytic bed</b>	<b>Adsorbent bed</b>
Characteristic length, $D_h / d_p$	$10^{-3}$ m	$4 \times 10^{-3}$ m
Bed porosity, $\epsilon_b$	63%	40%
Solid density, $\rho_S$	2300 kg/m <sup>3</sup>	1060 kg/m <sup>3</sup>
Solid heat capacity, $C_{PS}$	900 J/kg K	836 J/kg K
Solid thermal conductivity, $k_S$	2 W/m K	0.5 W/m K
Thermal inertia, $\rho_S(1 - \epsilon_b)C_{PS}$	766 kJ/m <sup>3</sup> <sub>bed</sub> K	532 kJ/m <sup>3</sup> <sub>bed</sub> K

5

6

7

1

2 Table 4 Expressions used to calculate physical, chemical and transport properties.

3

---

**Catalytic bed**


---

Kinetic equation (methane) [25]

$$r_{CH_4} = -\frac{k_w p_{CH_4}}{1 + K_{inh} p_{H_2O}} = -k'_w p_{CH_4}$$

$$k_w = 1.56 e^{-80000/RT_s} \text{ mol}/(\text{kg}_{\text{monolith}} \text{ s Pa})$$

$$K_{inh} = 8.07 \times 10^{-9} e^{67600/RT_s} \text{ Pa}^{-1}$$

Effectiveness factor (methane) [25]

$$\eta = \frac{\tanh \phi}{\phi}, \quad \phi = L_w \sqrt{\frac{k'_w \rho_{cat} RT_s}{f_w D_{ep}}}$$

Surface to volume ratio of the bed

$$a = (4/D_h) \epsilon_b$$

Mass transfer (methane) [25]

$$K_C = (D_{im}/D_h) \text{Sh}, \quad \text{Sh} = 2.977 \text{ (laminar)}$$

Heat transfer [25]

$$h = (k_g/D_h) \text{Nu}, \quad \text{Nu} = 2.977 \text{ (laminar)}$$

Axial dispersion (mass) [26]

$$D_{ax} = D_h v \left[ \frac{1}{\text{Re Sc}} + \frac{\text{Re Sc}}{192} \right]$$

Axial dispersion (energy) [26]

$$\kappa_{Gax} = D_h v \rho_G C_{PG} \left[ \frac{1}{\text{Re Pr}} + \frac{\text{Re Pr}}{192} \right]$$


---

**Adsorbent bed**


---

Adsorption equilibrium (water) [22]

$$n_i^* = K_{eqi} c_i^m \rightarrow c_{Si} = (n_i/K_{eqi})^{1/m}, \quad m = 0.5$$

$$K_{eqi} = 1.14 e^{4700/RT_s} \text{ (mol/kg}_{\text{ads}})(\text{m}^3/\text{mol})^{0.5}$$

Surface to volume ratio of the bed

$$a = (6/d_p)(1 - \epsilon_b)$$

Global mass transfer (water) [22]

$$K_C = 0.22 (T_s/373)^{-3.6} \text{ m/s}$$

Heat transfer [26]

$$h = (k_g/d_p) \text{Nu}, \quad \text{Nu} = 2 + \text{Re}^{1/2} \text{Pr}^{1/3}$$

Axial dispersion (mass) [26]

$$D_{ax} = d_p v \left[ \frac{0.73}{\text{Re Sc}} + \frac{0.5}{1 + \frac{9.7}{\text{Re Sc}}} \right]$$

Axial dispersion (energy) [26]

$$\kappa_{G,ax} = d_p v \rho_G C_{PG} \left[ \frac{0.73}{\text{Re Pr}} + \frac{0.5}{1 + \frac{9.7}{\text{Re Pr}}} \right]$$


---

4  $R = 8.314 \text{ J/mol K}$ 

5

1

2 Table 5 Composition of the ventilation air from different coal mine sites (concentrations  
3 in % Vol.)

4

Coal mine	Coal production (kt/year)	Average methane concentration	Water concentration
Site 1	187	0.40	2.0-4.0
Site 2	141	0.40	2.3-2.9
Site 3	334	0.20	3.3-4.0
Site 4	106	0.18	2.6-5.0

5

6

7

1

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3

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