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1 **Coal mine ventilation air methane combustion in a catalytic reverse**
2 **flow reactor: influence of emissions humidity**

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7 **Abstract**

8 The role of the humidity content on the performance of catalytic reverse flow reactors (RFR) for the
9 abatement of methane emissions from coal mines is studied in this manuscript. It has been
10 demonstrated that this technique is very useful for the abatement, and even upgrading, of these
11 emissions. However, the effect of humidity on the reactor performance has not been addresses yet,
12 in spite of being well known that water is an inhibitor in catalytic combustion.

13 Experimental studies in a lab-scale isothermal fixed bed reactor demonstrated that water decreases
14 the activity of a palladium on alumina catalyst for the combustion of methane, but this inhibition is
15 entirely reversible, results fitting well to a Langmuir-Hinshelwood kinetic model. Then, the influence
16 of water was studied in a bench-scale RFR operating at near adiabatic conditions at different
17 switching times (100-600 s) and methane feed concentrations (2700-7200 ppm). Finally, a
18 mathematical model for the reverse flow reactor, including the kinetic model with water inhibition,
19 has been validated using the experimental results. This model is of key importance for designing this
20 type of reactors for the treatment of mine ventilation emissions.

21

22 **Keywords:** precious metal catalyst; methane deep oxidation; monolithic catalyst; water inhibition;
23 unsteady state reactors; model-based design.

24

25 **1. Introduction**

26 In the last decades, environmental problems related to global warming have gained importance. Coal
27 mining is an activity with great influence on greenhouse emission, because of the huge amount of
28 methane emitted to the atmosphere during coal extraction through the ventilation system
29 (concentration 1000 to 10 000 ppm). Ventilation air methane represents the main contribution
30 (approximately 78%) to the carbon footprint of coal mining [1].

31 In the atmosphere, methane is accumulated and slowly oxidized with average lifetime of around 12
32 years. Nevertheless, the effect of methane as greenhouse gas is 21 times higher than the one of
33 carbon dioxide. For this reason, the combustion of methane to carbon dioxide before release has a
34 great interest to reduce the net warming potential [2, 4].

35 One suitable option for the treatment of ventilation air methane in coal mining is regenerative
36 oxidation, and in particular regenerative catalytic oxidation (RCO) in a reverse flow reactor [5,6].
37 Catalytic oxidation is an interesting alternative to thermal oxidation, since the use of a catalyst
38 significantly decreases the ignition temperature and, as a consequence, the size and thermal
39 requirements of the combustion device. Moreover, the formation of NO_x is negligible [7, 8].

40 Reverse flow reactors (RFR) consist of a catalytic fixed bed reactor in which the feed flow direction is
41 periodically reversed. RFRs present great potential advantages for the combustion of hydrocarbon
42 emissions. By selecting the appropriate switching time (t_{sw} , defined as the time elapsed between two
43 consecutive flow reversals), most of the combustion heat is stored inside the reactor in consecutive
44 cycles, so that autothermal operation is possible even for very slightly exothermic reactions. Hence,
45 RFRs allow the efficient treatment of very lean emissions of volatile organic compounds (VOC) (e.g.
46 originated from the use of organic solvents) or methane (e.g. coal mine vents) in air [9-11].

47 RFR advantages are a consequence of its forced unsteady state operation. However, this can also be
48 a drawback to maintain ignited operation in the presence of disturbances in the feed flow rate or
49 concentration. For example, if the feed becomes too lean, there is a risk of extinction, because the
50 amount of heat released by the reaction is very low; in these situations, the RFR regeneration

51 capacity is crucial to maintain autothermal operation. Under rich feed conditions, the heat released
52 and accumulated in the reactor can overheat the catalyst bed, leading to catalyst thermal
53 deactivation. Such issues have limited the industrial use of this type of reactors, and encouraged
54 research in the development of suitable control systems [12-15].

55 The catalyst performance is affected by the presence of side compounds (different of methane) in
56 the ventilation air. Among these compounds, water stands out because it is commonly present at
57 high concentration in these emissions (near to saturation at ambient temperature). It is well-known
58 that water has a negative effect on the activity of supported precious metal catalysts. The oxidation
59 of methane on palladium-supported catalysts has been studied by different authors, with a general
60 agreement on the existence of a reversible inhibitory effect [16-28]. Models based on Mars-van
61 Krevelen or Langmuir-Hinshelwood kinetics have been found to agree with the observations [17].

62 The combustion of methane in reverse flow reactors has been studied experimentally, and also by
63 means of simulations. Previous studies have been centred in the influence of operating conditions
64 [19, 20], optimization [21], model validation [20, 22], control of ignition state [13, 23], or heat
65 recovery [14, 24]. Although water is present in high concentration in coal mine ventilation air (20000-
66 50000 ppm) and the performance and stability of reverse flow reactors can be highly affected by the
67 decrease of the catalyst activity caused by water, to the best of our knowledge, this aspect has not
68 been studied. The main objective of this work is to fill this gap and assess the influence of water in
69 the oxidation of methane in catalytic reverse flow reactors.

70 For accomplishing this purpose, the effect of water on the reaction kinetic is firstly studied, and an
71 appropriate kinetic model is proposed. Then, the influence of water on the performance of reverse
72 flow reactors is analysed in a bench-scale device. Finally, a detailed mathematical model of the
73 reverse flow reactor is proposed and validated with the experimental data. This model is suitable to
74 be used in the design and optimization of commercial-scale devices for the treatment of methane
75 emissions in the presence of water.

76 **2. Methodology**

77 **2.1. Catalyst characterization**

78 The catalyst used in this work, representative of catalysts commonly used for methane combustion,
79 is a commercial palladium-based monolith supplied by BASF (reference FP-CPO-5M). The monolithic
80 catalyst is formed by an inert support (cordierite) with a cell density of 390 cpsi (cell size $1.02 \cdot 10^{-3}$ m,
81 open porosity 65% vol.) and a washcoating (average thickness $8.1 \cdot 10^{-5}$ m, fraction 20% vol.)
82 impregnated with the active phase (0.39% wt. palladium). Catalyst geometry was measured directly
83 using the images from a stereomicroscope (Stemi 2000-C, ZEISS).

84 Solid density (2300 kg/m^3) was measured experimentally, and the solid heat capacity (900 J/kg K) and
85 thermal conductivity (0.8 W/m K) were taken from the literature for cordierite-based monoliths.

86 Textural characteristics (specific internal surface area and pore volume) were measured by nitrogen
87 adsorption at 77 K in a Micromeritics ASAP 2020 surface area analyser. Obtained data have been
88 used for estimating internal porosity (12% vol.) and porous structure properties (mean pore diameter
89 12 nm), needed for the mathematical modelling of the reactor.

90

91 **2.2. Isothermal lab-scale reactor**

92 Catalyst stability and reaction kinetics for methane oxidation have been studied in an isothermal
93 fixed-bed reactor (0.6 m length and $9 \cdot 10^{-3}$ m internal diameter). The monolith was ground and sieved
94 to 100-250 μm , and then mixed with ground glass (355-710 μm) to avoid deviations from plug-flow
95 behaviour (tube diameter/particle diameter > 10).

96 The required feed methane/air mixture was prepared by mixing an air-methane mixture of 25 000
97 ppm methane, from a cylinder, and purified air from a compressor (Ingersoll-Rand), using two mass
98 flow regulators. Inlet and outlet streams were analysed in an Agilent gas chromatograph (GC).

99 Water was introduced in the air stream with the help of a bubbler. The concentration of water was
100 regulated using a temperature control system formed by a heating blanket and a temperature
101 controller. The water content is analysed using a hydrometer (VATSAIA HMI 32).

102 **2.3. Adiabatic bench-scale reverse flow reactor**

103 The bench-scale reverse-flow reactor used in the present work consists of a 0.8 m long 0.05 m
104 internal diameter 316 stainless steel tube. The tube contains three monolithic beds: one catalytic
105 (0.15 m long) situated in the middle, and two inert (0.125 m long each) situated at both ends. The
106 beds are surrounded by a glass wool layer, in order to avoid gas bypass near the reactor wall. The
107 temperature of the bed is measured in 5 points along the reactor axis using a multipoint
108 thermocouple array. The flow reversal is accomplished by using two pairs of solenoid valves (Parker-
109 Lucifer 121K46E), acting on the reactor inlet and outlet streams.

110 Reactor feed, consisting of methane-air mixtures with different methane concentrations, is set using
111 two mass flow meters (Bronkhorst F201C). The analysis of methane concentration at the inlet and
112 outlet streams is performed on-line (each 5 s) using an infrared spectrometer (ABB- PIR3502). The
113 reactor tube is surrounded by an oven, equipped with a dynamic temperature-control system able of
114 compensating the heat transfer through the reactor tube, and hence allowing a reactor operation
115 close to adiabatic [20,25,26].

116 The following protocol has been followed for each test. First, the reactor was fed with hot air, in
117 order to pre-heat the beds above the ignition temperature of the air-methane mixture ($T_{pre} =$
118 400°C). Then, the methane/air mixture was fed to the reactor (0.15 m/s n.t.p.) at room temperature
119 (20°C), and the flow reversal was started. The reactor was then operated until pseudo-steady state
120 or extinction.

121

122 **2.4. Reverse flow reactor model**

123 Based on previous experience on modelling reverse flow reactors [20, 27-29], in this work, a 1D
124 heterogeneous dynamic model has been selected (see equations in Table 1). The meaning of the
125 symbols is indicated in the list of symbols. The physical and transport properties appearing in the
126 equations of Table 1 must be specified or calculated by means of appropriate correlations, as
127 indicated in a previous work [22]. Danckwerts boundary conditions (see Table 2) have been used to

128 solve the model in MATLAB using the method of lines (ode15s) [20, 22]. The switch of the feed
129 direction is modelled by shifting the boundary conditions at both sides of the reactor.

130

131 **3. Results and discussion**

132 **3.1. Catalyst stability**

133 Catalyst stability at reaction conditions has been determined in the absence and presence of water.
134 Tests have been carried out in the isothermal fixed-bed reactor at 475°C and WHSV 1.22 m³ (n.t.p.)
135 kg_{cat}⁻¹ min⁻¹ with methane feed concentration 1000 ppm. Results are depicted in Figure 1. In the
136 absence of water, methane conversion decreases during the first 1.5 h and then remains constant.
137 Water is introduced in the reactor at t = 7 h with a concentration of 16000 ppm, causing a sudden
138 drop in conversion from 28% to 21%. Then, conversion remains nearly constant upon time. Finally,
139 when the water feeding is discontinued at t = 13 h, methane original conversion is recovered
140 immediately. This indicates that water causes inhibition of the methane oxidation reaction rather
141 than deactivation of the catalyst, as reported by other authors [17, 30-33].

142

143 **3.2. Kinetic modelling**

144 In the literature, several kinetic models have been proposed for the oxidation of methane in the
145 presence of water, the most commonly used being power-law, Mars-van Krevelen and Langmuir
146 Hinshelwood models [16, 35]. Langmuir-Hinshelwood models are based on mechanisms where
147 different species (methane, oxygen and water) are adsorbed on the catalyst surface, and the reaction
148 involves adsorbed oxygen and methane. The inhibition caused by water can be explained by
149 competitive adsorption of methane and water. The following kinetic equation can be derived based
150 on this mechanism (the terms corresponding to oxygen, in great excess, in the constants) [34]:

$$-r_{CH_4} = \frac{k_w p_{CH_4}}{1 + K_{H_2O} p_{H_2O}} = k'_w p_{CH_4} \quad (\text{Eq.1})$$

151 Where p_{CH_4} and p_{H_2O} are methane and water gas partial pressure, k_w is the kinetic constant and
 152 K_{H_2O} is the adsorption equilibrium constant of water. k_w and K_{H_2O} are assumed to have an
 153 exponential dependence with temperature according to Arrhenius and Van't Hoff equations,
 154 respectively. Water concentration in the reactor is nearly constant, so the kinetic equation is of first
 155 order with respect to methane with apparent kinetic constant k'_w .

156 The rate of methane oxidation has been measured in the isothermal fixed-bed reactor, operating at
 157 WHSV 0.98 m³ (n.t.p.) kg_{cat}⁻¹ min⁻¹. The following expression is obtained by solving the plug-flow
 158 reactor model with the previous kinetic model (Eq.1).

$$k'_w = \left(\frac{F_0}{p_0 W} \right) \ln \left(\frac{1}{1 - X_{CH_4}} \right) \quad (\text{Eq.2})$$

159 where F_0 is the total molar flow rate, p_0 is the total gas pressure and X_{CH_4} is methane conversion.

160 Figure 2a shows the light-off curves obtained at different methane feed concentrations (1000-5000
 161 ppm) in the absence of water. The different curves overlap, indicating that conversion is independent
 162 of methane concentration, like in Eq.2, and hence that reaction rate is first order on methane partial
 163 pressure. The kinetic constants calculated by Eq. 2 are used to calculate the Arrhenius parameters.
 164 An activation energy of 80 kJ mol⁻¹ was obtained, similar to the values reported in the literature for
 165 precious metal-catalysed methane combustion [30, 35].

166 The absence of diffusional limitations has been checked by calculating the parameters proposed in
 167 the literature for the most unfavourable conditions (highest temperature considered in the fitting,
 168 450°C): Carberry number (external mass transfer) $Ca = r_{obs}/K_G a_S C_G = 9 \cdot 10^{-4} < 0.05$, Wheeler-Weisz
 169 criteria (internal mass transfer) $\eta \phi^2 = r_{obs} d_p^2 / D_e C_S = 9 \cdot 10^{-2} < 0.1$, external heat transfer
 170 $|K_G (-\Delta H) C_G E_a C_a / h R T_G^2| = 1 \cdot 10^{-3} < 0.05$ and internal heat transfer $|D_e (-\Delta H) C_S E_a \eta \phi^2 / k_e R T_S^2| =$
 171 $5 \cdot 10^{-7} < 0.05$.

172 Light-off curves obtained for different water feed concentrations (20000 to 50000 ppm) at constant
 173 WHSV 1.22 m³ (n.t.p.) kg_{cat}⁻¹ min⁻¹ and methane feed concentration 1000 ppm are depicted in Figure
 174 2b. It is clearly observed that water reduces the activity of the catalyst, resulting in a decrease of

175 methane conversion at all temperatures. Moreover, the inhibition is stronger at high water
176 concentrations.

177 The parameters of this Eq.1 were fitted to the experimental data by the least-squares method using
178 the EXCEL Solver; the following parameters being obtained: $k_w = 2.44 e^{-80000/RT}$ mol kg_{cat}⁻¹ s⁻¹ Pa⁻¹
179 and $K_{H_2O} = 8.07 \cdot 10^{-9} e^{67600/RT}$ Pa⁻¹ ($R = 8.314$ J mol⁻¹ K⁻¹). These results agree with other
180 published results [17, 36].

181 Methane conversions predicted by the model with the fitted parameters are depicted in Figure 2b
182 (lines). The model accurately predicts the increase of conversion with temperature for the different
183 water concentrations.

184

185 3.3. RFR performance in presence of water

186 The experiments in the bench-scale reverse flow reactor have been planned according to an
187 experimental design, where the main operating variables are varied within the following ranges:
188 water concentration (20000 - 50000 ppm), methane concentration (2700-7200 ppm) and switching
189 time (100-600 s). The most representative results are compared in Figure 3 and 4 by means of the
190 temperature profiles at the middle of a cycle. These plots are very useful for studying the behaviour
191 of the reactor, being a measurement of the heat released (in the catalytic bed) and stored (in the
192 inert beds) in the reactor. The boundaries of the inert and catalytic beds are indicated by dashed
193 lines.

194 Figure 3 compares the performance of the reactor at high and low switching times. Switching time
195 determines the amount of heat stored in the reactor between cycles, and used for pre-heating the
196 feed in the next cycle, and for this reason is critical in achieving stable reactor operation (when
197 switching time is too long the reactor cools down gradually and finally extinction occurs). Results
198 show that, as expected, average temperature in the reactor centre are substantially higher for low
199 switching time (100 s) than for high switching time (600 s). As a result, at switching time 600 s stable

200 reactor operation is only achieved for methane feed concentration above 5400 ppm, while at 100 s
201 the reactor is stable for methane concentrations as low as 3600 ppm.

202 When the reactor is operated in the presence of water, the temperature plateau decreases; for
203 comparison purposes, the other operating variables are held constant. This can be explained by the
204 inhibition of the catalytic activity towards methane oxidation produced by water, which decreases
205 methane conversion, and hence, the heat released and stored in the reactor. As expected, this effect
206 is more marked at high water gas concentrations, because the catalyst inhibition is stronger.

207 The influence of methane and water gas feed concentrations are analysed in Figure 4 at constant
208 switching time (300 s). As expected, bed temperature is higher for the experiments at higher
209 methane concentration, and bed temperature decreases with increasing water content. The
210 difference between the experiments with and without water is more marked at high methane
211 concentration. In the test carried out at the highest water concentration (50000 ppm), the inhibition
212 is so strong that the reactor extinguished. These results demonstrate that water affects the thermal
213 stability of the reverse flow reactor and its long-term stable operation, reducing the interval of
214 operating conditions (methane concentration and switching time) for which the reactor operation is
215 stable.

216

217 **3.4. RFR model validation in the presence of water**

218 The mathematical model presented in the methodology section has been validated by simulating all
219 the experiments and comparing experiments and simulations in terms of temperature and methane
220 conversion.

221 Typical results are depicted in Figure 5 and 6. The evolution of temperature upon time at three
222 reactor positions ($z = 0.050, 0.116$ and 0.200 m, measured from a bed end; as the total bed length is
223 0.400 m, $z = 0.200$ m corresponds to the reactor centre) is depicted in Figure 5 for two experiments.

224 It must be considered that bed temperature profiles are symmetric due to the periodic behaviour of
225 the reactor. At the beginning of the experiments ($t = 0$), the reactor bed is pre-heated uniformly to

226 400°C. Then, the methane feed is introduced at room temperature and the flow reversal is started.
227 This produces a temperature wave that moves forward and backward along the reactor bed. In the
228 temperature versus time plots, this movement is observed as saw teeth, which are characteristic of
229 the behaviour of reverse flow reactors. The temperature evolution trend in the different reactor
230 positions indicates how the reactor is performing.

231 The experiment shown in Figure 5 a, c and e is unstable, because temperature decreases upon time
232 in all bed positions (except a slight increase at the beginning at $z = 0.200$ m) and the reactor proceeds
233 to extinction. In this particular case, methane feed concentration is not enough to achieve **long-term**
234 **stable operation of the reactor with water inhibition**. The correspondence between experiments and
235 simulations is good (except at $z = 0.200$ m, where the model predicts a temperature slightly lower),
236 and the model succeeds in predicting the inhibition and associated temperature decrease caused by
237 water.

238 The experiment analysed in Figure 5 b, d, f is stable. The evolution of temperature with time shows
239 that the system reaches a stable pseudo-steady state in which the same temperature evolution is
240 repeated after successive cycles. There is good agreement between simulations and experiments,
241 though there are small discrepancies for $z = 0.200$ m, as in the previous experiment. These
242 discrepancies are explained by a poorer temperature control in the middle of the reactor, because
243 the temperature is higher, which results in deviations from the adiabatic behaviour of the bench-
244 scale reactor. The temperature evolution at the other positions of the reactor is predicted accurately.

245 Bed temperature profiles are also very useful to determine the validity of the model. In Figure 6,
246 profiles at different stages of a cycle (at beginning, the middle and the end) are compared for
247 experiments and simulations. In general, the model is able of predicting the reactor behaviour. As
248 indicated before, the major discrepancies are found in the bed centre.

249 In conclusion, the 1D heterogeneous mathematical model with catalyst inhibition proposed in this
250 work can be considered as validated with the experiments carried out in a bench-scale reverse flow
251 reactor operating at near-adiabatic conditions. The simple Langmuir-Hinshelwood kinetic model,

252 obtained from conventional light-off curves, is useful for modelling methane combustion in the
253 presence of water in RFR. This RFR model can now be used in the design and optimization of RFR
254 commercial-scale units for methane combustion from sources where catalyst inhibition by water is
255 expected, such as coal mine vents and landfill lean emissions, among others.

256

257 **3.5. Considerations for the design of a RFR in the presence of water**

258 This section is devoted to the study of the RFR stability at different operating conditions and its
259 consequences in the design of commercial scale units. In Figure 7, all the experiments carried out in
260 this work are depicted as a function of the operating conditions (switching time and methane feed
261 concentration) for the case of (a) water-free conditions and (b) 40 000 ppm water (corresponding to
262 a relative humidity of 75%). The experiments that resulted in stable operation of the reactor appear
263 at the upper part of the graph with a solid marker; the unstable ones at the bottom with an open
264 marker. A line, obtained by simulations using the mathematical model, determines the limit between
265 the stable and unstable zones. Reactor stability is determined by the combination of the heat
266 released by the reaction (given by methane concentration) and switching time; reactor stability
267 increasing for higher methane concentration and lower switching time. Switching times lower than
268 50 s are not considered, as they cause important by-pass of un-reacted methane (*wash-out*) as
269 explained in the literature, and mechanical problems (flow reversal valves premature ageing) [10-12].

270 **It can be observed that the presence of water reduces notably the range of operation conditions at**
271 **which stable operation can be achieved.** Thus, for the same switching time an increase of
272 approximately 1500 ppm in the feed concentration is required. The heat released by the additional
273 1500 ppm increases the catalyst temperature, so that it compensates the decrease in activity caused
274 by water. The same effect can also be achieved by reducing the switching time, which increases the
275 heat trapped in the reactor, and hence the temperature of the catalyst. It should also be considered
276 that the temperature of the catalyst cannot be increased indefinitely to compensate the lower

277 activity of the catalyst. The catalyst has maximum recommended operating temperature to prevent
278 overheating.

279 Figure 7 demonstrates that the decrease in catalyst activity caused by water highly affects the
280 performance of the reverse flow reactor, reducing the range of operating conditions in which its
281 stable operation is possible. However, autothermal reactor operation is still possible, by increasing
282 methane feed concentration or, within certain limits, lowering switching time.

283

284 **4. Conclusions**

285 Coal mine ventilation air contains appreciable amounts of methane, but also water that undoubtedly
286 affects the catalytic combustion of methane and, consequently, the operation of catalytic reverse
287 flow reactors. The aim of this study is to get new insights on the influence of this water on the
288 operation of catalytic reverse flow reactors.

289 It was found that water produces a reversible inhibition on precious metal-based catalysts, which
290 was successfully modelled using a Langmuir-Hinshelwood kinetic model. The study was extended to a
291 bench-scale reverse flow reactor equipped with a precious-metal based monolithic catalyst, operated
292 at different feed water concentrations. The results of the experiments show that the decrease in the
293 catalyst activity produced by water reduces methane conversion, and hence the heat released in the
294 reactor. This decreases the temperature of the catalytic bed and the stability of the reverse flow
295 reactor.

296 A mathematical model for the reverse flow monolithic reactor, capable of modelling the inhibition
297 caused by water, was proposed and validated with the experimental data. This model is very useful
298 for the study of the influence of reactor design and operating conditions on the reactor performance
299 and the design of commercial scale reverse flow reactors. It was demonstrated that the design of
300 efficient reactors in the presence of water in the feed requires special attention. As an illustration,
301 the operating conditions (methane and water concentration and switching time) resulting on stable
302 RFR operation or reaction extinction were determined for a particular reactor design, showing that

303 the effect of water can be overcome by increasing methane concentration or decreasing switching
304 time.

305

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309 **Nomenclature**

310 a geometric external surface to volume ratio ($\text{m}^2/\text{m}^3_{\text{bed}}$)

311 C molar concentration (mol/m^3)

312 C_p heat capacity ($\text{J}/\text{kg K}$)

313 D diffusion coefficient (m^2/s)

314 E_a Activation energy (kJ/mol)

315 F_0 total molar flow rate (mol/s)

316 h gas to solid heat transfer coefficient ($\text{W}/\text{m}^2 \text{K}$)

317 k thermal conductivity ($\text{W}/\text{m K}$)

318 K_G gas to solid mass transfer coefficient (m/s)

319 K_{H_2O} adsorption equilibrium constant for water (Pa^{-1})

320 k_w kinetic constant ($\text{mol}/\text{kg}_{\text{cat}} \text{s Pa}$)

321 p pressure (Pa)

322 r reaction rate ($\text{mol}/\text{kg}_{\text{cat}} \text{s}$)

323 R ideal gas constant ($8.314 \text{ J}/\text{mol K}$)

324 t time (s)

325 T temperature (K)

326 t_{sw} switching time (s)

327 u gas superficial velocity (m/s)

328 W catalyst weight (kg)

329	X	conversion (-)
330	y	molar fraction (-)
331	z	spatial coordinate (m)
332	Greek symbols	
333	ΔH	heat of reaction (J/mol)
334	ϵ_b	bed porosity (-)
335	ϕ	Thiele modulus (-)
336	η	internal effectiveness factor of the catalyst (-)
337	ρ	density (kg/m ³)
338	Subscripts	
339	0	inlet
340	ax	axial
341	e	effective
342	G	gas
343	S	solid
344		
345		
346		

347 **Caption to figures**

348 Figure 1 Catalyst stability at constant reaction conditions: 475°C, 1000 ppm methane,
349 WHSV 1.22 m³ (n.t.p.) kg_{cat}⁻¹ min⁻¹. (◆) methane conversion. (—) water
350 concentration (ppm).

351 Figure 2 Light-off curves of the ground monolith at different conditions.
352 (a) Methane feed concentration: (■) 1000 ppm, (✕) 2000 ppm, (◆) 3000 ppm,
353 (△) 5000 ppm. WHSV = 0.98 m³ (n.t.p.) kg_{cat}⁻¹ min⁻¹. No water.
354 (b) Water feed concentration: (◆) 3000, (▲) 8000, (■) 15000, (●) 23000 and
355 (✕) 33000 ppm. WHSV = 1.22 m³ (n.t.p.) kg_{cat}⁻¹ min⁻¹. 1000 ppm methane.

356 Figure 3 Temperature profiles in the reverse flow reactor at mid cycle. Influence of the
357 water feed concentration: (■) 0, (◆) 30000 and (▲) 40000 ppm.
358 (a) $t_{sw} = 600$ s, $y_{G0} = 5400$ ppm.
359 (b) $t_{sw} = 100$ s, $y_{G0} = 3600$ ppm.

360 Figure 4 Temperature profiles in the reverse flow reactor at mid cycle: influence of the
361 water feed molar fraction: (■) 0, (◆) 30000 and (▲) 40000 ppm.
362 (a) $t_{sw} = 300$ s, $y_{G0} = 3600$ ppm.
363 (b) $t_{sw} = 300$ s, $y_{G0} = 4500$ ppm.

364 Figure 5 Model validation: evolution of reactor temperature at 0.050, 0.116 and 0.200 m.
365 (—) Experiment, (—) simulation.
366 (a). (c) and (e): $y_{G0} = 3600$ ppm, $t_{sw} = 200$ s, $y_{H20} = 33000$ ppm.
367 (b). (d) and (f): $y_{G0} = 5400$ ppm, $t_{sw} = 300$ s, $y_{H20} = 37000$ ppm.

368 Figure 6 Model validation: evolution of temperature profiles during a half-cycle (gas flow
369 from left to right), beginning (◆), middle (■) and end of half-cycle (▲). Symbols:
370 experiments; lines: simulations.
371 (a). $y_{G0} = 3600$ ppm, $t_{sw} = 200$ s, $y_{H20} = 33000$ ppm.
372 (b). $y_{G0} = 5400$ ppm, $t_{sw} = 300$ s, $y_{H20} = 37000$ ppm.

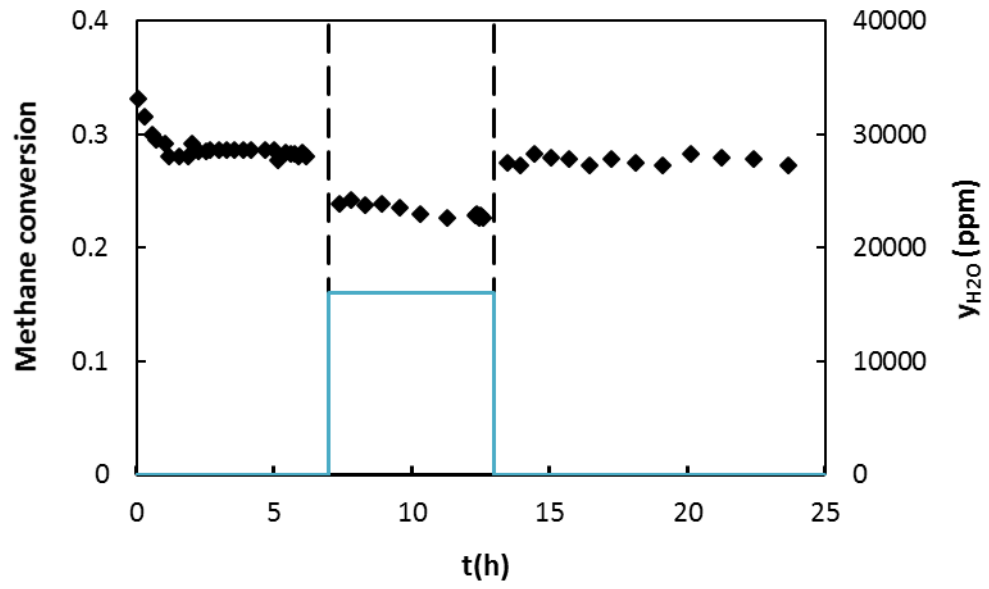
373 Figure 7 Influence of water in the reverse flow reactor performance and stability.
374 (a). Free of water: stable (◆) and unstable (◇) experiment.
375 (b). Water concentration = 37000 ppm: stable (▲) and unstable (△) experiment.
376 Stability limit: free of water (— —) and water concentration = 37000 ppm (···).

377

378

379 **Figure 1**

380



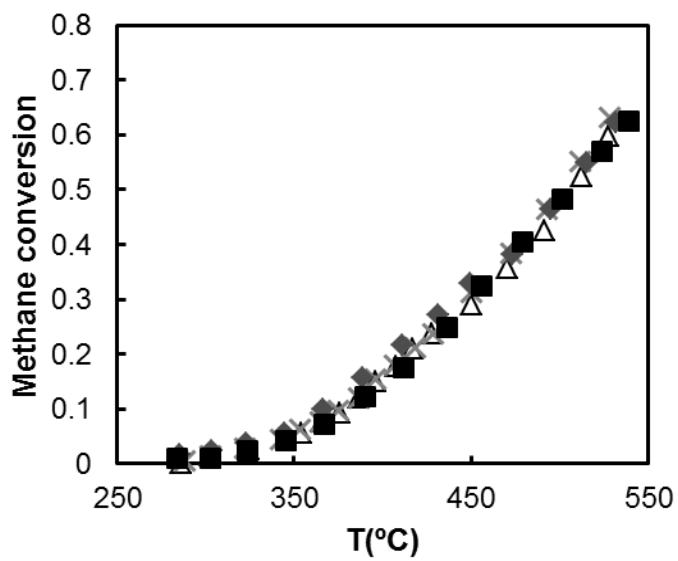
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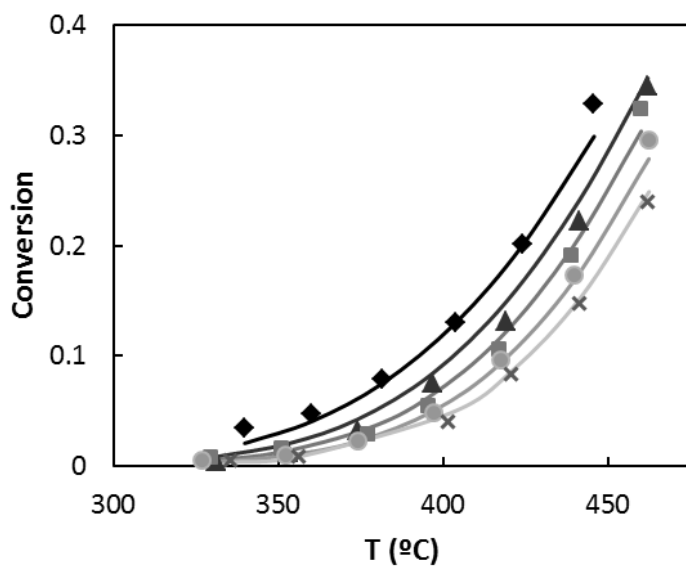
383

384

385 **Figure 2**



386 **(a)**



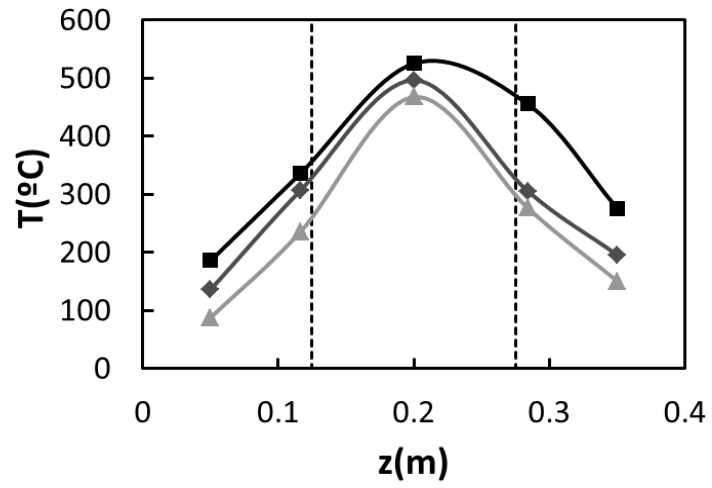
387 **(b)**

388

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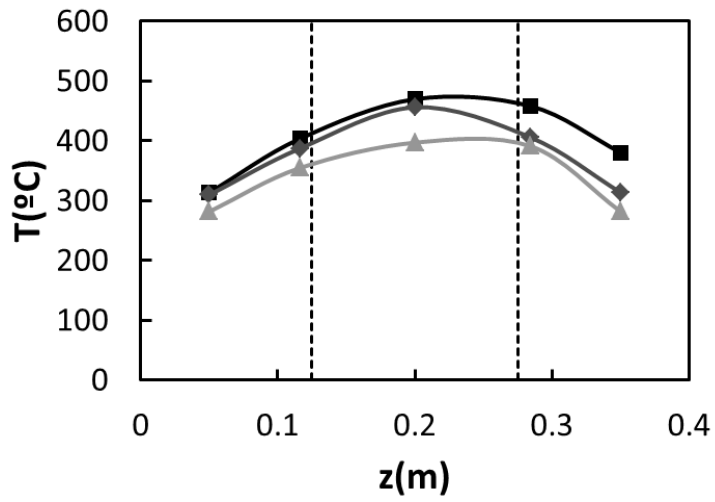
390 **Figure 3**

391



392

(a)



393

(b)

394

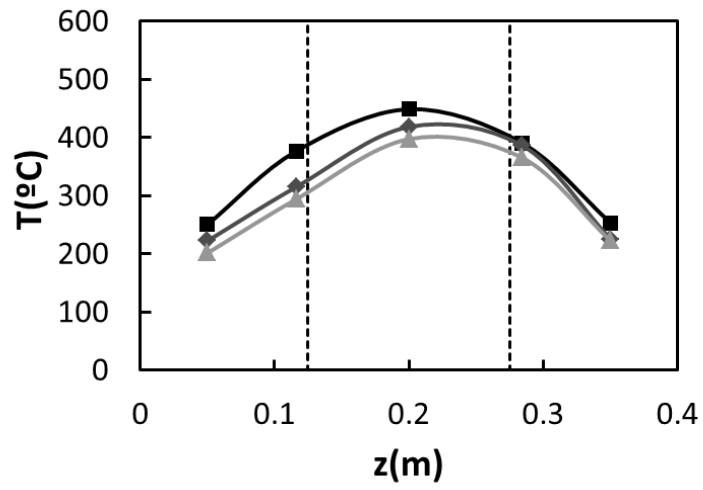
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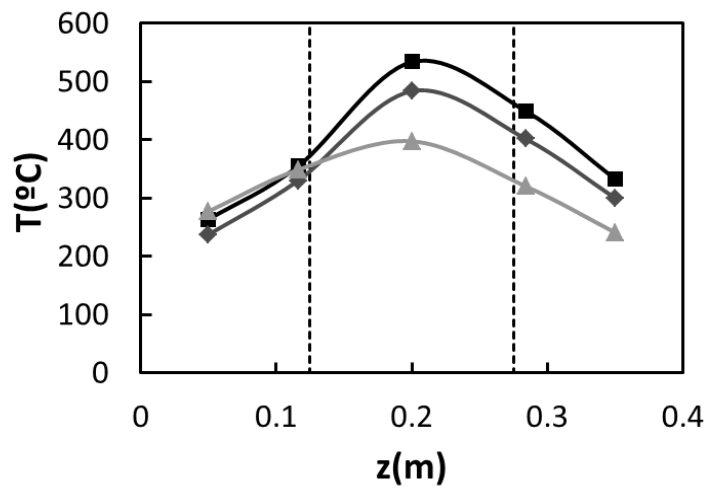
398 **Figure 4**

399



400

(a)



401

(b)

402

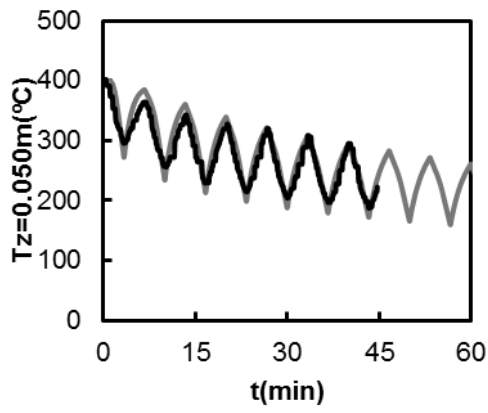
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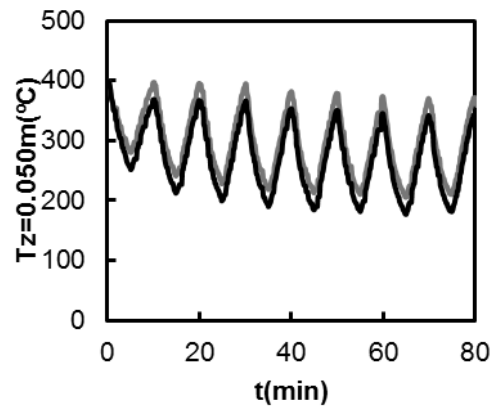
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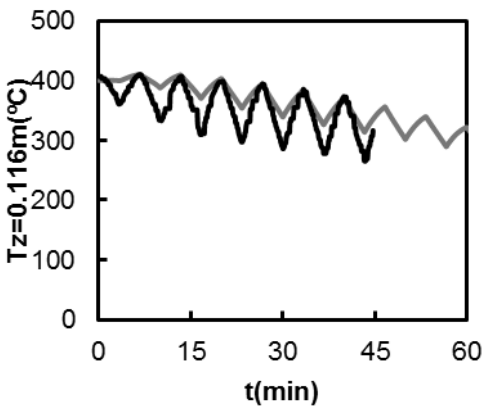
407 **Figure 5**



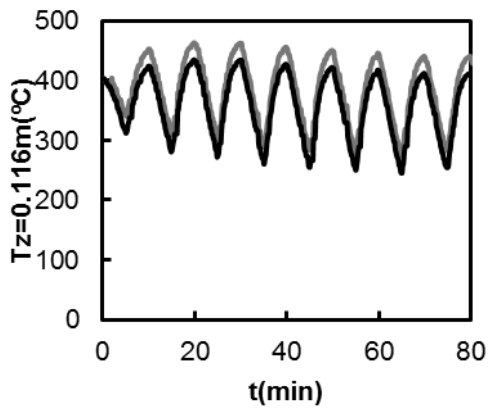
408 (a)



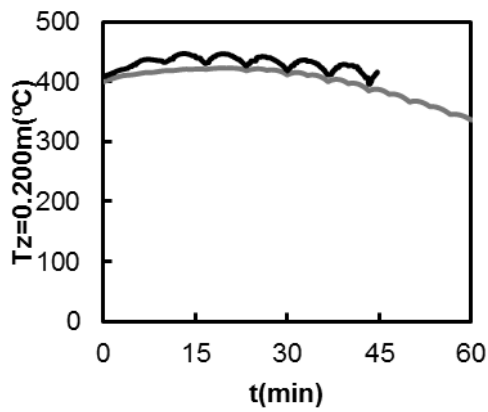
(b)



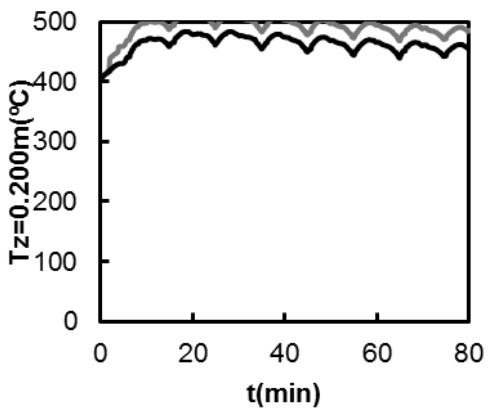
409 (c)



(d)



410 (e)



(f)

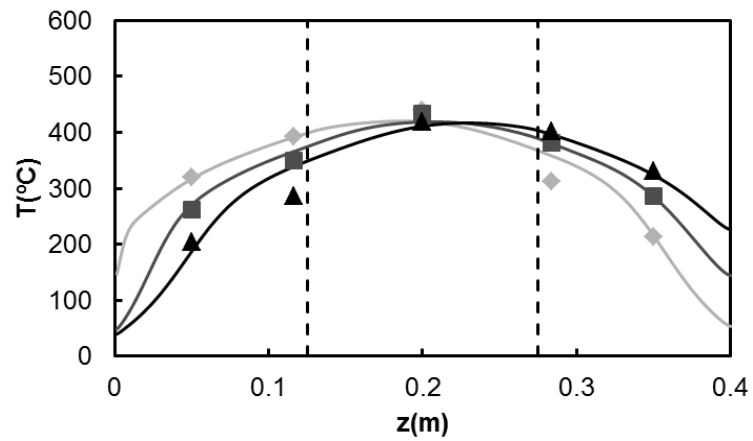
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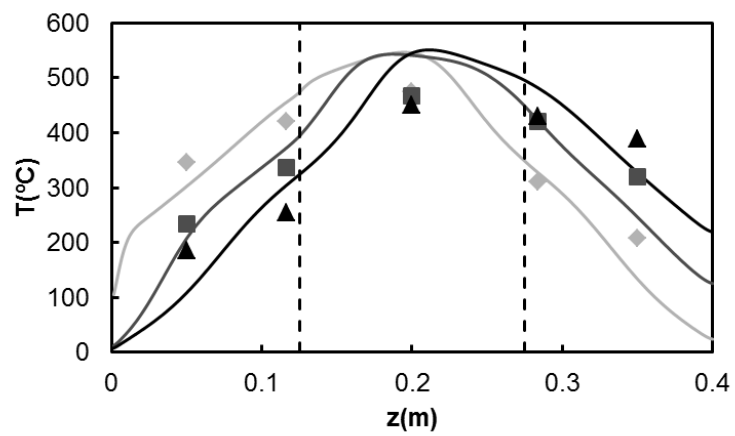
414 **Figure 6**

415



416

(a)



417

(b)

418

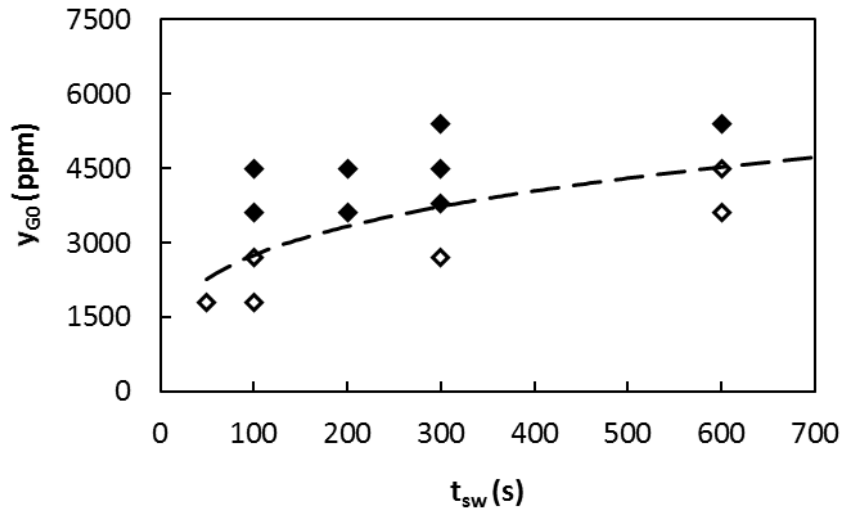
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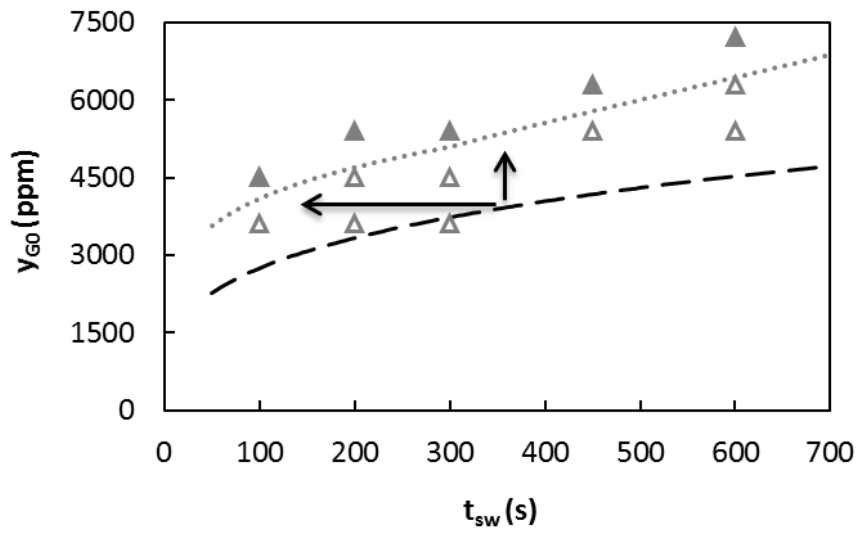
421

422 **Figure 7**

423



424 (a)



425 (b)

426

427

428

429

430

431 **List of tables**

432

433 Table 1 Summary of the main equation of the mathematical model proposed for the
434 modelling of the reverse flow reactor.

435 Table 2 Boundary and initial conditions of the mathematical model proposed for the
436 modelling of the reverse flow reactor.

437

438

439

440

441 Table 1

442

 Mass balance to the gas phase

$$\frac{\partial y_G}{\partial t} = -\frac{u_0}{\epsilon_b} \frac{\rho_{G0}}{\rho_G} \frac{\partial y_G}{\partial z} + D_{ax} \frac{\partial^2 y_G}{\partial z^2} - \frac{aK_G}{\epsilon_b} (y_G - y_S)$$

 Mass balance to the solid phase

$$\frac{\partial y_S}{\partial t} = \frac{aK_G}{(1 - \epsilon_b)} (y_G - y_S) + \frac{\rho_S \eta r_{CH_4}}{c_G}$$

 Energy balance to the gas phase

$$\frac{\partial T_G}{\partial t} = -\frac{u_0 \rho_{G0}}{\epsilon_b \rho_G} \frac{\partial T_G}{\partial z} + \frac{k_{Gax}}{\rho_G C_{PG}} \frac{\partial^2 T_G}{\partial z^2} + \frac{ah}{\rho_G C_{PG} \epsilon_b} (T_S - T_G)$$

 Energy balance to the solid phase

$$\frac{\partial T_S}{\partial t} = \frac{k_S}{\rho_S C_{PS}} \frac{\partial^2 T_S}{\partial z^2} + \frac{ah}{\rho_S C_{PS} (1 - \epsilon_b)} (T_G - T_S) + \frac{\rho_S \eta r_{CH_4} \Delta H}{\rho_S C_{PS}}$$

443

444

445

446 Table 2

447

Initial conditions

$$y_G|_{t=0} = y_S|_{t=0} = 0$$

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

Boundary conditions

$$(y_{Gj})_{0^-} = (y_{Gj})_{0^+} - \frac{\epsilon_b D_{ax}}{u_0} \left(\frac{\partial y_{Gj}}{\partial z} \right)_{0^+}$$

$$(T_G)_{0^-} = (T_G)_{0^+} - \frac{\epsilon_b \kappa_{G,ax}}{u_0 \rho_{G0} C_{PG}} \left(\frac{\partial T_G}{\partial z} \right)_{0^+}$$

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

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

$$\left(\frac{\partial y_{Gj}}{\partial z} \right)_{z=L_R} = \left(\frac{\partial y_{Sj}}{\partial z} \right)_{z=L_R} = 0$$

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

448

449

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