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# Separation of carbon dioxide from flue emissions using Endex principles

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## Abstract

In an Endex reactor endothermic and exothermic reactions are directly thermally coupled and kinetically matched to achieve intrinsic thermal stability, efficient conversion, autothermal operation, and minimal heat losses. Applied to the problem of in-line carbon dioxide separation from flue gas, Endex principles hold out the promise of effecting a CO<sub>2</sub>-capture technology of unprecedented economic viability. In this work we describe an Endex Calcium Looping reactor, in which heat released by chemisorption of carbon dioxide onto calcium oxide is used directly to drive the reverse reaction, yielding a pure stream of CO<sub>2</sub> for compression and geosequestration. In this initial study we model the proposed reactor as a continuous-flow dynamical system in the well-stirred limit, compute the steady states and analyse their stability properties over the operating parameter space, flag potential design and operational challenges, and suggest an optimum regime for effective operation.

*Keywords:* Calcium Looping, Endex reactor, CO<sub>2</sub> separation, Carbon capture, Clean coal

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## 1. Introduction

In this paper we introduce a method of reactive endothermic-exothermic coupling, known as an Endex system (1; 2), for the in-line separation of carbon dioxide from flue and fuel gas emissions. Endex principles are applied to obtain a highly efficient modification of the Calcium Looping separation technique, in which calcium oxide ( $\text{CaO}$ , or lime) is used to scrub  $\text{CO}_2$  from a flue gas (3). The Endex process involves direct thermal coupling of a carboniser reactor segment, in which the lime sorbent reacts with  $\text{CO}_2$  to produce calcium carbonate ( $\text{CaCO}_3$ ) and a scrubbed gas effluent stream, and a calciner reactor segment to which the loaded sorbent is transported and where the sorbent is regenerated and reinjected into the carboniser segment, with production of a pure  $\text{CO}_2$  gas stream. The same methodology can be applied to other sorbents and to fuel gas mixtures such as syngas. Since the Endex Calcium Looping reactor is a thermoreactive system an important first step in a project to build and operate a demonstration plant is to assess the thermal stability of the system. In this work we model the reactor as a coupled dynamical system in the well-stirred limit and map the linear stability of the steady states over the operational parameter space.

Technologies for scrubbing carbon dioxide from flue gas to reduce greenhouse gas emissions must satisfy the following criteria, at least, in order to be accepted by society and implemented by industry: they must (1) effect  $\text{CO}_2$  capture for less than  $\sim\text{US}\$30$  per tonne with an increased cost of electricity of less than about 15%, (2) preferably be retrofittable to existing fossil-fueled plants, (3) not cause additional environmental harm, and (4) operate safely. The best available technologies may not be able to comply with all of these requirements (4). There is a drive to develop second generation technologies which have been purpose-designed to meet the stringent demands of  $\text{CO}_2$  capture, rather than adapt existing technologies.

Calcium Looping was first proposed by (5) for post-combustion  $\text{CO}_2$  emissions reduction, although its use on an industrial scale for removal of  $\text{CO}_2$  from syngases dates from the 1960s (6). (7) proposed that oxyfuel combustion of additional fossil fuel be used to drive the high temperature calcination process. (8) showed that the  $\text{CO}_2$ -lime chemical bond strength is such that the thermal energy required is about 30–40% of the thermal energy of the plant that produces the flue gas. This additional consumption of energy results in higher  $\text{CO}_2$  production, but this is offset by use of the heat liberated from the carboniser at about 873–1023 K to produce additional

38 power.

39 The major drawback of Calcium Looping is the rapid loss of carbonation  
40 capacity due to sintering of the lime sorbent. Sintering occurs at the high  
41 temperatures used in the conventional calcination cycle, about 1123–1223 K  
42 in an atmosphere of carbon dioxide (9; 10) and, more importantly, reactive  
43 sintering results in irreversible loss of the mesopore surface area due to pore  
44 filling (11).

45 Sintering was recognised as a problem by (6) and by (12) and has been  
46 the subject of intensive research since. For example, (13) showed that the  
47 sorption capacity degrades from a capacity of about 80% of the theoretical  
48 limit of 0.78 kg of CO<sub>2</sub> per kg of CaO to about 17% after about 10 cycles, and  
49 reactivation studies were carried out by (14) and (15). Even though (16)  
50 showed that CO<sub>2</sub> capture using Calcium Looping with sintering meets criteria  
51 (1)–(3) above, sorbent sintering remains the largest barrier to adoption of  
52 Calcium Looping. In the Endex Calcium Looping process described in the  
53 present paper the sintering problem is neatly sidestepped by inversion of the  
54 usual temperature difference between carboniser and calciner and by using  
55 light carbonation over fast cycling.

56 The Endex approach to thermal control and heat recovery was first de-  
57 scribed and analysed in mathematical terms by (1) and (2). It involves  
58 using the heat generated by an exothermic reaction to drive an endothermic  
59 reaction directly, in real time. The reactions are thermally coupled via direct  
60 heat transfer or mass transfer or both, and for the reactions to effectively  
61 “see” each other they must be matched kinetically. Since the kinetic param-  
62 eters (activation energies and pre-exponential factors) of a selected Endex  
63 couple do not match in general, kinetic matching is achieved (to an accept-  
64 able approximation) by manipulation of residence times. Several studies of  
65 specific Endex systems have been carried out since with promising results,  
66 although none has referred to the original works of (1) and (2). Terms such  
67 as “recuperative coupling” and “co-current thermally coupled reactor” are  
68 used for Endex systems and principles in those works, which are reviewed in  
69 the study of a thermally coupled reactor by (17).

70 (18) and (19) proposed that an Endex configuration could be used in  
71 which the temperature of the calciner is held below that of the carboniser  
72 by thermally coupling the reactor segments. This configuration is counter-  
73 intuitive because it is usually assumed that the endothermic, bond-breaking,  
74 process in the calciner would occur at a higher temperature than that of the  
75 carboniser, and all previous approaches to Calcium Looping are based on this

76 conventional configuration. Inversion of the temperature difference between  
77 carboniser and calciner is achieved by control of the pressure. Operation  
78 using this new configuration has three consequences: the lower temperature  
79 of the calciner reduces thermal sintering, partial carbonation reduces the  
80 loss of surface area by pore-filling, and the unreacted sorbent promotes heat  
81 transfer. The intent was to greatly reduce the impact of thermal and reactive  
82 sintering, and remove this barrier to adoption of Calcium Looping. The most  
83 desirable property of the Endex configuration is that CO<sub>2</sub> separation can be  
84 achieved, in principle, without the need for additional heat. (19) conclude  
85 that the Endex configuration has the potential to significantly reduce the  
86 cost of CO<sub>2</sub> capture below that of current technologies, principally because  
87 of this property.

88 Thermal coupling of reactive systems creates additional nonlinearities in  
89 the dynamics. In the Endex reactor configuration for CaO Looping, CO<sub>2</sub>  
90 separation can be considered as a gas switch in which the CO<sub>2</sub> pressure  
91 in the calciner, for example, can be used to control the CO<sub>2</sub> output mass  
92 flow. However, reactor coupling can amplify perturbations with adverse ef-  
93 fects, and a more detailed analysis of the Endex configuration is required that  
94 deals with its response to perturbations, and the start-up and shut down pro-  
95 cesses. This analysis is performed in this paper. In section 2 we review the  
96 properties of Endex systems, and outline the rationale for stability analysis of  
97 thermoreactive systems generally and of the proposed Endex configuration in  
98 particular. The methodology used is described in section 3, and the dynam-  
99 ical model is presented. In section 4 the results are presented and discussed  
100 for: standalone carboniser, Endex carboniser/calciner with sorbent cycling  
101 but without wall thermal coupling, Endex carboniser-calciner with both sor-  
102 bent cycling and wall thermal coupling, and transient analysis (start-up and  
103 shutdown dynamics). We summarize these results in section 5.

## 104 **2. Carbonation, calcination, and Endex principles**

105 The chemisorption of carbon dioxide onto calcium oxide is highly exother-  
106 mic, releasing 170 kJ/mol CO<sub>2</sub> at 1073 K. Housed in a reactor where ther-  
107 mostatting is necessarily imperfect such a reaction may become thermally  
108 unstable and either self-quench or self-heat uncontrollably. Both situations  
109 are obviously undesirable from safety and economic considerations.

110 Traditionally, reactors housing exothermic reactions are fitted with ther-  
111 mostatted cooling jackets, but the problem of maintaining thermal stability

112 becomes much more difficult (and expensive) as the reactor is scaled up be-  
113 cause the heat removal rate is linear in the temperature and scales as  $L^2$   
114 while the reactive heat generation rate is exponential in the temperature and  
115 scales as  $L^3$ , where  $L$  is a characteristic reactor dimension. This scale-up  
116 problem is particularly relevant to reactive flue gas  $\text{CO}_2$  capture, because  
117 the emitter is typically a large fossil-fueled power station.

118 Reaction heat that is removed by the cooling system in traditional chem-  
119 ical reactor plants is either dissipated into the environment, or sometimes, in  
120 large and sophisticated plants, partially recovered by an indirect route and  
121 used for another purpose.

122 It is important to appreciate the potential for adiabatic, or thermally in-  
123 sulated, operation of an Endex configured reactor. A conventional chemical  
124 reactor is almost never run adiabatically (unless it is a bomb calorimeter)  
125 because for most common industrial reactions the adiabatic temperature rise  
126 for full conversion is dangerously high. Purpose-built cooling systems are  
127 usually necessary, which can become technically very elaborate, and expen-  
128 sive, when the reactor is large. The concept of an *ideal adiabatic* Endex  
129 reactor, where the additional conservation condition of enthalpy flux conser-  
130 vation holds to a good approximation, suggests the very appealing possibility  
131 that scaling problems may be eliminated, in the same way that surface-to-  
132 volume ratios are irrelevant in the single conventional adiabatic reactor, while  
133 good conversion, thermal safety, and direct recovery of reaction heat are also  
134 achieved.

135 An Endex system is a coupled nonlinear dynamical system, and there-  
136 fore has the potential to exhibit thermal instabilities and is capable of more  
137 complex behavior than a single insulated or thermostatted exothermic re-  
138 action system. However, in the work of (1) and (2) it was shown that a  
139 general Endex-configured reaction system can operate stably, autothermally,  
140 and economically, achieving almost full recovery of chemical energy and co-  
141 production of valuable products. The tradeoff is that the stability regime  
142 must be mapped for specific Endex systems in order to avoid or control (or  
143 even, perhaps, exploit) the coupled relaxation oscillator dynamics that are  
144 inherent to coupled dynamical systems.

145 In the proposed Endex reactor the exothermic carbonation reaction  
146  $\text{CaO} + \text{CO}_2 \rightleftharpoons \text{CaCO}_3$  is thermally coupled and kinetically matched with the  
147 reverse reaction, the endothermic calcination reaction  
148  $\text{CaCO}_3 \rightleftharpoons \text{CaO} + \text{CO}_2$ . To show that, in principle, this system can be  
149 operated effectively within a large margin of thermal safety we have carried

150 out a linear stability analysis on the steady-state solutions of a dynamical  
151 model for the reactor.

152 Stability analysis is a valuable reactor system design tool, and an essential  
153 step in the design of thermoreactive systems. Typically we are interested in  
154 running a continuous-flow thermoreactive system at a particular steady state,  
155 or set-point. Stability analysis tells us whether small perturbations around  
156 the steady state—which are inevitable in any real system—will decay and  
157 settle back onto the steady state, or grow in amplitude leading to thermal  
158 oscillations or uncontrollable thermal runaway. When stability analysis is  
159 carried out over a range of the design and operational parameters of the  
160 system it is often called bifurcation analysis, and it can provide a valuable  
161 stability map of the system.

162 The mathematical theory and methodology behind stability analysis are  
163 well-established and accepted. Briefly, at each steady state solution of the  
164 parent dynamical system we construct a dynamical system for the perturba-  
165 tion to that steady state. Since the perturbation is small we can write it as  
166 a Taylor series expansion and retain only the first-order terms. According to  
167 the theory of linear differential equations, the solution can be written as a  
168 superposition of terms of the form  $e^{\lambda_j t}$  where  $\{\lambda_j\}$  is the set of eigenvalues of  
169 the Jacobian matrix of coefficients of the linearized perturbation system. A  
170 nonzero complex part of an eigenvalue contributes an oscillatory component  
171 to the solution. If the real part of an eigenvalue is positive the perturbation  
172 must grow exponentially with time. A stable steady state, therefore, is one  
173 for which *all* the eigenvalues of the Jacobian of the linearized perturbation  
174 system have negative real components.

### 175 **3. Methodology and dynamical model**

#### 176 *3.1. Methodology*

177 The following general procedure for stability analysis of thermoreactive  
178 systems was applied:

- 179 1. Write down dynamical coupled mass and enthalpy balances for the  
180 reaction system.
- 181 2. Choose a primary *bifurcation parameter*, usually a parameter that can  
182 be tuned experimentally, such as an inlet temperature or flow rate.
- 183 3. Compute the steady state solutions as a function of the bifurcation  
184 parameter.

- 185 4. Evaluate the stability of each solution by computing the characteristic  
186 eigenvalues of the linear perturbation at each point.  
187 5. Flag each change in sign of the real parts of the eigenvalues. These are  
188 the singular points.  
189 6. Compute the amplitude, period, and stability of any periodic solutions  
190 as a function of the bifurcation parameter.  
191 7. If appropriate, repeat the analysis using another bifurcation parameter.  
192 If singular points are found compute their loci using a second parameter  
193 to obtain a stability map of the dynamical system.

194 This modelling and analysis was carried out in the well-stirred approxima-  
195 tion. Results from this analysis provide essential guidance for design and  
196 operation of an economically and safety optimised reactor system, and may  
197 be used to inform expensive convective simulations that require substantial  
198 high-performance computational resources.

199 *3.2. Endex-coupled carboniser-calciner: dynamical model*

Enthalpy summation and mass balances for the gas-phase reactant lead to the following dynamical equations for the Endex carboniser-calciner system:

$$V_1 \frac{dc_1}{dt} = -V_1 v_1(T_1, p_1) + F_1(c_{1,\text{in}} - c_1) \quad (1)$$

$$V_1 \bar{C}_1 \frac{dT_1}{dt} = V_1(-\Delta H)v_1(T_1, p_1) + F_1 \bar{C}_{1,\text{g}}(T_{1,\text{in}} - T_1) + (F_s C_s + L_{\text{ex}})(T_2 - T_1) \quad (2)$$

$$V_2 \frac{dc_2}{dt} = -V_2 v_2(T_2, p_2) - F_2 c_2 \quad (3)$$

$$V_2 \bar{C}_2 \frac{dT_2}{dt} = V_2 \Delta H v_2(T_2, p_2) - F_2 \bar{C}_{2,\text{g}} T_2 + (F_s C_s + L_{\text{ex}})(T_1 - T_2). \quad (4)$$

200 The quantities and notation are defined in table A.1, Appendix A. Equations  
201 (1)–(4) describe an Endex system that is heat-coupled through cycling of  
202 loaded and unloaded sorbent between the carboniser (denoted by subscript 1)  
203 and calciner (denoted by subscript 2), and via direct common wall transfer.  
204 The overall system is treated as fully insulated. In reality it is expected that  
205 heat losses to the environment will be small, less than around 5%.



The solid-gas surface reaction rates are functions of temperature, pressure, and of fractional surface coverage  $\theta_i$ , ( $i = 1, 2$ ),

$$v_1(T_1, p_1) = \left( \frac{p_1}{p_{1,\text{eq}}} - 1 \right) \theta_1 \epsilon k(T_1) \zeta_1 S \quad (5)$$

$$v_2(T_2, p_2) = \left( 1 - \frac{p_2}{p_{2,\text{eq}}} \right) (1 - \theta_2) \epsilon k(T_2) \zeta_2 S, \quad (6)$$

206 where  $k(T_i)$ , ( $i = 1, 2$ ) has the usual Arrhenius temperature dependence, and  
207  $\theta_i$  is given by the Langmuir isotherm

$$\theta_i = \frac{\left( \frac{p_i}{p_{i,\text{eq}}} \right)^{1/2}}{1 + \left( \frac{p_i}{p_{i,\text{eq}}} \right)^{1/2}}. \quad (7)$$

208 In this model, the isotherm is based on the  $\text{CO}_2$  molecule occupying two  
209 surface sites and the saturation pressure of  $\text{CO}_2$  is pinned to the equilibrium  
210 pressure of  $\text{CO}_2$  in the sorbent.

### 211 3.3. Data source

212 Physicochemical data and reaction rates for the surface reaction system  
213  $\text{CaO}_{(s)} + \text{CO}_{2(g)} \rightleftharpoons \text{CaCO}_{3(s)}$  were taken from the published literature and  
214 tabulated by (20). The reactor design parameters and solids and gas flow  
215 rates are those given by (20) for a demonstration unit for scrubbing the  
216 emissions from a 5 MW lignite fuelled power plant. Numerical values of data  
217 and quantities used in this analysis are given in table A.1, Appendix A.

## 218 4. Results and discussion

### 219 4.1. Standalone carboniser

The first step in the analysis of the Endex dynamical system, equations (1)–(4), is to analyse the carboniser segment in standalone mode. The dynamics of this system will be a subset of the Endex dynamics. The standalone carboniser is described by the following smaller, simpler dynamical system:

$$V_1 \frac{dc_1}{dt} = -V_1 v_1(T_1, p_1) + F_1(c_{1,\text{in}} - c_1) \quad (1)$$

$$V_1 \bar{C}_1 \frac{dT_1}{dt} = V_1 (-\Delta H) v_1(T_1, p_1) + F_1 \bar{C}_{1,g} (T_{1,\text{in}} - T_1) + F_s C_s (T_{s,\text{in}} - T_1). \quad (8)$$

220 Steady state solutions of equations (1) and (8), using equation 5, were com-  
221 puted as a function of the gas residence time,  $\tau_1 \equiv V_1/F_1$ , and are rendered  
222 in figure 1 in terms of the dynamical variables  $p_1$  (a),  $c_1$  (b), and  $T_1$  (c). The  
223 computations were carried out for four values of the solids flow rate  $F_s$  as in-  
224 dicated. The real parts of the two eigenvalues of the linear perturbation were  
225 positive at each point, thus the steady states are stable within this regime.

226 In (a) the equilibrium partial pressure,  $p_{1,\text{eq}}$ , corresponding to each  $F_s$   
227 has also been plotted as dotted lines. We see that the condition  $p_1 \gg p_{1,\text{eq}}$   
228 holds over the range of residence times considered, thus carbonation proceeds  
229 spontaneously.

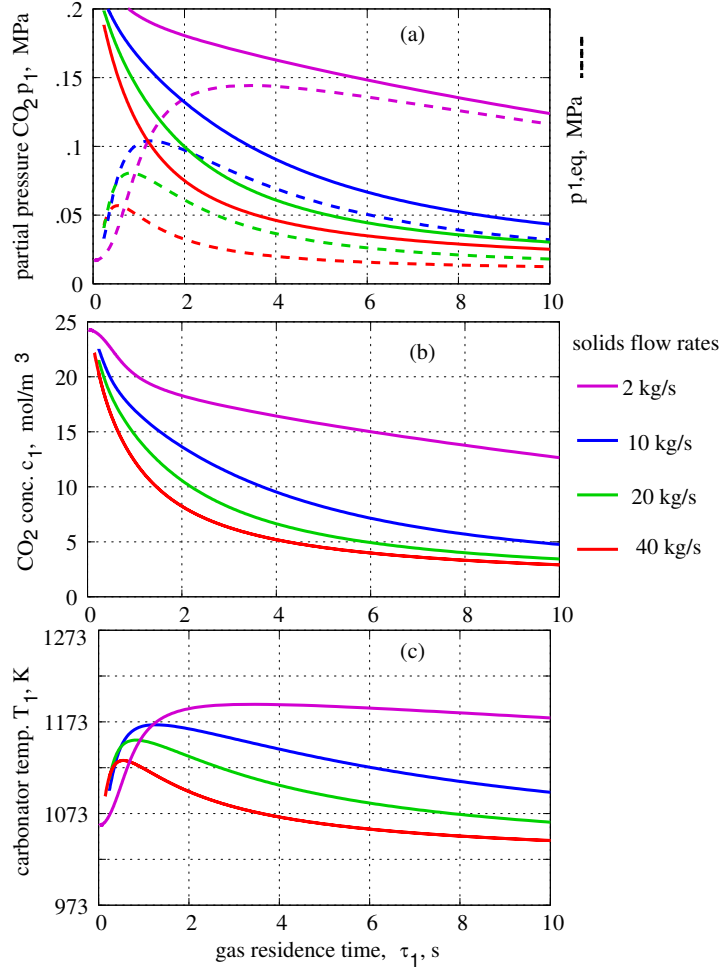


Figure 1: Steady state analysis of the standalone carboniser.  $T_{1,in} = 1060$  K,  $T_{s,in} = 1021$  K.

230 In (b) we see that higher mass flow rates of solid sorbent allow improved  
 231 uptake of the  $\text{CO}_2$  by the sorbent at shorter gas residence times. For exam-  
 232 ple, to achieve a  $\text{CO}_2$  concentration of  $\sim 7$  mol/m<sup>3</sup> (corresponding to a  $\text{CO}_2$   
 233 conversion of 71%) requires a residence time of  $\sim 7.2$  s at a solids flow rate of  
 234 10 kg/s, but only 4 s if the solids flow rate is 20 kg/s.

235 However, if it is desired to maintain the temperature below  $\sim 1123$  K  
 236 and achieve appreciable  $\text{CO}_2$  conversion we see from (c) that gas residence  
 237 times  $> 6$  s and solids flow rates  $> 10$  kg/s are required.

238 *4.2. Endex-coupled carboniser-calciner: analysis*

239 In the standalone carboniser the heat carried by the partially carbonated  
240 sorbent was discarded into the environment. In effect the standalone car-  
241 boniser loses the heat generated by the adsorption reaction to a heat bath  
242 held at the constant temperature  $T_{s,in}$  at the rate indicated by the last term  
243 in equation (8).

244 In the Endex-coupled system, modelled by equations (1)–(4), the heat  
245 generated by adsorption and carried by the partially carbonated sorbent  
246 is recovered directly to drive the calcination of the sorbent. There is no  
247 external thermostat or heat bath; instead, the dynamical temperature of the  
248 carboniser  $T_1$  and that of the calciner  $T_2$  are coupled at the rate indicated  
249 by the last term in equations (2) and (4).

250 *Zero wall heat exchange*

251 Assuming in the first instance that  $L_{ex} = 0$ , i.e., the carboniser and  
252 calciner communicate thermally only via transfer of the sorbent, we have the  
253  $\text{CO}_2$  residence time in the calciner  $\tau_2 \equiv V_2/F_2$  as the only additional tunable  
254 parameter.

255 The first task is to select an optimum range for the gas inlet temperature,  
256  $T_{1,in}$ . The putative set-point for  $T_{1,in}$  is around 1023 K. In figures 2 and 3  
257 steady state solutions of equations 1–4 are plotted with  $T_{1,in}$  as the bifurcation  
258 parameter. The eigenvalue analysis gave the steady states as stable over this  
259 range.

260 In figure 2 the calciner gas residence time  $\tau_{2,gas}$  is set at 30 s, and in  
261 figure 3  $\tau_{2,gas}$  is set at 60 s. The steady state solutions have been computed  
262 and plotted for two values of the carboniser gas residence time  $\tau_{1,gas}$ .

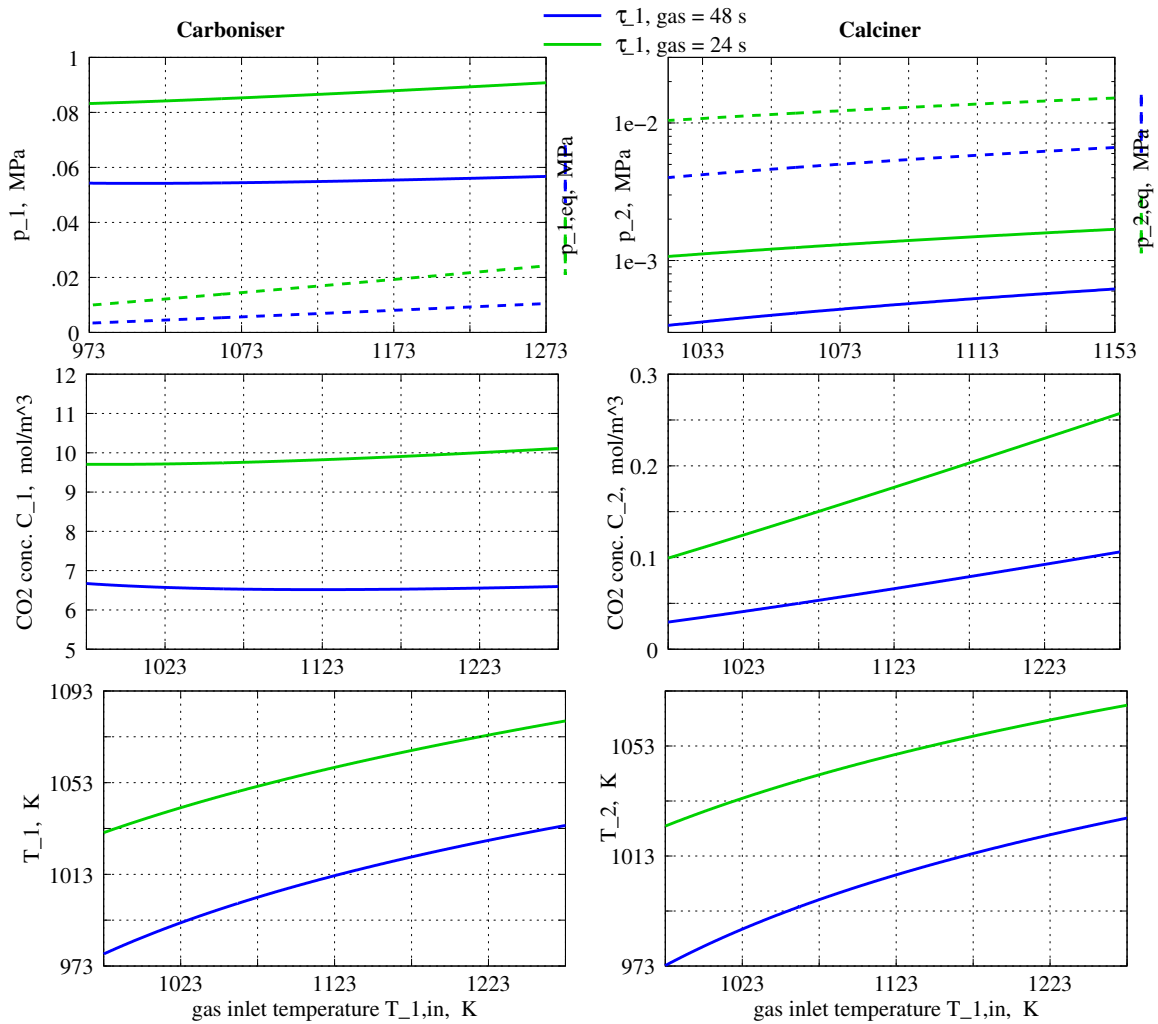


Figure 2: Left subfigures: carboniser, right subfigures: calciner.  $\tau_{2,\text{gas}} = 30$  s.

263 It is interesting to observe that the longer carboniser gas residence time  
 264  $\tau_{1,\text{gas}}$  (blue lines) gives much improved CO<sub>2</sub> uptake by the sorbent over the  
 265 shorter  $\tau_{1,\text{gas}}$  (green lines), yet the dynamical carboniser temperature  $T_1$  is  
 266 depressed. One normally expects that an exothermic reacting system will  
 267 become hotter for higher conversion of the reactant. The occurrence of the

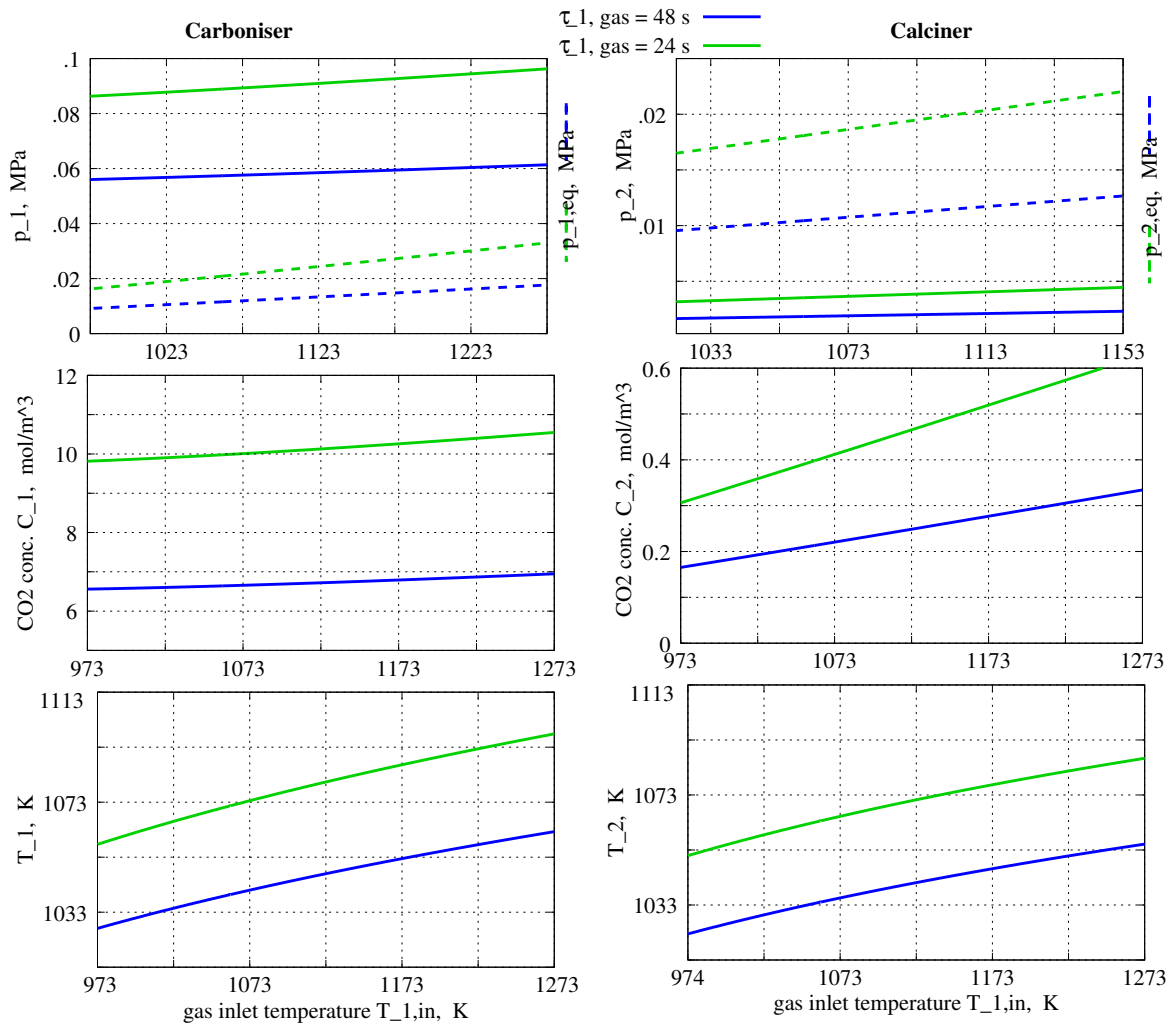


Figure 3: Left subfigures: carboniser, right subfigures: calciner.  $\tau_{2,gas} = 60$  s.

268 back reaction (calcination) at higher conversion of the  $\text{CO}_2$  should work  
 269 against this, but the positive enthalpy change associated with the back re-  
 270 action is not built into equation 4. In this case it is the high rate of thermal  
 271 transport provided by the mass flow of sorbent with high thermal capacitance  
 272 that allows this “temperature inversion”. When the sorbent mass flow rate  
 273  $F_s$  is set to zero, the carboniser and calciner are decoupled and the normal  
 274 increase in  $T_1$  with longer gas residence time occurs.

275 What this means is that the sorbent mass flow is an important control  
 276 tool for the system. We now know, for example, that  $\tau_{1,\text{gas}}$  can be made  
 277 as long as you like without risking overheating of the carboniser, provided  
 278  $F_s$  is maintained above some critical rate. In figure 4 the partial pressure  
 279 steady states are compared for two values of  $F_s$ . The higher sorbent flow  
 rate evidently gives better performance.

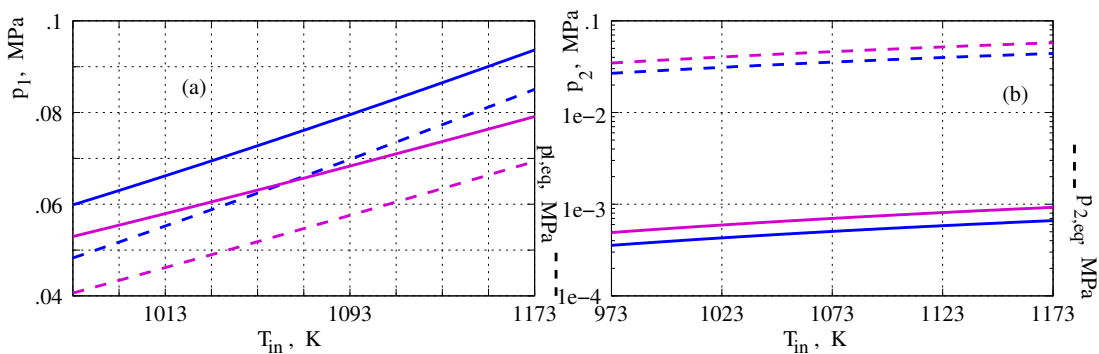


Figure 4: Blue:  $F_s = 10$  kg/s, magenta:  $F_s = 40$  kg/s.  $\tau_{1,\text{gas}} = 15$  s,  $\tau_{2,\text{gas}} = 15$  s,  $L_{\text{ex}} = 0$ .

280

281 Comparing figures 2 and 3 we note another interesting effect of thermal  
 282 coupling of the reactors: the carboniser “sees” the calciner gas residence time  
 283  $\tau_{1,\text{gas}}$ . Since the negative enthalpy change of the back reaction (carbonation)  
 284 is not built into equation 4, it is the longer  $\tau_{1,\text{gas}}$  that results in warmer sorbent  
 285 entering the carboniser at  $T_2$ , which in turn increases  $T_1$ . This improved  
 286 thermal coupling decreases  $T_1 - T_2$ , consistent with the rigorous ideal Endex  
 287 result (1):  $\lim_{\sigma \rightarrow 0} |T_1 - T_2| = 0$ , where  $\sigma = 1/F_s$ .

288 For both figures, in the carboniser segment the condition  $p_1 \gg p_{1,\text{eq}}$  holds  
 289 and in the calciner segment the condition  $p_2 \ll p_{2,\text{eq}}$  holds. The solutions  
 290 are stable over the computed regime. However, dynamical stability—i.e., the  
 291 behaviour of complex conjugate pairs of eigenvalues, or the occurrence of

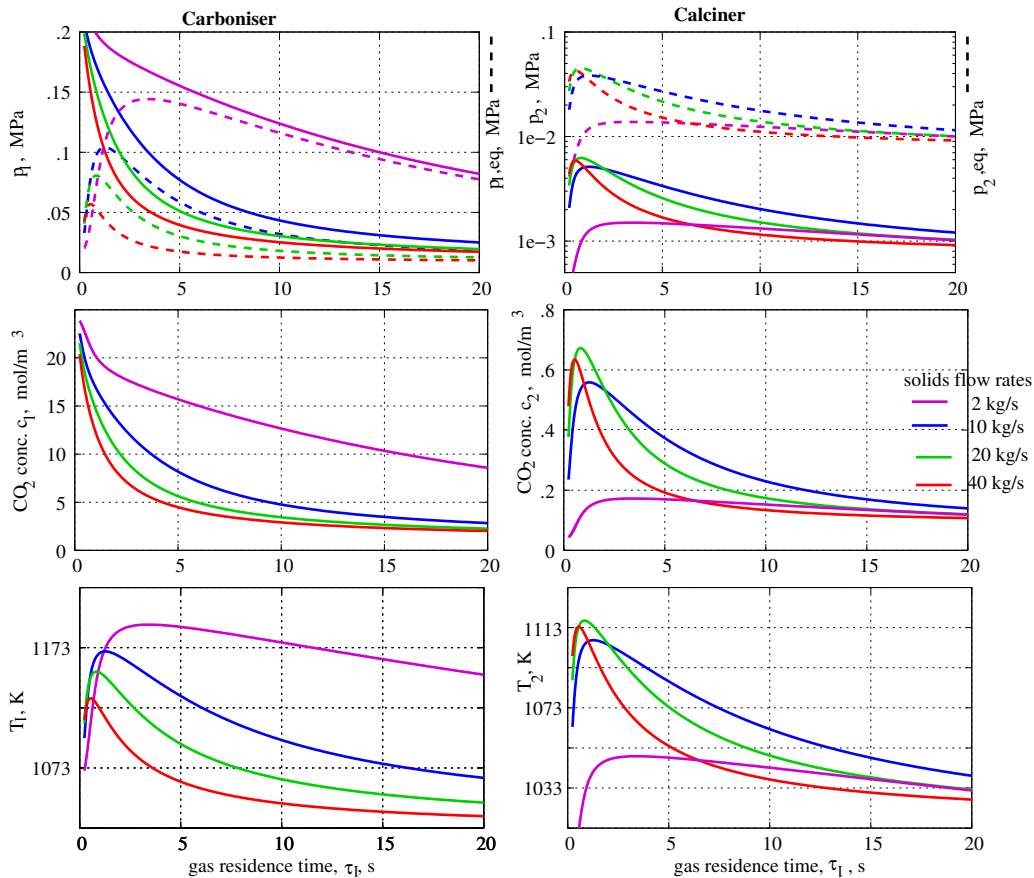


Figure 5: Left subfigures: carboniser, right subfigures: calciner. Endex steady states as a function of carboniser gas residence time  $\tau_{1,\text{gas}}$ .  $\tau_{2,\text{gas}} = 30$  s,  $L_{\text{ex}} = 0$ .

292 Hopf bifurcations—is governed by the volumetric specific heats. A system  
 293 with low thermal capacitance is likely to become thermally unstable, and in  
 294 fact Hopf bifurcations do occur in this system if artificially low specific heats  
 295 are used.

296 The steady state solutions with  $\tau_1$  as bifurcation parameter are plotted in  
 297 figure 5, for four solids flow rates. In the carboniser a residence time greater  
 298 than 10 s is required to achieve a  $\text{CO}_2$  uptake of 90% or more. However,  
 299 residence times longer than about 15 s do not lead to appreciably more uptake  
 300 of  $\text{CO}_2$ .



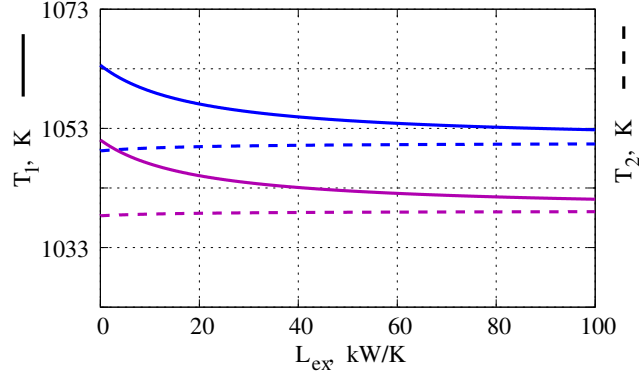


Figure 6: Blue lines:  $\tau_{1,\text{gas}} = 10$  s; Magenta lines:  $\tau_{1,\text{gas}} = 15$  s.  $T_1$  is plotted with solid lines,  $T_2$  with dashed lines.  $\tau_{2,\text{gas}} = 30$  s,  $F_s = 20$  kg/s.

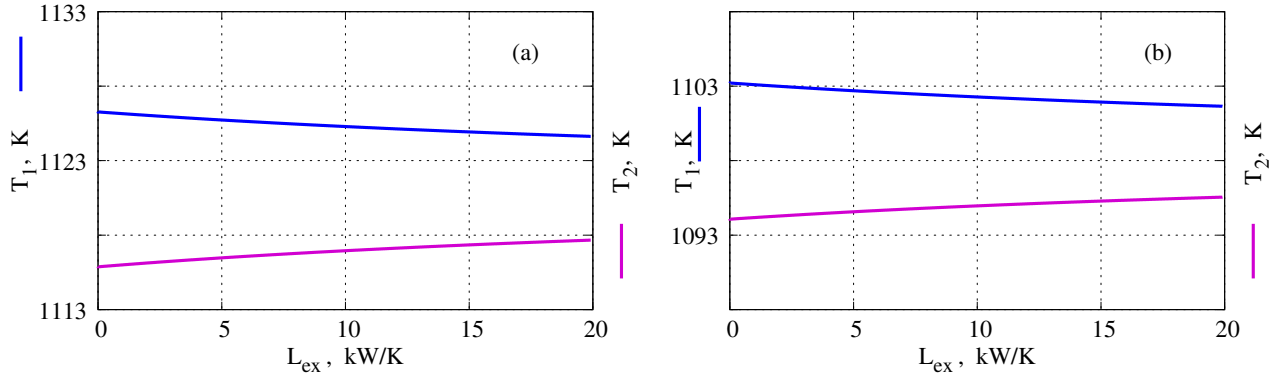


Figure 7: (a)  $\tau_{1,\text{gas}} = 15$  s, (b)  $\tau_{1,\text{gas}} = 20$  s.  $\tau_{2,\text{gas}} = 30$  s,  $F_s = 40$  kg/s.  $T_1$  is plotted with blue lines,  $T_2$  with magenta lines.

### 301 *Non-zero wall heat transfer*

302 In this scenario the carboniser and calciner share a common wall or walls,  
 303 which are also heat exchangers. For cylindrical reactor segments the car-  
 304 boniser cylinder would be embedded in the calciner segment. (The volume  
 305 displacement is negligible and has not been corrected for in this analysis.

306 For the purpose of simulating the effects of wall heat exchange we now  
 307 regard the combined heat transfer coefficient  $L_{\text{ex}}$  as a tunable bifurcation  
 308 parameter, and the steady state solutions are plotted in figures 6 and 7. The  
 309 theoretical limit as  $1/L_{\text{ex}} \rightarrow 0$  is  $T_1 = T_2$ . However a reasonable upper limit  
 310 of  $L_{\text{ex}}$  for this configuration would be around 10 kW/K. It will be shown in

311 subsection **C** below that nonzero wall heat transfer is desirable from safety  
 312 considerations.

313 *Start-up and shut-down dynamics*

314 *Start-up:* The trajectories plotted in figure 8 indicate that full steady  
 315 state operation can be achieved in less than 60s, whiler quasi steady-state  
 316 operation of the carboniser segment is achieved in less than 5s. The time  
 317 lag is due to the much higher effective activation energy for the calcination,  
 318 and it could be reduced by employing operational strategies that achieve  
 319 improved effective kinetic matching of the reactions, for example, increasing  
 the pumpout rate  $F_2$ .

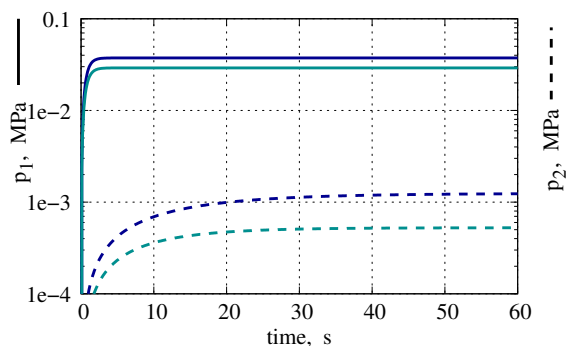


Figure 8: Cyan coloured lines:  $\tau_{2,\text{gas}} = 10$  s. Indigo coloured lines:  $\tau_{2,\text{gas}} = 10$  s. In both cases  $\tau_{1,\text{gas}} = 15$  s,  $F_s = 20$  kg/s,  $L_{\text{ex}} = 0$ . In each case the initial  $\text{CO}_2$  concentrations are zero and the initial temperatures are set equal to the steady state temperatures.

320

321 *Shutdown:* In a normal shutdown scenario the carboniser-calciner shut-  
 322 down dynamics are coupled to the shutdown dynamics of the flue gas gener-  
 323 ator. Assuming the  $\text{CO}_2$  partial pressure  $p_{c,\text{in}}$  at the inlet is reduced linearly  
 324 and quasistatically we may simulate this type of shutdown as a quasi steady-  
 325 state procedure, using  $p_{c,\text{in}}$  as the bifurcation parameter. In figure 9 the  
 326 carboniser partial pressure  $p_1$  ebbs slowly until  $p_{c,\text{in}}$  is about 0.025 MPa then  
 327 drops off dramatically. The calciner gas pressure  $p_2$  declines smoothly as the  
 328 loading of the sorbent declines.

329 *Possible danger:* For an Endex carboniser-calciner reactor system with-  
 330 out wall thermal contact the only channel for heat transfer to the calciner  
 331 is via the sorbent. If the sorbent flow  $F_s$  is interrupted (perhaps by me-  
 332 chanical failure) the cooling capacity of the calciner is unavailable. The

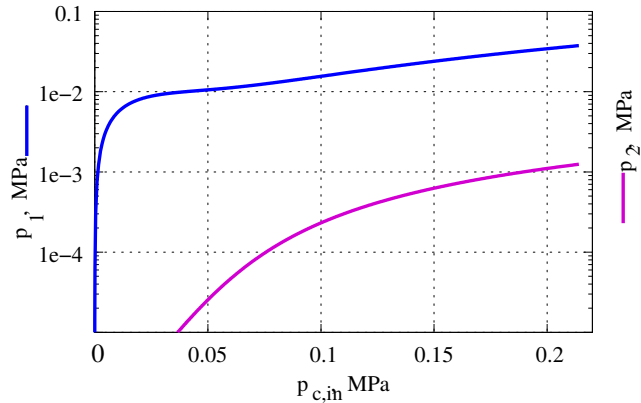


Figure 9: The gas inlet pressure is allowed to ebb quasistatically.  $F_s = 20$  kg/s,  $\tau_{1,gas} = 15$  s,  $\tau_{2,gas} = 15$  s,  $T_{1,in} = 1060$  K,  $L_{ex} = 0$ .

333 only channel for heat removal from the carboniser is then via the outflow of  
 334 scrubbed flue gas. The adiabatic temperature rise for complete conversion of  
 335  $24.28 \text{ mol/m}^{-3}$  of  $\text{CO}_2$  to carbonate is around 650 K. Although a tempera-  
 336 ture rise of this magnitude would not in practice occur, because the scrubbed  
 337 gas outflow would continue to remove heat, the scenario in which  $F_s$  is in-  
 338 terrupted is of concern. It is simulated in figure 10, in which steady state  
 339 operation is interrupted by switching off the solids flow. The time series  
 340 were computed for zero wall heat transfer,  $L_{ex} = 0$ , and for  $L_{ex} = 1, 5$  and  
 341  $10$  kW/K. The thermal excursion is large and dramatic for  $L_{ex} = 0$ , more  
 342 than 80 K and possibly exceeding the safety limits of the vessel. Where the  
 343 calciner and carboniser have efficient wall thermal contact, however, the ther-  
 344 mal excursion is much smaller and quite manageable. In the case of  $L_{ex} =$   
 345  $10$  kW/K the maximum temperature increase of 15 K occurs 100 s after the  
 346 solids flow is switched off, after which the temperature declines slowly.

347 Thus the inclusion of efficient wall thermal contact in the Endex reactor  
 348 design may be an important safety consideration.

#### 349 *D Instabilities in the system*

350 In the subsections above we found that within a broad range of the ex-  
 351 pected normal operating conditions the Endex carboniser-calciner reactor  
 352 is free of instabilities. This raises the question of where, exactly, in the pa-  
 353 rameter space may instability occur in this system, since there are no global

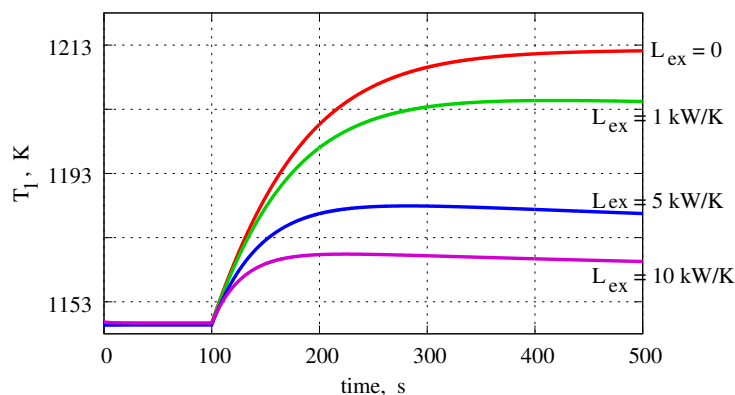


Figure 10: At  $t = 100$  s the solids flow rate  $F_s$  is switched from  $40$  kg/s to zero.  $\tau_{1,\text{gas}} = 15$  s,  $\tau_{2,\text{gas}} = 15$  s,  $T_{1,\text{in}} = 1060$  K.

354 constraints on the nonlinear dynamical system, equations (1)–(4) that forbid  
 355 the occurrence of a positive real eigenvalue part.

356 In fact multiplicity and hysteresis may occur at low temperatures of the  
 gas inlet. In figure 11 the steady states have been computed and plotted

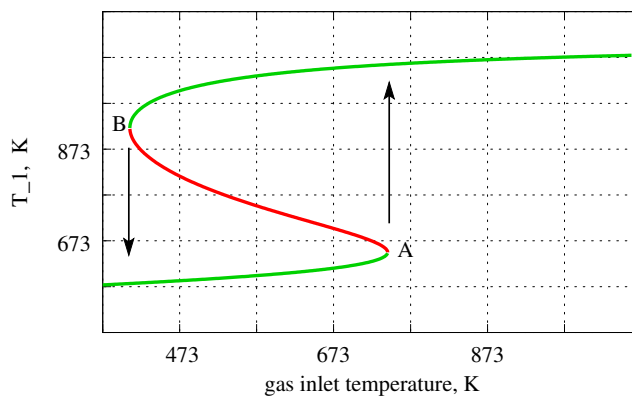


Figure 11: Green curves are the stable steady states, red curves are the unstable steady states.  $F_s = 5$  kg/s,  $\tau_{1,\text{gas}} = 2.4$  s,  $\tau_{2,\text{gas}} = 15$  s,  $L_{\text{ex}} = 0$ .

357  
 358 as a function of the gas inlet temperature  $T_{1,\text{in}}$ . The eigenvalues were also  
 359 monitored, and the stability of the steady states is colour-coded.

360 One may, in principle, carry out an experiment in which the gas inlet  
 361 temperature is increased quasistatically from, say,  $473$  K. On this lower green  
 362 curve the reaction temperature  $T_1$  increases slowly but small perturbations

363 decay. When the gas inlet temperature reaches the value marked A on the  
364 figure the solutions change character. A real eigenvalue passes through zero  
365 and becomes positive. Small perturbations now grow in amplitude. A rapid  
366 transition to the high-temperature stable branch occurs, indicated by an ar-  
367 row on the figure. The inlet temperature may then be tuned up to its normal  
368 set-point at 1060 K, or it may be tuned down along the upper green curve.  
369 When it reaches the point marked B on the figure an abrupt temperature  
370 collapse must occur, since the solutions again lose stability.

371 Although this hysteresis loop may be exploited in start-up and shut-down  
372 procedures, it can be seen that it is not relevant over the normal operating  
373 regime of the reactor.

374 Thermal oscillations associated with nonzero complex components of the  
375 eigenvalues do not occur in this system. This is because such behaviour  
376 is typically governed by the dynamics of the exothermic reaction, i.e., the  
377 left hand side of equation (2). The high thermal capacitance provided by  
378 the solids fraction effectively damps any oscillatory components, or complex  
379 parts of the eigenvalues.

## 380 5. Summary and conclusions

381 A dynamical system model was derived for an Endex coupled carboniser-  
382 calciner housing the  $\text{CaO}/\text{CaCO}_3$  surface reactions, in the well-stirred fully  
383 insulated approximation.

384 Steady state and stability analysis of the carboniser compartment in stan-  
385 dalone mode provided a subset of states from which to begin the more difficult  
386 task of analysing the full Endex system. Approximate lower bounds for the  
387 gas residence time  $\tau_1$  and solids flow rate  $F_s$  were obtained. In the steady  
388 state and stability analysis of the full Endex system it was observed that the  
389 sorbent mass flow rate is an important control parameter, because the ther-  
390 mal transport from carboniser to calciner provided by the sorbent depresses  
391 the carboniser temperature at long gas residence times.

392 The equilibrium partial pressures in carboniser and calciner segments  
393 were monitored. Over the parameter regime studied  $p_{1,\text{eq}} < p_1$  and  $p_{2,\text{eq}} > p_2$ ,  
394 as required by the surface reaction thermokinetics for spontaneous carbona-  
395 tion and calcination respectively.

396 The parameter regime studied is given in the following table:

397

$T_{1,\text{in}}$	973 – 1273 K
$\tau_1$	0.1 – 20 s
$F_s$	10 – 40 kg/s
$\tau_2$	15 – 60 s
$L_{\text{ex}}$	0 – 100 kW/K

398 The real parts of the eigenvalues of the solutions remain negative over the  
399 parameter regime studied, hence steady state operation is stable over these  
400 ranges; i.e., perturbations to the system set-point decay rather than grow.

401 Start-up time to steady state operation was found to be less than 60 s  
402 for initial CO<sub>2</sub> partial pressure of zero and initial temperatures equal to the  
403 steady state temperatures. Quasi steady state operation of the carboniser  
404 segment can be achieved in less than 5 s. The shut-down dynamics of the  
405 reactor were modelled as the gradual decline in pressure of the gas inflow.  
406 The carboniser partial pressure fell slowly until the temperature became too  
407 low to sustain the reaction, whereupon the partial pressure drops off rapidly.

408 Interruption of the sorbent flow was flagged as a possible source of dynam-  
409 ical thermal instability, in a reactor with no or poor wall thermal coupling.  
410 It was found that a reactor design with significant wall heat exchange be-  
411 tween the carboniser and calciner compartments insured against temperature  
412 surges in the carboniser in the event of an interruption to the solids flow.

413 To complete the stability analysis, the location of instabilities in this En-  
414 dex system was pinpointed as a region of thermal multiplicity over tempera-  
415 tures well below the normal operating regime. It was noted that oscillatory  
416 instabilities are fully damped by the high thermal capacitance provided by  
417 the sorbent.

418 These modelling and analysis results confirm that the proposed reactor  
419 configuration for the Calcium Looping reactor is a stable Endex configura-  
420 tion that can, in principle, scrub CO<sub>2</sub> from a flue gas stream efficiently and  
421 regenerate a pure stream of CO<sub>2</sub> for geosequestration without additional en-  
422 ergy requirements. The system has the potential to capture more than 90%  
423 of the CO<sub>2</sub> from flue gas emissions and release it in a pure stream, in a ther-  
424 mally safe reactor that requires no thermostating. The system is stable to  
425 perturbations and exhibits gas switching during start-up.

426 **Appendix A. Notation**

Table A.1: For compactness the subscript  $i$  is used as appropriate, where  $i = 1, 2$ ; 1 refers to the carboniser and 2 refers to the calciner.

$c_i$	concentration of CO <sub>2</sub>	mol/m <sup>3</sup>
$c_{1,\text{in}}$	inflow concentration of CO <sub>2</sub>	$p_{c,\text{in}}/RT_{1,\text{in}} = 24.3 \text{ mol m}^{-3}$
$k(T_i)$	rate constant	$114 \exp(-E/RT_1) \text{ mol}/(\text{m}^3\text{s}^1)$
$p_0$		4.147e06 MPa
$p_{c,\text{in}}$	inlet partial pressure CO <sub>2</sub>	MPa
$p_i$	partial pressure CO <sub>2</sub>	MPa
$p_{i,\text{eq}}$	equilibrium partial pressure of CO <sub>2</sub>	$p_0 \exp(- \Delta H /RT_i) \text{ MPa}$
$v_i$	reaction rate	$\text{mol m}^{-3}\text{s}^{-1}$
$\bar{C}_1$	weighted volumetric specific heat of carboniser contents	$160 \text{ kJ K}^{-1}\text{m}^{-3}$
$\bar{C}_{1,g}$	weighted volumetric specific heat of gas	$5.8 \text{ kJ K}^{-1}\text{m}^{-3}$
$\bar{C}_2$	weighted volumetric specific heat of calciner contents	$25 \text{ kJ K}^{-1}\text{m}^{-3}$
$\bar{C}_{2,g}$	volumetric specific heat of calciner gas	$25 \text{ J K}^{-1}\text{m}^{-3}$
$C_s$	specific heat of sorbent	$975 \text{ J K}^{-1}\text{kg}^{-1}$
$E$	activation energy for calcination	205 kJ/mol
$F_1$	volumetric flow rate of gas into the carboniser	$V_1/\tau_1 \text{ m}^3\text{s}^{-1}$
$F_2$	volumetric outflow rate of gas from the calciner	$V_2/\tau_2 \text{ m}^3\text{s}^{-1}$
$F_s$	mass flow rate of sorbent	$\text{kg s}^{-1}$
$L_{\text{ex}}$	heat exchange rate coefficient	$\text{kW K}^{-1}$
$R$	gas constant	$8.314 \text{ J}/(\text{mol K})$
$S$	surface area	$5e07 \text{ m}^2/\text{m}^3$
$T_i$	reactor segment temperature	K
$T_{1,\text{in}}$	temperature of gas at the inlet	K
$V_1$	internal volume of carboniser	$\pi \times 0.25^2 \times 12 = 2.356 \text{ m}^3$
$V_2$	internal volume of calciner	$\pi \times 2^2 \times 12 = 150.8 \text{ m}^3$
$\Delta H$	reaction enthalpy	$-170 \text{ kJ}/\text{mol CO}_2$
$\epsilon$	porosity of nascent lime	0.51
$\tau_i$	gas residence time	s
$\theta_i$	fractional sorbent surface coverage	
$\zeta_1$	carboniser solid fraction	0.5
$\zeta_2$	calciner solid fraction	0.008

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