Electronic Supplementary Information

Screening and Property Targeting of Thermochemical Energy Storage Materials in Concentrated Solar Power using Thermodynamics-based Insights and Mathematical Optimization

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S1 Reaction list and comparison of properties

Table S1 lists the reactions generated based on stoichiometry. For each of the reactions, equilibrium temperature (T^{eq}) is estimated:

$$T^{eq} = -\frac{\Delta G^r}{R \log p_c^{\nu_c}}$$

where ΔG^r, R, p_C, ν_C are the Gibbs energy of reaction, universal gas constant, partial pressure of gas C, and stoichiometry coefficient, respectively. Partial pressure of gas C in oxide reactions is fixed to 0.21, whereas it is taken to be 1 bar for hydroxide and carbonate reaction systems. Reaction enthalpy (ΔH^r) is also reported and estimated at T^{eq}.

Table S1. List of reaction considered and their estimated properties.

No.	Reactions	T^{eq} (K)	ΔH^r (kJ/mol)
1	$Mn_2O_3 <--> 0.66667\ Mn_3O_4 + 0.16667\ O_2$	1174.1	32.136
2	$Mn_2O_3 <--> 2\ MnO + 0.5\ O_2$	1646.7	173.85
3	$MnO_2 <--> 0.5\ Mn_2O_3 + 0.25\ O_2$	717.69	39.764
4	$Mn_3O_4 <--> 3\ MnO + 0.5\ O_2$	1846.2	196.46
5	$MnO_2 <--> 0.33333\ Mn_3O_4 + 0.33333\ O_2$	809.44	56.15
6	$V_2O_5 <--> V_2O_4 + 0.5\ O_2$	1835.4	174.72
7	$V_2O_5 <--> V_2O_3 + O_2$	2405.1	384.59
8	$V_2O_5 <--> 2\ VO_2 + 0.5\ O_2$	2714.6	886.8
9	$V_2O_5 <--> 2\ VO + 1.5\ O_2$	2945	717.73
10	$V_2O_4 <--> V_2O_3 + 0.5\ O_2$	3680.7	139.68
11	$V_2O_4 <--> 2\ VO + O_2$	3909.6	451.06
12	$BaO_2 <--> BaO + 0.5\ O_2$	1015.3	80.479
13	$CuO <--> 0.5\ Cu_2O + 0.25\ O_2$	1304.9	64.907
14	$Fe_2O_3 <--> 0.66667\ Fe_3O_4 + 0.16667\ O_2$	1613.1	77.754
15	$Fe_2O_3 <--> 2\ FeO + 0.5\ O_2$	2011.9	319.48
16	$Fe_3O_4 <--> 3\ FeO + 0.5\ O_2$	2431.4	229.07
17	SrO2 $<--> SrO + 0.5\ O_2$	393.51	40.425
18	$MnO_2 <--> MnO + 0.5\ O_2$	1178.7	131.17
19	$RhO_2 <--> 0.5\ Rh_2O_3 + 0.25\ O_2$	38.006	-19.778
20	$Li_2O_2 <--> Li_2O + 0.5\ O_2$	374.75	33.702
21	$LiO <--> 0.5\ Li_2O + 0.25\ O_2$	3413	-298.33
22	$CrO_3 <--> 0.5\ Cr_2O_3 + 0.75\ O_2$	149.23	19.338
23	$CrO_2 <--> 0.5\ Cr_2O_3 + 0.25\ O_2$	73163	1.03E+05
24	$Cr_2O_3 <--> 2\ CrO + 0.5\ O_2$	3483.2	1240.3
25	$PbO_2 <--> PbO + 0.5\ O_2$	532.88	54.465
26	PbO_2 $<--> 0.33333\ Pb_3O_4 + 0.33333\ O_2$	487.73	34.855
27	$Sb_2O_5 <--> Sb_2O_4 + 0.5\ O_2$	570.22	67.489

28	$Sb_2O_5 < --> 2\ SbO + 1.5\ O_2$	1139.1	755.25
29	$Sb_2O_5 < --> Sb_2O_3 + O_2$	1095.7	341.34
30	$Sb_2O_5 < --> 0.5\ Sb_4O_6 + O_2$	1143.1	371.04
31	$Pb_3O_4 < --> 3\ PbO + 0.5\ O_2$	638.72	57.949
32	$Sb_2O_4 < --> 2\ SbO + O_2$	1271.7	675.31
33	$Sb_2O_4 < --> Sb_2O_3 + 0.5\ O_2$	1441.4	277.85
34	$Sb_2O_4 < --> 0.5\ Sb_4O_6 + 0.5\ O_2$	1508.7	292.71
35	$UO_3 < --> 0.33333\ U_3O_8 + 0.16667\ O_2$	860.96	34.881
36	$UO_3 < --> 0.25\ U_4O_9 + 0.375\ O_2$	1340.3	98.232
37	$UO_3 < --> UO_2 + 0.5\ O_2$	1544.4	139.18
38	$U_3O_8 < --> 0.75\ U_4O_9 + 0.625\ O_2$	2066.7	180.41
39	$U_3O_8 < --> 3\ UO_2 + O_2$	2260.8	278.36
40	$Na_2O_2 < --> Na_2O + 0.5\ O_2$	1141.2	87.077
41	$NaO_2 < --> 0.5\ Na_2O + 0.75\ O_2$	632.37	46.146
42	$NaO < --> 0.5\ Na_2O + 0.25\ O_2$	2770	-213.11
43	$NaO_2 < --> 0.5\ Na_2O_2 + 0.5\ O_2$	120.96	5.9705
44	$NaO_2 < --> NaO + 0.5\ O_2$	1817.3	270.81
45	$AlO_2 < --> 0.5\ Al_2O_3 + 0.25\ O_2$	5064.2	-449.07
46	$AlO_2 < --> 0.5\ Al_2O_2 + 0.5\ O_2$	24.604	73.764
47	$AlO_2 < --> 0.5\ Al_2O + 0.75\ O_2$	2906.8	114.71
48	$Al_2O_3 < --> Al_2O_2 + 0.5\ O_2$	4875.1	843.8
49	$Al_2O_3 < --> Al_2O + O_2$	4417.4	1182.6
50	$Al_2O_2 < --> Al_2O + 0.5\ O_2$	3474	299.25
51	$SiO_2 < --> SiO + 0.5\ O_2$	3184.2	735.54
52	$Co_3O_4 < --> 3\ CoO + 0.5\ O_2$	1166.1	197.78
53	$CrO_3 < --> CrO_2 + 0.5\ O2$	7.7802	154.61
54	$CrO_3 < --> CrO + O_2$	2547.1	651.31
55	$KO_2 < --> 0.5\ K_2O_2 + 0.5\ O_2$	1158.8	22.337
56	$K_2O_2 < --> K_2O + 0.5\ O_2$	1343.7	167.17
57	$KO_2 < --> KO + 0.5\ O_2$	1871.2	300.17
58	$KO_2 < --> 0.5\ K_2O + 0.75\ O_2$	1304	96.809
59	$KO < --> 0.5\ K_2O + 0.25\ O_2$	2345.2	-196.81
60	$CaO_2 < --> CaO + 0.5\ O_2$	277.86	18.128
61	$TiO_2 < --> 0.5\ Ti_2O_3 + 0.25\ O_2$	3864.6	161.3
62	$Ti_2O_3 < --> 2\ TiO + 0.5\ O_2$	5120.6	407.32
63	$Ti_3O_5 < --> 1.5\ Ti_2O_3 + 0.25\ O_2$	26855	1477.6
64	$Ti_4O_7 < --> 2\ Ti_2O_3 + 0.5\ O2$	6042.6	230.33
65	$TiO_2 < --> TiO + 0.5\ O_2$	4484.6	358.38
66	$TiO_2 < --> 0.33333\ Ti_3O_5 + 0.16667\ O_2$	3152.6	123.72
67	$TiO_2 < --> 0.25\ Ti_4O_7 + 0.125\ O_2$	3018.8	88.533
68	$Ti_3O_5 < --> 3\ TiO + O_2$	5728.7	691.21
69	$Ti_4O_7 < --> 4\ TiO + 1.5\ O_2$	5306.5	1068.3

70	$Ti_4O_7 <--> 1.3333\ Ti_3O_5 + 0.16667\ O_2$	3544.2	140.81
71	$VO_2 <--> 0.5\ V_2O_3 + 0.25\ O_2$	3019.1	-241.06
72	$V_2O_3 <--> 2\ VO + 0.5\ O_2$	4015.8	318.46
73	$VO_2 <--> VO + 0.5\ O_2$	2080.8	-99.259
74	$CrO_2 <--> CrO + 0.5\ O_2$	3970.1	510.35
75	$GaO <--> 0.5\ Ga_2O + 0.25\ O_2$	4079.2	-222.39
76	$Ga_2O_3 <--> Ga_2O + O_2$	2720.3	762.97
77	$Ga_2O_3 <--> 2\ GaO + 0.5\ O_2$	3105.2	1166.1
78	$GeO_2 <--> GeO + 0.5\ O_2$	1988.5	463.65
79	$As_2O_3 <--> 2\ AsO + 0.5\ O_2$	9.1384	246
80	$As_2O_5 <--> 2\ AsO + 1.5\ O_2$	1230.3	752.14
81	$As_4O_6 <--> 4\ AsO + O_2$	1366.7	925.76
82	$As_2O_5 <--> As_2O_3 + O_2$	90782	9.90E+05
83	$As_2O_5 <--> 0.5\ As_4O_6 + O_2$	1062.5	299.57
84	$SeO_2 <--> SeO + 0.5\ O_2$	1093.4	261.16
85	$RbO_2 <--> 0.5\ Rb_2O + 0.75\ O_2$	1411.3	78.472
86	$ZrO_2 <--> ZrO + 0.5\ O_2$	4674	1023.9
87	$Nb_2O_5 <--> 2\ NbO_2 + 0.5\ O_2$	3654	331.03
88	$Nb_2O_5 <--> 2\ NbO + 1.5\ O_2$	4333.3	953.56
89	$NbO_2 <--> NbO + 0.5\ O_2$	4777.5	317.97
90	$MoO_2 <--> MoO + 0.5\ O_2$	3376.8	737.47
91	$MoO_3 <--> MoO_2 + 0.5\ O_2$	4103.4	218.94
92	$MoO_3 <--> MoO + O_2$	3496.9	865.24
93	$Tc_2O_7 <--> 2\ TcO_2 + 1.5\ O_2$	995.25	158.82
94	$Tc_2O_7 <--> 2\ TcO_3 + 0.5\ O_2$	393	34.149
95	$TcO_3 <--> TcO_2 + 0.5\ O_2$	1227	42.06
96	$RuO_4 <--> RuO_2 + O_2$	10.621	275.75
97	$RuO_3 <--> RuO_2 + 0.5\ O_2$	2970.7	-139.11
98	$RuO_4 <--> RuO_3 + 0.5\ O_2$	1155.8	100.99
99	$In_2O_3 <--> In_2O + O_2$	2300.2	784.9
100	$SnO_2 <--> SnO + 0.5\ O_2$	2633.7	285.79
101	$Sb_2O_3 <--> 2\ SbO + 0.5\ O_2$	1177.9	409.1
102	$Sb_4O_6 <--> 4\ SbO + O_2$	1135.2	768.69
103	$CeO_2 <--> CeO + 0.5\ O_2$	3915.9	771.64
104	$PrO_2 <--> 0.14286\ Pr_7O_{12} + 0.14286\ O_2$	690.92	13.759
105	$Pr_7O_{12} <--> 3.5\ Pr_2O_3 + 0.75\ O_2$	1131.4	186.46
106	$PrO_2 <--> 0.5\ Pr_2O_3 + 0.25\ O_2$	947.26	35.203
107	$CsO_2 <--> 0.5\ Cs_2O + 0.75\ O_2$	1452.7	85.226
108	$La_2O_3 <--> 2\ LaO + 0.5\ O_2$	4106.9	1274.2
109	$TbO_2 <--> 0.5\ Tb_2O_3 + 0.25\ O_2$	765.24	39.378
110	$TbO_{1.72} <--> 0.5\ Tb_2O_3 + 0.11\ O_2$	931.21	20.02
111	$TbO_{1.81} <--> 0.5\ Tb_2O_3 + 0.155\ O_2$	928.46	28.928
112	$TbO_2 <--> TbO_{1.72} + 0.14\ O_2$	641.59	18.716
113	$TbO_2 <--> TbO_{1.81} + 0.095\ O_2$	504.15	9.7468
114	$TbO_{1.81} <--> TbO_{1.72} + 0.045\ O_2$	922.33	8.8912
115	$ThO_2 <--> ThO + 0.5\ O_2$	4991	1046.7

116	$U_4O_9 <--> 4\,UO_2 + 0.5\,O_2$	2856.5	101.48
117	$PuO_2 <--> 0.5\,Pu_2O_3 + 0.25\,O_2$	2220.4	163.99
118	$Pu_2O_3 <--> 2\,PuO + 0.5\,O_2$	9.4951	-1333.5
119	$PuO_2 <--> PuO + 0.5\,O_2$	6713.8	372.18
120	$Ta_2O_5 <--> 2\,TaO_2 + 0.5\,O_2$	4030.8	1222.4
121	$Ta_2O_5 <--> 2\,TaO + 1.5\,O_2$	4518.8	2004.3
122	$TaO_2 <--> TaO + 0.5\,O_2$	5459.3	430.12
123	$W_2O_6 <--> 0.66667\,W_3O_8 + 0.33333\,O_2$	36.217	-64.501
124	$W_2O_6 <--> 2\,WO_{2.72} + 0.28\,O_2$	1905.9	-363.04
125	$W_2O_6 <--> 2\,WO_{2.9} + 0.1\,O_2$	2023.9	-433.11
126	$W_2O_6 <--> 2\,WO_{2.96} + 0.04\,O_2$	2073.2	-459.17
127	$W_2O_6 <--> 2\,WO_2 + O_2$	153.92	-13.651
128	$W_2O_6 <--> 2\,WO + 2\,O_2$	4505	1890.9
129	$W_4O_{12} <--> 1.3333\,W_3O_8 + 0.66667\,O_2$	2956.7	485.6
130	$W_4O_{12} <--> 4\,WO_{2.72} + 0.56\,O_2$	1563.1	-291.88
131	$W_4O_{12} <--> 4\,WO_{2.9} + 0.2\,O_2$	1857.1	-424.83
132	$W_4O_{12} <--> 4\,WO_{2.96} + 0.08\,O_2$	1958.5	-474.52
133	$W_4O_{12} <--> 4\,WO_2 + 2\,O_2$	3233	328.4
134	$W_4O_{12} <--> 4\,WO + 4\,O_2$	4066.2	4216.5
135	$W_3O_9 <--> W_3O_8 + 0.5\,O_2$	3512.9	294.63
136	$W_3O_9 <--> 3\,WO_{2.72} + 0.42\,O_2$	1610.1	-289.73
137	$W_3O_9 <--> 3\,WO_{2.9} + 0.15\,O_2$	1840.5	-391.21
138	$W_3O_9 <--> 3\,WO_{2.96} + 0.06\,O_2$	1924.3	-429.16
139	$W_3O_9 <--> 3\,WO_2 + 1.5\,O_2$	-1443.2	426.06
140	$W_3O_9 <--> 3\,WO + 3\,O_2$	4186.2	3096
141	$WO_{2.72} <--> 0.33333\,W_3O_8 + 0.026667\,O_2$	2242.1	184.77
142	$WO_{2.9} <--> 0.33333\,W_3O_8 + 0.11667\,O_2$	2329.6	220.21
143	$WO_{2.96} <--> 0.33333\,W_3O_8 + 0.14667\,O_2$	2371.8	233.18
144	$W_3O_8 <--> 3\,WO_2 + O_2$	474.07	-59.706
145	$W_3O_8 <--> 3\,WO + 2.5\,O_2$	4271.8	2801.6
146	$WO_3 <--> 0.33333\,W_3O_8 + 0.16667\,O_2$	2939.6	135.05
147	$WO_{2.9} <--> WO_{2.72} + 0.09\,O_2$	2875.1	37.887
148	$WO_{2.96} <--> WO_{2.72} + 0.12\,O_2$	2982	51.835
149	$WO_{2.72} <--> WO_2 + 0.36\,O_2$	15.558	-406.57
150	$WO_{2.72} <--> WO + 0.86\,O_2$	3760.5	1072.2
151	$WO_3 <--> WO_{2.72} + 0.14\,O_2$	15276	893.93
152	$WO_{2.96} <--> WO_{2.9} + 0.03\,O_2$	3320.5	13.78
153	$WO_{2.9} <--> WO_2 + 0.45\,O_2$	14.222	-481.31
154	$WO_{2.9} <--> WO + 0.95\,O_2$	3721.1	1113.1
155	$WO_3 <--> WO_{2.9} + 0.05\,O_2$	19116	1408.6
156	$WO_{2.96} <--> WO_2 + 0.48\,O_2$	3709.7	-0.41559
157	$WO_{2.96} <--> WO + 0.98\,O_2$	3715.6	1127

160	$WO_3 <--> WO_{2.96} + 0.02\ O_2$	20129	1549
161	$WO_2 <--> WO + 0.5\ O_2$	3715.4	1130.4
162	$WO_3 <--> WO_2 + 0.5\ O_2$	13.344	-532.46
163	$WO_3 <--> WO + O_2$	4069.5	1026.6
164	$ReO_3 <--> ReO_2 + 0.5\ O_2$	1775.3	124.29
165	$Re_2O_7 <--> 2\ ReO_3 + 0.5\ O_2$	37.466	-225.19
166	$Re_2O_7 <--> 2\ ReO_2 + 1.5\ O_2$	7842.2	527.61
167	$Mn_2O_3 <--> 2\ Mn + 1.5\ O_2$	3450.2	902.63
168	$Mn_3O_4 <--> 3\ Mn + 2\ O_2$	3641.1	1421.1
169	$V_2O_5 <--> 2\ V + 2.5\ O_2$	4028.1	1463.3
170	$V_2O_4 <--> 2\ V + 2\ O_2$	5116.8	1146.3
171	$BaO_2 <--> Ba + O_2$	47372	61591
172	$BaO <--> Ba + 0.5\ O_2$	-1949.6	985.31
173	$Cu_2O <--> 2\ Cu + 0.5\ O_2$	2477.6	110.2
174	$CuO <--> Cu + 0.5\ O_2$	1647	157.89
175	$Fe_2O_3 <--> 2\ Fe + 1.5\ O_2$	2945.3	920.67
176	$Fe_3O_4 <--> 3\ Fe + 2\ O_2$	3633.8	996.77
177	$SrO <--> Sr + 0.5\ O_2$	6639.3	465.98
178	$MnO <--> Mn + 0.5\ O_2$	4849.7	377.29
179	$Rh_2O_3 <--> 2\ Rh + 1.5\ O_2$	1304.3	332.07
180	$RhO_2 <--> Rh + O_2$	-1665.7	352.25
181	$Li_2O_2 <--> 2\ Li + O_2$	91553	1.03E+06
182	$Li_2O <--> 2\ Li + 0.5\ O_2$	10.55	-1219.2
183	$Cr_2O_3 <--> 2\ Cr + 1.5\ O_2$	4374.6	1003.3
184	$PbO_2 <--> Pb + O_2$	1322.6	265.29
185	$Sb_2O_5 <--> 2\ Sb + 2.5\ O_2$	1806	1028.1
186	$PbO <--> Pb + 0.5\ O_2$	20.531	-520.99
187	$Sb_2O_4 <--> 2\ Sb + 2\ O_2$	2180.7	933.33
188	$UO_3 <--> U + 1.5\ O_2$	4461.9	1195
189	$U_3O_8 <--> 3\ U + 4\ O_2$	5458.1	3136.7
190	$Na_2O <--> 2\ Na + 0.5\ O_2$	3760.6	444.23
191	$Na_2O_2 <--> 2\ Na + O_2$	2353	496.77
192	$NaO_2 <--> Na + O_2$	1957.5	197.2
193	$AlO_2 <--> Al + O_2$	7513.1	275.08
194	$Al_2O_3 <--> 2\ Al + 1.5\ O_2$	5767.5	1331
195	$Al_2O_2 <--> 2\ Al + O_2$	7701.1	618.06
196	$Al_2O <--> 2\ Al + 0.5\ O_2$	-699.32	216.84
197	$SiO_2 <--> Si + O_2$	4680.5	884.81
198	$SiO <--> Si + 0.5\ O_2$	-1017.8	129.11
199	$CoO <--> Co + 0.5\ O_2$	3336.5	190.79
200	$Co_3O_4 <--> 3\ Co + 2\ O_2$	2299.9	821.2
201	$FeO <--> Fe + 0.5\ O_2$	4296.4	250.45
202	$MnO_2 <--> Mn + O_2$	2632.5	529.49
203	$CrO_3 <--> Cr + 1.5\ O_2$	2775.3	514.5
204	$K_2O_2 <--> 2\ K + O_2$	1951.4	787.56
205	$KO_2 <--> K + O_2$	2038.1	251.82
206	$LiO <--> Li + 0.5\ O_2$	1358.3	-71.349
207	$NaO <--> Na + 0.5\ O_2$	1498.3	-69.871

208	$KO \Longleftrightarrow K + 0.5\,O_2$	1358.6	-58.286
209	$K_2O \Longleftrightarrow 2\,K + 0.5\,O_2$	2988.4	364.67
210	$CaO_2 \Longleftrightarrow Ca + O_2$	4367.3	599.98
211	$CaO \Longleftrightarrow Ca + 0.5\,O_2$	6837.4	496.72
212	$Ti_2O_3 \Longleftrightarrow 2\,Ti + 1.5\,O_2$	6452.5	1296.2
213	$TiO_2 \Longleftrightarrow Ti + O_2$	5727	795.11
214	$TiO \Longleftrightarrow Ti + 0.5\,O_2$	7330	438.19
215	$Ti_3O_5 \Longleftrightarrow 3\,Ti + 2.5\,O_2$	6693.9	1999.2
216	$V_2O_3 \Longleftrightarrow 2\,V + 1.5\,O_2$	5347.7	1055.6
217	$VO2 \Longleftrightarrow V + O_2$	-2264.8	534.23
218	$VO \Longleftrightarrow V + 0.5\,O_2$	6202.2	376.28
219	$CrO_2 \Longleftrightarrow Cr + O_2$	35037	14412
220	$CrO \Longleftrightarrow Cr + 0.5\,O_2$	1962.8	-161.07
221	$Ga_2O \Longleftrightarrow 2\,Ga + 0.5\,O_2$	-241.37	156.66
222	$GaO \Longleftrightarrow Ga + 0.5\,O_2$	2248.3	-137.62
223	$Ga_2O_3 \Longleftrightarrow 2\,Ga + 1.5\,O_2$	25557	6876.9
224	$GeO_2 \Longleftrightarrow Ge + O_2$	2920.6	535.33
225	$GeO \Longleftrightarrow Ge + 0.5\,O_2$	-532.64	57.143
226	$AsO \Longleftrightarrow As + 0.5\,O_2$	-613.36	78.044
227	$As_2O_3 \Longleftrightarrow 2\,As + 1.5\,O_2$	38.653	40.797
228	$As_2O_5 \Longleftrightarrow 2\,As + 2.5\,O_2$	1942.7	849.73
229	$As_4O_6 \Longleftrightarrow 4\,As + 3\,O_2$	2670.2	2227.4
230	$SeO_2 \Longleftrightarrow Se + O_2$	1163.7	213.84
231	$SeO \Longleftrightarrow Se + 0.5\,O_2$	855.19	-48.541
232	$Rb_2O \Longleftrightarrow 2\,Rb + 0.5\,O_2$	2866.4	350.51
233	$RbO_2 \Longleftrightarrow Rb + O_2$	2172.7	220.9
234	$SrO_2 \Longleftrightarrow Sr + O_2$	4396.4	211.72
235	$ZrO_2 \Longleftrightarrow Zr + O_2$	5989.1	1005.1
236	$ZrO \Longleftrightarrow Zr + 0.5\,O_2$	764.4	-54.53
237	$Nb_2O_5 \Longleftrightarrow 2\,Nb + 2.5\,O_2$	4953.5	1566.1
238	$NbO_2 \Longleftrightarrow Nb + O_2$	5427.2	630.59
239	$NbO \Longleftrightarrow Nb + 0.5\,O_2$	6277.6	312.95
240	$MoO_2 \Longleftrightarrow MO + O_2$	3323.4	520.95
241	$MoO \Longleftrightarrow MO + 0.5\,O_2$	3509.4	-219.06
242	$MoO_3 \Longleftrightarrow MO + 1.5\,O_2$	3492.6	646.02
243	$Tc_2O_7 \Longleftrightarrow 2\,Tc + 3.5\,O_2$	1950.5	954.38
244	$TcO_2 \Longleftrightarrow Tc + O_2$	2357.8	404.38
245	$TcO_3 \Longleftrightarrow Tc + 1.5\,O_2$	72753	5.81E+05
246	$RuO_2 \Longleftrightarrow Ru + O_2$	1797.7	268.37
247	$RuO_4 \Longleftrightarrow Ru + 2\,O_2$	1070.6	179.7
248	$RuO_3 \Longleftrightarrow Ru + 1.5\,O_2$	977.36	78.112
249	$In_2O \Longleftrightarrow 2\,In + 0.5\,O_2$	-383.31	121.89
250	$In_2O_3 \Longleftrightarrow 2\,In + 1.5\,O_2$	4498.1	574.09
251	$SnO_2 \Longleftrightarrow Sn + O_2$	2739.1	534.62
252	$SnO \Longleftrightarrow Sn + 0.5\,O_2$	2871.1	246.37
253	$SbO \Longleftrightarrow Sb + 0.5\,O_2$	31935	7043.2
254	$Sb_2O_3 \Longleftrightarrow 2\,Sb + 1.5\,O_2$	2864.4	606.9
255	$Sb_4O_6 \Longleftrightarrow 4\,Sb + 3\,O_2$	2734.7	1279.9

256	$CeO_2 <--> Ce + O_2$	5424.1	951.45
257	$CeO <--> Ce + 0.5\,O_2$	-1258.3	181.39
258	$Pr_7O_{12} <--> 7\,Pr + 6\,O_2$	5740.6	5412.4
259	$PrO_2 <--> Pr + O_2$	7551.1	288.06
260	$Pr_2O_3 <--> 2\,Pr + 1.5\,O_2$	6701	1400.1
261	$CsO_2 <--> Cs + O_2$	2100.6	214
262	$Cs_2O <--> 2\,Cs + 0.5\,O_2$	2758.5	259.26
263	$LaO <--> La + 0.5\,O_2$	-1256.1	159.57
264	$La_2O_3 <--> 2\,La + 1.5\,O_2$	6647.6	1598.3
265	$Tb_2O_3 <--> 2\,Tb + 1.5\,O_2$	5993.1	2457.9
266	$TbO_2 <--> Tb + O_2$	5136.7	838.39
267	$TBO_{1.72} <--> TB + 0.86\,O_2$	6449.7	676.01
268	$TBO_{1.81} <--> TB + 0.905\,O_2$	5627.5	841.93
269	$ThO_2 <--> Th + O_2$	6215.9	1171.2
270	$ThO <--> Th + 0.5\,O_2$	-366.19	43.927
271	$U_4O_9 <--> 4\,U + 4.5\,O_2$	5787.6	4325.2
272	$UO_2 <--> U + O_2$	7480	773.49
273	$Pu_2O_3 <--> 2\,Pu + 1.5\,O_2$	4.2962	-3411.2
274	$PuO_2 <--> Pu + O_2$	6475.1	856.79
275	$PuO <--> Pu + 0.5\,O_2$	6307.5	496.57
276	$Ta_2O_5 <--> 2\,Ta + 2.5\,O_2$	5359.3	1719.8
277	$TaO_2 <--> Ta + O_2$	-2047.9	429.39
278	$TaO <--> Ta + 0.5\,O_2$	2384.2	-175.79
279	$W_2O_6 <--> 2\,W + 3\,O_2$	4192.8	1243.5
280	$W_4O_{12} <--> 4\,W + 6\,O_2$	3692.1	2900.6
281	$W_3O_9 <--> 3\,W + 4.5\,O_2$	3827.7	2112.9
282	$W_3O_8 <--> 3\,W + 4\,O_2$	3883.9	1820.5
283	$WO_{2.72} <--> W + 1.36\,O_2$	3328.1	712.03
284	$WO_{2.9} <--> W + 1.45\,O_2$	3301.7	750.79
285	$WO_{2.96} <--> W + 1.48\,O_2$	3302	764.57
286	$WO_2 <--> W + O_2$	3250.1	601.72
287	$WO <--> W + 0.5\,O_2$	5279.7	-309.93
288	$WO_3 <--> W + 1.5\,O_2$	3686.3	711.58
289	$ReO_3 <--> Re + 1.5\,O_2$	2168.6	539.15
290	$ReO_2 <--> Re + O_2$	2319.3	415.47
291	$Re_2O_7 <--> 2\,Re + 3.5\,O_2$	2777	1006.8
292	$IrO_2 <--> Ir + O_2$	1311.5	226.02
293	$IrO_3 <--> Ir + 1.5\,O_2$	26.102	47.791
294	$Ti_4O_7 <--> 4\,Ti + 3.5\,O_2$	6417.8	2812
295	$Pb_3O_4 <--> 3\,Pb + 2\,O_2$	1803.8	653.75
296	$BeO <--> Be + 0.5\,O_2$	8481.4	405.64
297	$MgO <--> Mg + 0.5\,O_2$	5725.6	486.51
298	$Sc_2O_3 <--> 2\,Sc + 1.5\,O_2$	6839.4	1608.6
299	$NiO <--> Ni + 0.5\,O_2$	2577.6	196.57
300	$ZnO <--> Zn + 0.5\,O_2$	3492.8	280.17
301	$Y_2O_3 <--> 2\,Y + 1.5\,O_2$	5998.4	1985.2
302	$PdO <--> Pd + 0.5\,O_2$	1045.9	115.33
303	$Ag_2O <--> 2\,Ag + 0.5\,O_2$	425.45	30.527

304	$CdO < --> Cd + 0.5 O_2$	2411.2	247.77
305	$TeO_2 < --> Te + O_2$	1765.1	274.45
306	$TeO < --> Te + 0.5 O_2$	1117.1	-44.591
307	$CsO < --> Cs + 0.5 O_2$	1271.3	-50.874
308	$Cs_2O_3 < --> 2 Cs + 1.5 O_2$	2160.9	419.78
309	$HfO_2 < --> Hf + O_2$	7903.6	848.26
310	$Ce_2O_3 < --> 2 Ce + 1.5 O_2$	7385.9	1596.4
311	$PrO_{1.833} < --> Pr + 0.9165 O_2$	60388	1.55E+05
312	$Nd_2O_3 < --> 2 Nd + 1.5 O_2$	5939.6	1824.6
313	$Sm_2O_3 < --> 2 Sm + 1.5 O_2$	5033	2452.5
314	$Eu_2O_3 < --> 2 Eu + 1.5 O_2$	5797.4	1371.6
315	$Gd_2O_3 < --> 2 Gd + 1.5 O_2$	5415.9	2576.2
316	$Dy_2O_3 < --> 2 Dy + 1.5 O_2$	6512	1638.3
317	$Ho_2O_3 < --> 2 Ho + 1.5 O_2$	6029.3	1900.7
318	$Er_2O_3 < --> 2 Er + 1.5 O_2$	6204.4	1813.5
319	$Tm_2O_3 < --> 2 Tm + 1.5 O_2$	5851.8	1936.5
320	$Yb_2O_3 < --> 2 Yb + 1.5 O_2$	5993.7	1814.3
321	$Lu_2O_3 < --> 2 Lu + 1.5 O_2$	5916.6	1901.6
322	$PtO_2 < --> Pt + O_2$	28.433	27.12
323	$Au_2O_3 < --> 2 Au + 1.5 O_2$	41.723	30.735
324	$HgO < --> Hg + 0.5 O_2$	724.85	145.56
325	$Tl_2O_3 < --> 2 Tl + 1.5 O_2$	1355	379.15
326	$Tl_2O < --> 2 Tl + 0.5 O_2$	4319.1	27.197
327	$Bi_2O_3 < --> 2 Bi + 1.5 O 2$	29387	13995
328	$NpO_2 < --> Np + O_2$	5433.3	964.47
329	$Al(OH)_3 < --> 0.5 Al_2O_3 + 1.5 H_2O$	317.67	75.328
330	$Ba(OH)_2 < --> BaO + H_2O$	1319.9	100.64
331	$Be(OH)_2 < --> BeO + H_2O$	353.74	52.118
332	$Cd(OH)_2 < --> CdO + H_2O$	388.8	77.2
333	$Ca(OH)_2 < --> CaO + H_2O$	794.14	99.377
334	$CsOH < --> 0.5 Cs_2O + 0.5 H_2O$	3816.5	147.59
335	$Co(OH)_2 < --> CoO + H_2O$	368.26	59.09
336	$Cu(OH)_2 < --> CuO + H_2O$	312.75	44.949
337	$Cs_2(OH)_2 < --> Cs_2O + H_2O$	3566.3	298.64
338	$Li_2(OH)_2 < --> Li_2O + H_2O$	30.956	320.97
339	$K_2(OH)_2 < --> K_2O + H_2O$	2902.8	161.22
340	$Na_2(OH)_2 < --> Na_2O + H_2O$	32.987	134.33
341	$Fe(OH)_2 < --> FeO + H_2O$	341.17	54.436
342	$Fe(OH)_3 < --> 0.5 Fe_2O_3 + 1.5 H_2O$	218.04	47.351
343	$LiOH < --> 0.5 Li_2O + 0.5 H_2O$	1312.5	25.64
344	$Mg(OH)_2 < --> MgO + H_2O$	540.99	77.818
345	$KOH < --> 0.5 K_2O + 0.5 H_2O$	3530.1	99.207
346	$NaOH < --> 0.5 Na_2O + 0.5 H_2O$	2264.4	93.979
347	$Sr(OH)_2 < --> SrO + H_2O$	1013.6	89.44
348	$BaCO_3 < --> BaO + CO_2$	1811.1	212.36
349	$CdCO_3 < --> CdO + CO_2$	567.85	96.308
350	$CaCO_3 < --> CaO + CO_2$	1169	166.55
351	$Cs_2CO_3 < --> Cs_2O + CO2$	4045.1	149.68

352	$Pb_2CO_4 <--> 2PbO + CO_2$	611.28	82.83
353	$FeCO_3 <--> FeO + CO_2$	412.68	75.133
354	$PbCO_3 <--> PbO + CO_2$	583.52	83.031
355	$Li_2CO_3 <--> Li_2O + CO_2$	1884.8	190.13
356	$MgCO_3 <--> MgO + CO_2$	580.58	98.803
357	$MnCO_3 <--> MnO + CO_2$	618.73	112.59
358	$NiCO_3 <--> NiO + CO_2$	370.68	60.904
359	$K_2CO_3 <--> K_2O + CO_2$	13.946	-867.91
360	$Rb_2CO_3 <--> Rb_2O + CO_2$	5.8455	-772.73
361	$Ag_2CO_3 <--> Ag_2O + CO_2$	487.22	79.348
362	$Na_2CO_3 <--> NA2O + CO2$	5.332	-751.22
363	$SrCO_3 <--> SrO + CO_2$	1432.2	199.1
364	$ZnCO_3 <--> ZnO + CO_2$	393.48	68.277

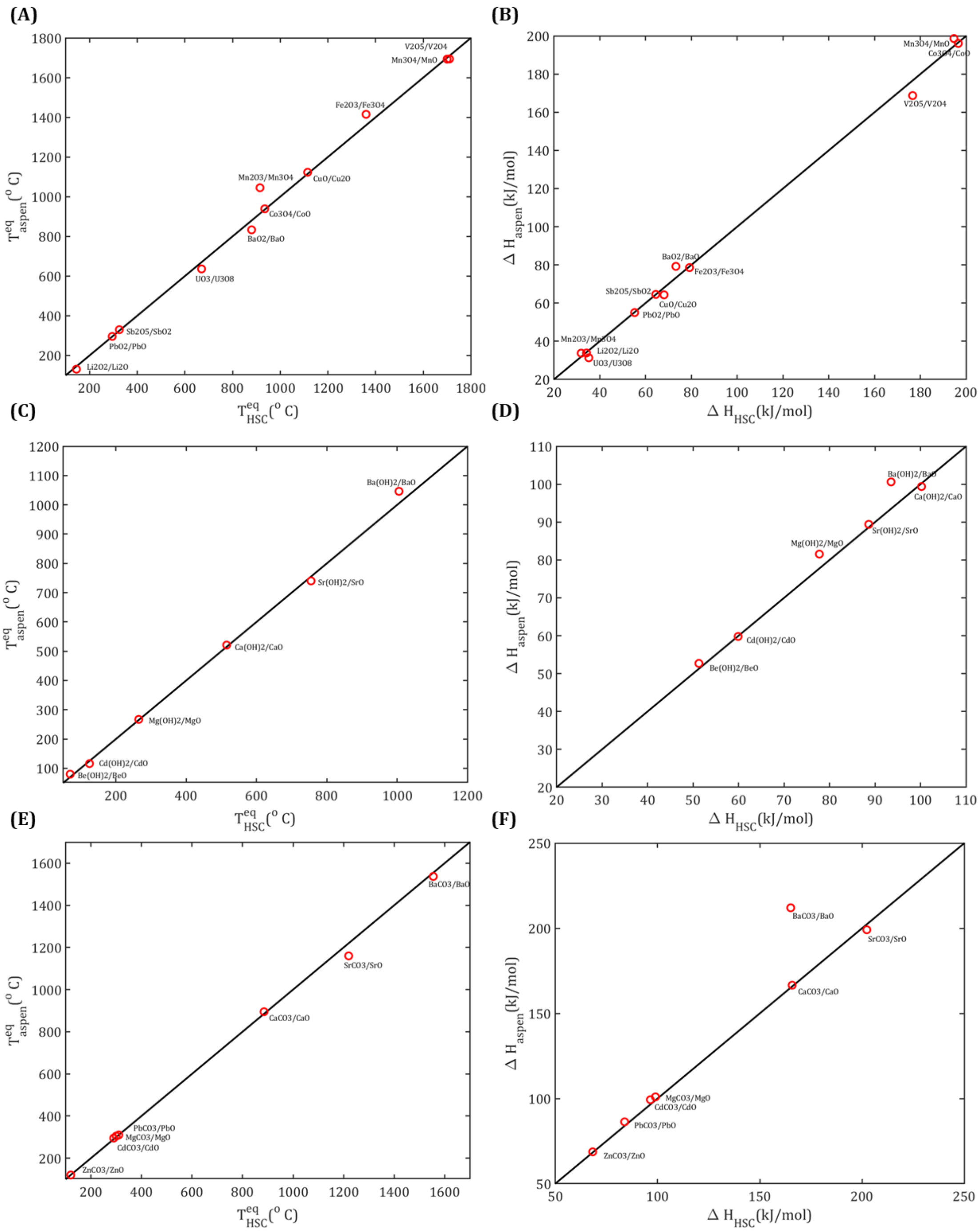

Figure S1. Comparison of the estimated equilibrium temperature and reaction enthalpy with those obtained by Pardo et al. [1] for select redox (A-B), hydroxide (C-D), and carbonate reaction (E-F) systems.

S2 Reactions obtained after thermodynamic screening

Table S2 lists the reactions obtained after thermodynamic screening and properties including equilibrium temperature, reaction enthalpy, average heat capacities of A and B, and densities of A and B. Average heat capacity of A ($\overline{\mathrm{Cp_A}}$) is estimated as follows:

$$\overline{Cp_A} = \frac{\int_{T^L}^{T^U} Cp_A(T)\, dT}{T^U - T^L}$$

where $Cp_A(T)$ is the heat capacity of A as a function of temperature, $T^L = \max\,(T^{eq} - 500, 250)$ and $T^U = \min(1750, T^{eq} + 500)$.

Table S2. List of reactions obtained after performing thermodynamic screening and their corresponding properties.

No.	Reactions	T^{eq} (K)	ΔH^r (kJ/mol)	$\overline{\mathrm{Cp_A}}$ (kJ/kg-K)	$\overline{\mathrm{Cp_B}}$ (kJ/kg-K)	ρ_A (g/cm^3)	ρ_B (g/cm^3)	Price ($/MT)
1	Mn_2O_3/Mn_3O_4	1174.1	32.136	0.908	0.870	4.72	4.59	1837
2	Mn_2O_3/MnO	1646.7	173.85	1.002	0.820	4.72	5.19	1837
3	MnO_2/Mn_2O_3	717.69	39.764	0.815	0.789	4.01	4.72	2270
4	MnO_2/Mn_3O_4	809.44	56.15	0.837	0.792	4.01	4.59	2270
5	BaO_2/BaO	1015.3	80.479	0.516	0.372	5.39	5.75	1364
6	CuO/Cu_2O	1304.9	64.907	0.725	0.627	5.94	6.03	6220
7	Fe_2O_3/Fe_3O_4	1613.1	77.754	0.898	0.868	5.07	4.95	805
8	MnO_2/MnO	1178.7	131.17	0.900	0.784	4.01	5.19	2270
9	Pb_3O_4/PbO	638.72	57.949	0.278	0.135	8.22	8.47	8500
10	UO_3/U_3O_8	860.96	34.881	0.344	0.361	6.57	8.3	77093
11	UO_3/U_4O_9	1340.3	98.232	0.364	0.362	6.57	10.97	77093
12	UO_3/UO_2	1544.4	139.18	0.369	0.336	6.57	11.26	77093
13	Na_2O_2/Na_2O	1141.2	87.077	1.454	1.565	2.52	2.35	150
14	NaO_2/Na_2O	632.37	46.146	1.602	1.387	2.19	2.35	150
15	Co_3O_4/CoO	1166.1	197.78	0.967	0.775	5.4	6.31	36132
16	KO_2/K_2O_2	1158.8	22.337	1.304	0.195	2.22	2.31	436
17	TcO_3/TcO_2	1227	42.06	1.435	0.622	3.64	6.58	60000000
18	PrO_2/Pr_7O_{12}	690.92	13.759	0.532	0.416	6.12	6.08	52200
19	Pr_7O_{12}/Pr_2O_3	1131.4	186.46	0.458	0.453	6.08	6.09	52200
20	PrO_2/Pr_2O_3	947.26	35.203	0.576	0.437	6.12	6.09	52200
21	CsO_2/Cs_2O	1452.7	85.226	0.696	0.405	3.73	4.05	2227600
22	TbO_2/Tb_2O_3	765.24	39.378	0.398	0.367	7.74	7.84	501000
23	$TbO_{1.72}/Tb_2O_3$	931.21	20.02	0.412	0.381	7.78	7.84	501000
24	$TbO_{1.81}/Tb_2O_3$	928.46	28.928	0.410	0.381	7.8	7.84	501000
25	$TbO_2/TbO_{1.72}$	641.59	18.716	0.390	0.382	7.74	7.78	501000
26	$TbO_{1.81}/TbO_{1.72}$	922.33	8.891	0.409	0.411	7.8	7.78	501000
27	Rh_2O_3/Rh	1304.3	332.07	0.637	0.333	7.97	12.03	72000000
28	IrO_2/Ir	1311.5	226.02	0.376	0.165	11.3	21.93	43000000
29	PdO/Pd	1045.9	115.33	0.467	0.283	7.79	11.41	33000000
30	$Ba(OH)_2/BaO$	1319.9	100.64	0.822	0.388	4.46	5.75	1981
31	$Ca(OH)_2/CaO$	794.14	99.377	1.519	0.917	2.2	3.29	150
32	$LiOH/Li_2O$	1312.5	25.64	3.634	3.084	1.4	1.96	15246
33	$Sr(OH)_2/SrO$	1013.6	89.44	1.216	0.54	3.35	4.88	2111

34	$CaCO_3/CaO$	1169	166.55	1.29	0.971	2.61	3.29	100
35	Pb_2CO_4/PbO	611.28	82.83	0.385	0.139	6.87	8.47	2800
36	$PbCO_3/PbO$	583.52	83.031	0.492	0.144	6.27	8.47	2800
37	$MgCO_3/MgO$	580.58	98.803	1.302	1.159	2.9	3.47	242
38	$MnCO_3/MnO$	618.73	112.59	0.970	0.713	3.56	5.19	1837
39	$SrCO_3/SrO$	1432.2	199.1	0.935	0.572	3.48	4.88	863

S3 Power cycle

We employ supercritical CO_2 Brayton cycle with a simple recuperative configuration consisting of a compressor, turbine, recuperator, heater/reactor, and cooler. The schematic of the cycle and temperature-entropy diagram of the cycle is shown in Figure S2.

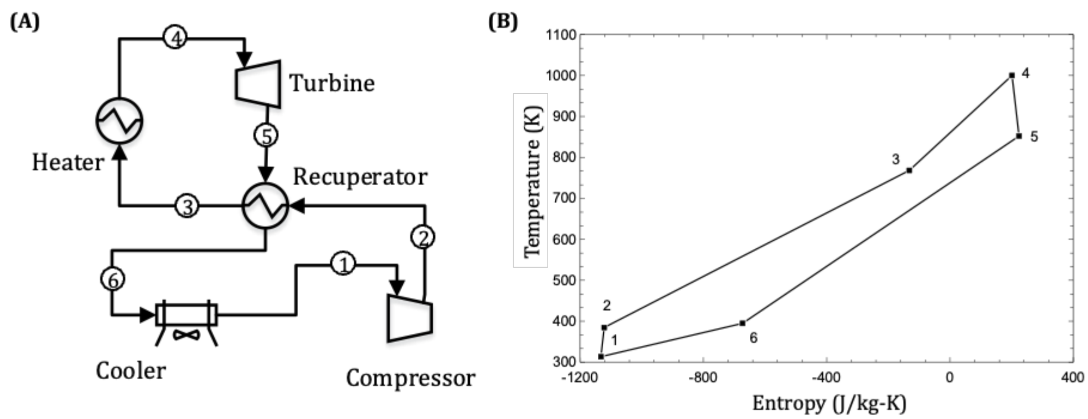

Figure S2. Schematic of s-CO2 Brayton cycle with a simple recuperative configuration. (B) T-S diagram of the s-CO2 power cycle.

S4 Model equations

An optimization model is developed to assess the economic viability of various reactions. The objective of the model is to minimize the levelized cost of electricity. The constraints of the plant include performance considerations of plant components, mass and energy balances, equipment design, and cost calculations. Based on Figures 1 and 2, we develop process models for the three reactions. However, for the sake of brevity, process model for carbonate reactions employing closed configuration (Figure S3) is provided in this section.

Notation

We denote indices by lower-case italic roman characters, variables as upper-case italic roman characters, and sets and subsets by upper-case bold roman characters. The parameters are denoted by italic Greek characters.

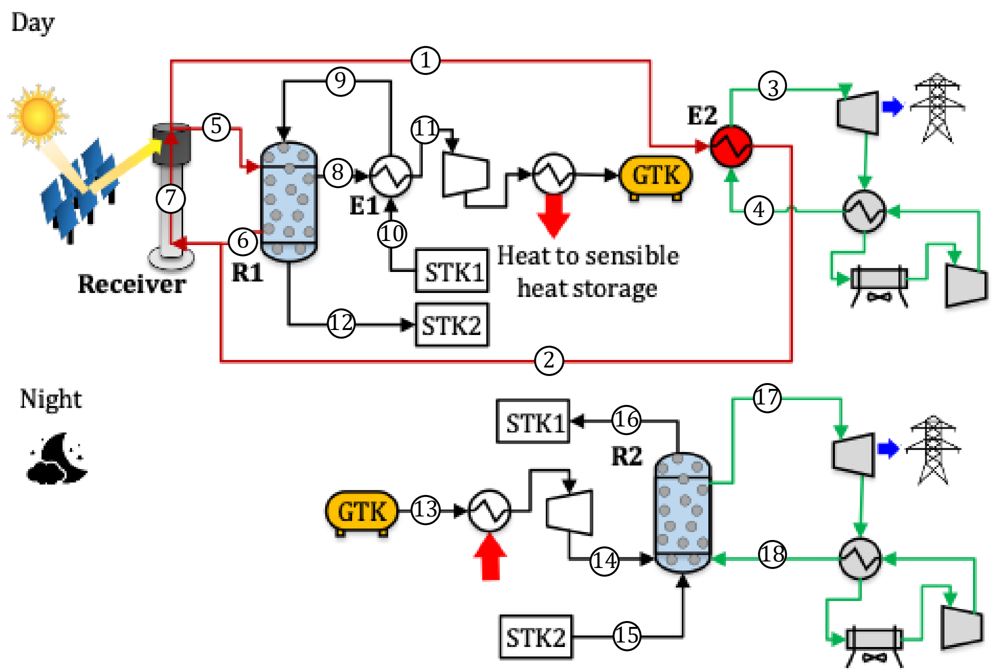

Figure S3. Process flowsheet for carbonate reactions.

Sets and Subsets

$i \in \mathbf{I}$	Units
$\mathbf{I^R}$	Reaction units
$\mathbf{I^{TK}}$	Storage tanks
$j \in \mathbf{J}$	Streams
$\mathbf{JPS_i^{IN}}$	Inlet process streams to unit i
$\mathbf{JS_i^{C}}$	Streams containing C from/to unit i
$\mathbf{JPS_i^{OUT}}$	Outlet process streams from unit i
$\mathbf{JUS_i^{IN}}$	Inlet utility streams to unit i
$\mathbf{JUS_i^{OUT}}$	Outlet utility streams from unit i
$k \in \mathbf{K}$	Components
$\mathbf{K^R}$	Components involved in reaction
$\mathbf{K^F}$	Components in fluid phase
$s \in \mathbf{S}$	Scenarios

Parameters

ω_k	Molecular weight of component k (g/mol)
ν_k	Stoichiometry coefficient of component k
Cp_k	Specific heat capacity of component k (kJ/kg/K)
T^{eq}	Equilibrium temperature (K)
T^{amb}	Ambient temperature (K)
ΔH^r	Reaction enthalpy at T^{eq} (kJ/kg)
δ^e	External tube diameter in reactors (m)

δ^{in}	Internal tube diameter in reactors (m)
δ^{dc}	Distance between tube centers in reactors (m)
γ	Reaction conversion
ρ_k	Density of material k (kg/m^3)
ϵ^r	Void fraction in reactor
ϵ^{stk}	Void fraction in solid storage tanks
ζ^t	Thermal conductivity of tube wall (W/m/K)
ζ_k^f	Thermal conductivity of fluid $k \in \mathbf{K^F}$ (W/m/K)
μ_k	Viscosity of component $k \in \mathbf{K^F}$ (kg/m/s)
σ	Stefan-Boltzmann constant (W/m^2/K^4)
ξ	Convective heat transfer coefficient of air (W/m^2/K)
ξ^{HTC}	Heat transfer coefficient in E1 (W/m^2/K)
ψ^t	Emissivity of tube surface
ψ^b	Emissivity of bed
ϕ^{col}	concentration ratio of collector
α^{rec}	receiver solar absorptance
ψ^{rec}	receiver thermal emittance
λ^{CRF}	Capital recovery factor
υ_s	Solar direct normal irradiance in scenario s (kW/m^2)
θ^{conv}	Conveyor unit power consumption (kW/kg/s)
ϕ^C	Sensible heat of cooling of gas from τ^{eq} to 298 K (kJ/kg)
ϕ^{comp}	Compression power to compress CO_2 from 1 bar to 75 bar (MW/kg/s)
$\lambda^{indirect}$	Indirect cost factor
λ^{cont}	Contingency cost factor
θ^{rate}	CSP plant rated capacity (MW)
$\theta^{rec,ref}$	Reference size of receiver (MWh$_t$)
δ^T	Minimum approach temperature during heat transfer (K)
κ_s^{day}	Duration of daytime in scenario s (h)
κ_s^{night}	Duration of nighttime in scenario s (h)
β^{rec}	Scaling factor of receiver
η^{col}	Collector efficiency
η^{bop}	Balance of plant efficiency (0.9, considering 10% parasitic load in the plant)
λ^{col}	Collector price (\$/m^2)
λ^{conv}	Conveyor price (\$/MW)
λ^{E1}	Price of E1 (\$/m^2)
λ^{comp}	Compressor price (\$/MW)
λ^{sens}	Sensible heat storage price (\$/MWh$_t$)
λ^{rec}	Receiver price at size $\theta^{r,ref}$ (\$/MWh$_t$)
λ^p	Power block price (\$/MW)
$\lambda^{reactor}$	Reactor price (\$/m^2 of heat exchange area)

λ^{sm}	Storage media price (\$/ton)
λ^{stk}	Solid storage tank price (\$/m^3)
λ^{gtk}	Gas storage tank price (\$/m^3)
$\lambda^{om,fix}$	Operation and maintenance, fixed cost (\$/MW/year)
$\lambda^{om,vary}$	Operation and maintenance, variable cost (\$/MWh)
π_s	Occurrence frequency of scenario s

First stage variables

A^{col}	Collector area (m^2)
A_i^r	Heat exchange area of reactor $i \in \mathbf{I^R}$ (m^2)
A^{E1}	Heat exchange area of E1 (m^2)
$CAPEX$	Plant total capital cost (\$)
C^{conv}	Conveyor cost (\$)
C^{comp}	Compressor cost (\$)
C^{sen}	Sensible heat storage cost (\$)
C^{TCES}	TCES system cost (\$)
$LCOE$	Levelized cost of electricity (₵/kWh)
M^{sm}	Storage media weight (ton)
$OPEX$	Annual operational cost (\$/year)
QT^{rec}	Receiver size (MWh_t)
V_i	Volume of unit $i \in \mathbf{I^R} \cup \{STK1, STK2\}$ (m^3)
L_i	Length of unit $i \in \mathbf{I^R}$ (m)
W^{ele}	Annual total electricity output (MWh/year)
T_j	Temperature of stream j (K)
TP_i	Pinch temperature in unit $i \in \mathbf{I^R}$
$AMTD_i$	Average mean temperature difference between hot and cold streams in unit $i \in \mathbf{I^R} \cup$ E1 (K)

Second stage variables

$F_{j,k,s}$	Mass flow rate of component k in stream j under scenario s (kg/sec)
$Q_{i,s}$	Heat transfer rate in unit $i \in \mathbf{I^R} \cup$ E1 under scenario s (MW)
QS_s	Sensible heat stored under scenarios s (MWh)
$TO_{i,s}$	Average temperature of tube surface on the bed side of unit $i \in \mathbf{I^R}$ under scenario s
$H_{i,s}$	Overall heat transfer coefficient of unit $i \in \mathbf{I^R}$ under scenario s (W/m^2/K)
$HO_{i,s}$	Heat transfer coefficient of fluidized bed in unit $i \in \mathbf{I^R}$ under scenario s (W/m^2/K)
$HI_{i,s}$	Convection heat transfer coefficient between tube surface and HTF in unit $i \in \mathbf{I^R}$ under scenario s (W/m^2/K)
$SRT_{i,s}$	Solid residence time in unit $i \in \mathbf{I^R}$ under scenario s (sec)
$U_{j,s}$	Superficial velocity of stream $j \in \mathbf{JUS_i^{IN}} \cup \mathbf{JUS_i^{OUT}} \cup \mathbf{JS_i^{C}}$, $i \in \mathbf{I^R}$ under scenario s (m/sec)
$XB_{j,s}$	Mole fraction of stream $j \in \mathbf{JPS_i^{OUT}}$, $i \in \mathbf{I^R}$ under scenario s (m/sec)

W_s^{day}	Daytime power generated under scenario s (MWh)
W_s^{night}	Nighttime power generated under scenario s (MWh)
P_s^{conv}	Conveyor power under scenario s (MW)
P_s^{comp}	Compressor power under scenario s (MW)
$QT_s^{curtail}$	Energy curtailed through heliostat defocus under scenario s (MWh)
Q_s^{HTF}	HTF thermal energy requirement during charging under scenario s (MW)
DT_s^c	Duration of daytime power generation (h)
NT_s^d	Duration of nighttime power generation (h)
E_s^{rec}	Receiver efficiency in scenario s
$E_s^{p,day}/E_s^{p,night}$	Daytime/ nighttime power block efficiency in scenario s

Equations

$$F_{j,k,s} = 0, \forall i \in \mathbf{I}, j \in \mathbf{JUS_i^{IN}} \cup \mathbf{JUS_i^{OUT}}, k \in \mathbf{K^R}, s \in \mathbf{S} \tag{1}$$

$$F_{7,k,s} = F_{5,k,s} + F_{1,k,s}, \forall k \in \mathbf{K}, s \in \mathbf{S} \tag{2}$$

$$T_1 = T_5 \tag{3}$$

$$T_5 \geq T_7 + 100 \tag{4}$$

$$F_{7,k,s} = F_{2,k,s} + F_{6,k,s}, \forall k \in \mathbf{K}, s \in \mathbf{S} \tag{5}$$

$$TP_i \geq T_j + \delta^T, \forall i = \mathrm{R1}, j \in \mathbf{JPS_i^{OUT}}, s \in \mathbf{S} \tag{6}$$

$$TP_i + \delta^T \leq T_j, \forall i = \mathrm{R2}, j \in \mathbf{JPS_i^{OUT}}, s \in \mathbf{S} \tag{7}$$

$$T_5 \geq T_8 + \delta^T \tag{8}$$

$$T_6 \geq T_9 + \delta^T \tag{9}$$

$$\sum_{j \in \mathbf{JUS_i^{IN}}} F_{j,k,s} \cdot (T_7 - T_j) = 0, \forall k \in \mathbf{K}, i = Rec, s \in \mathbf{S} \tag{10}$$

$$E_s^{rec} = \alpha^{rec} - \frac{\psi^{rec} \cdot \sigma \cdot (T_1^4) + \xi \cdot (T_1 - T^{amb})}{\upsilon_s \cdot \eta^{col} \cdot \phi^{col}}, \forall s \in \mathbf{S} \tag{11}$$

$$F_{j,k,s} = F_{j',k,s}, \forall i = E1 \cup \mathbf{I^R}, j' \in \mathbf{JUS_i^{IN}}, j \in \mathbf{JUS_i^{OUT}}, k = \mathbf{K}, s \in \mathbf{S} \tag{12}$$

$$10^3 \cdot Q_{i,s} = \sum_k F_{7,k,s} \cdot Cp_k \cdot (T_5 - T_7), \forall i = Rec, s \in \mathbf{S} \tag{13}$$

$$10^3 \cdot Q_{i,s} = \sum_k F_{10,k,s} \cdot Cp_k \cdot (T_9 - T_{10}), \forall i = E1, s \in \mathbf{S} \tag{14}$$

$$T_8 \geq T_9 + \delta^T \tag{15}$$

$$T_{11} \geq T_{10} + \delta^T \tag{16}$$

$$10^3 \cdot Q_{i,s} = \sum_k F_{8,k,s} \cdot (T_8 - T_{11}), \forall i = E1, s \in \mathbf{S} \tag{17}$$

$$AMTD_i = \frac{T_8 + T_{11} - T_9 - T_{10}}{2}, \forall i = E1 \tag{18}$$

$$A^{E1} \cdot \xi^{HTC} \cdot AMTD_{E1} \geq Q_{E1,s}, \forall s \in \mathbf{S} \tag{19}$$

$$\left(F_{j,B,s} - F_{j',B,s}\right) \cdot \nu_k \cdot \omega_k = \left(F_{j,k,s} - F_{j',k,s}\right) \cdot \nu_B \cdot \omega_B, \forall i \in \mathbf{I^R}, j \in \mathbf{JPS_i^{OUT}}, j' \in \mathbf{JPS_i^{IN}}, k = \{\mathrm{A}, \mathrm{C}\}, s \in \mathbf{S} \tag{20}$$

$$F_{j,A,s} = (1-\gamma) \cdot F_{j',A,s}, \forall\ i = \mathrm{R1}, j \in \mathbf{JPS_i^{OUT}}, j' \in \mathbf{JPS_i^{IN}}, s \in \mathbf{S} \tag{21}$$

$$F_{j,B,s} = (1-\gamma) \cdot F_{j',B,s}, \forall i = R2, j \in \mathbf{JPS_i^{OUT}}, j' \in \mathbf{JPS_i^{IN}}, s \in \mathbf{S} \tag{22}$$

$$F_{j,k,s} = F_{j',k,s}, \forall\ i \in \mathbf{I^R},\ j \in \mathbf{JUS_i^{OUT}},\ j' \in \mathbf{JUS_i^{IN}},\ k \in \mathbf{K},\ s \in \mathbf{S} \tag{23}$$

$$10^3 \cdot Q_{i,s} = \left(-F_{j,A,s} + F_{j',A,s}\right) \cdot \Delta H^r \ + \ \sum_{k \in \mathbf{K^R}} \left[F_{j,k,s} \cdot Cp_k \cdot \left(T_j - T^{eq}\right) + F_{j',k,s} \cdot Cp_k \cdot \left(T^{eq} - T_{j'}\right)\right], \forall i \in \mathbf{I^R}, j \in \mathbf{JPS_i^{OUT}}, j' \in \mathbf{JPS_i^{IN}}, s \in \mathbf{S} \tag{24}$$

$$10^3 \cdot Q_{i,s} = \sum_k F_{j,k,s} \cdot Cp_k \cdot (T_{j'} - T_j), \forall i \in \mathbf{I^R}, j \in \mathbf{JUS_i^{OUT}}, j' \in \mathbf{JUS_i^{IN}}, s \in \mathbf{S} \tag{25}$$

$$A_i^r \cdot AMTD_i \cdot H_{i,s} = 10^6 \cdot Q_{i,s}, \forall\ i \in \mathbf{I^R},\ s \in \mathbf{S} \tag{26}$$

$$V_i = \frac{A_i^r \cdot \left(\delta_i^{dc}\right)^2}{\pi \cdot \delta_i^e}, \forall\ i \in \mathbf{I^R} \tag{27}$$

$$AMTD_i = \frac{\left[\left(T_{j''} + T_{j'''}\right) - \left(T_j + T_{j'}\right)\right]}{2}, \forall i \in \mathbf{I^R}, j \in \mathbf{JPS_i^{OUT}}, j' \in \mathbf{JPS_i^{IN}}, j'' \in \mathbf{JUS_i^{OUT}}, j''' \in \mathbf{JUS_i^{IN}} \tag{28}$$

$$\frac{1}{H_{i,s}} = \frac{1}{HO_{i,s}} + \frac{\delta^e - \delta^{in}}{2\zeta^t} + \frac{\delta^e}{\delta^{in} \cdot HI_{i,s}}, \forall\ i \in \mathbf{I^R},\ s \in \mathbf{S} \tag{29}$$

$$HO_{i,s} = \frac{0.66 \cdot \zeta_k^f}{\delta^e} \left(\frac{Cp_k \cdot \mu_k}{\zeta_k^f}\right)^{0.3} \left[\left(\frac{U_{j',s} \cdot \rho_k \cdot \delta^e}{\mu_k}\right) \cdot \left(\frac{XB_{j,s} \cdot \rho_B + \left(1 - XB_{j,s}\right) \cdot \rho_A}{\rho_k}\right) \cdot \left(\frac{1-\epsilon^r}{\epsilon^r}\right)\right]^{0.44} + \frac{\sigma \cdot \left(TO_{i,s}^4 - T_j^4\right)}{\left(\frac{1}{\psi^b} + \frac{1}{\psi^t} - 1\right) \cdot \left(TO_{i,s} - T_j\right)}, \forall\ i \in \mathbf{I^R},\ j \in \mathbf{JPS_i^{OUT}},\ j' \in \mathbf{JS_i^C},\ k \in \mathbf{K},\ s \in \mathbf{S} \tag{30}$$

$$\frac{HI_{i,s} \cdot \delta^{in}}{\zeta_k^f} = 0.023 \cdot \left(\frac{Cp_k \cdot \mu_k}{\zeta_k^f}\right)^{0.4} \left(\frac{U_{j,s} \cdot \rho_k \cdot \delta^{in}}{\mu_k}\right)^{0.8}, \forall\ i = \mathrm{R1},\ j \in \mathbf{JUS_i^{OUT}},\ \ k \in \mathbf{K},\ s \in \mathbf{S} \tag{31}$$

$$\frac{HI_{i,s} \cdot \delta^{in}}{\zeta_k^f} = 0.023 \cdot \left(\frac{Cp_k \cdot \mu_k}{\zeta_k^f}\right)^{0.3} \left(\frac{U_{j,s} \cdot \rho_k \cdot \delta^{in}}{\mu_k}\right)^{0.8}, \forall\ i = \mathrm{R2},\ j \in \mathbf{JUS_i^{OUT}},\ \ k \in \mathbf{K},\ s \in \mathbf{S} \tag{32}$$

$$TO_{i,s} = \frac{T_j + T_{j'}}{2} - \frac{10^6 \cdot Q_{i,s}}{A_i^r} \cdot \left(\frac{\delta^e}{\delta^{in} \cdot HI_{i,s}} + \frac{\delta^e - \delta^{in}}{2\zeta^t}\right), \forall\ i \in \mathbf{I^R},\ j \in \mathbf{JUS_i^{OUT}},\ j' \in \mathbf{JUS_i^{IN}}, s \in \mathbf{S} \tag{33}$$

$$10^3 \cdot V_{R1} = \frac{F_{9,A,s} \cdot SRT_{R1,s}}{\rho_A \cdot (1 - \epsilon^r)}, \forall s \in \mathbf{S} \tag{34}$$

$$10^3 \cdot V_{R2} = \frac{F_{15,B,s} \cdot SRT_{R2,s}}{\rho_B \cdot (1 - \epsilon^r)}, \forall s \in \mathbf{S} \tag{35}$$

$$U_{j,s} = \frac{F_{j,k,s}}{\rho_k \cdot A_i^r \cdot \left[\frac{(\delta^{dc})^2}{\pi \delta^e \cdot L_i} - \frac{\delta^e}{4 L_i}\right]}, \forall\ i \in \mathbf{I^R}, j \in \mathbf{JS_i^C},\ k \in \mathbf{K},\ s \in \mathbf{S} \tag{36}$$

$$U_{j,s} = \frac{F_{j,k,s}}{\rho_k \cdot A_i^r \left[\frac{(\delta^{in})^2}{4 \cdot \delta^e \cdot L_i}\right]}, \forall\ i \in \mathbf{I^R},\ j \in \mathbf{JUS_i^{IN}} \cup \mathbf{JUS_i^{OUT}},\ k \in \mathbf{K},\ s \in \mathbf{S} \tag{37}$$

$$TO_{i,s} \geq \frac{T_j + T_{j'}}{2}, \forall\ i \in \mathrm{R1},\ j \in \mathbf{JPS_i^{OUT}},\ j' \in \mathbf{JPS_i^{IN}},\ s \in \mathbf{S} \tag{38}$$

$$TO_{i,s} \leq \frac{T_j + T_{j'}}{2}, \forall\ i \in \mathrm{R2},\ j \in \mathbf{JPS_i^{OUT}},\ j' \in \mathbf{JPS_i^{IN}},\ s \in \mathbf{S} \tag{39}$$

$$\frac{10^3 \cdot Q_{i,s} \cdot (T_{j'} - TP_i)}{(T_{j'} - T_j)} = (-F_{j,A,s} + F_{j',A,s}) \cdot \Delta H^r + \sum_{j'' \in \mathbf{JP_i^{OUT}}} \sum_k F_{j'',k,s} \cdot Cp_k \cdot (T_{j''} - T^{eq}), \quad \forall i = \mathrm{R1}, j \in \mathbf{JUS_i^{OUT}}, j' \in \mathbf{JUS_i^{IN}}, s \in \mathbf{S} \tag{40}$$

$$\frac{10^3 \cdot Q_{i,s} \cdot (T_j - TP_i)}{(T_{j'} - T_j)} = \sum_{j'' \in \mathbf{JP_i^{IN}}} \sum_k F_{j'',k,s} \cdot Cp_k \cdot (T_{j''} - T_{j'''}), \quad \forall i = \mathrm{R2}, j \in \mathbf{JUS_i^{OUT}}, j' \in \mathbf{JUS_i^{IN}}, j''' \in \mathbf{JPS_i^{OUT}}, s \in \mathbf{S} \tag{41}$$

$$T_1 = T_3 + \delta^T \tag{42}$$

$$T_2 = T_4 + \delta^T \tag{43}$$

$$E^{p,day} = -0.25 \cdot \left(\frac{T_3}{1000}\right)^2 + 0.87 \cdot \left(\frac{T_3}{1000}\right) - 0.15 \tag{44}$$

$$E^{p,night} = -0.25 \cdot \left(\frac{T_{17}}{1000}\right)^2 + 0.87 \cdot \left(\frac{T_{17}}{1000}\right) - 0.15 \tag{45}$$

$$T_j = 0.87 \cdot T_{j'} - 98.3, \forall i = \{E2, R2\}, j \in \mathbf{JUS_i^{IN}}, j' \in \mathbf{JUS_i^{OUT}} \tag{46}$$

$$10^3 \cdot Q_{i,s} = \sum_k F_{1,k,s} \cdot Cp_k \cdot (T_1 - T_2), \forall i = E2, s \in \mathbf{S} \tag{47}$$

$$Q_{i,s} \cdot E^{p,day} \cdot \eta^{bop} = \theta^{rate} \tag{48}$$

$$DT_s^c \leq \kappa_s^{day}, \forall s \in \mathbf{S} \tag{49}$$

$$NT_s^d \leq \kappa_s^{night}, \forall s \in \mathbf{S} \tag{50}$$

$$F_{12,k,s} \cdot DT_s^c = F_{15,k,s} \cdot NT_s^d, \forall k \in \mathbf{K}, s \in \mathbf{S} \tag{51}$$

$$F_{10,k,s} \cdot DT_s^c = F_{16,k,s} \cdot NT_s^d, \forall k \in \mathbf{K}, s \in \mathbf{S} \tag{52}$$

$$Q_{R2,s} \cdot E_s^{p,night} \cdot \eta^{bop} = \theta^{rate}, \forall s \in \mathbf{S} \tag{53}$$

$$Q_s^{HTF} = \theta^{rate} / E^{p,day} / \eta^{bop} + Q_{R1,s}, \forall s \in \mathbf{S} \tag{54}$$

$$QT^{rec} \cdot E_s^{rec} \cdot \kappa_s^{day} \geq Q_s^{HTF} \cdot DT_s^c, \forall s \in \mathbf{S} \tag{55}$$

$$A^{col} \cdot \upsilon_s \cdot \eta^{col} \cdot E_s^{rec} \cdot \kappa_s^{day} = Q_s^{HTF} \cdot DT_s^c + QT_s^{curtail}, \forall s \in \mathbf{S} \tag{56}$$

$$P_s^{conv} = \theta^{\,conv} \cdot \sum_k F_{2,k,s}\,, \forall s \in \mathbf{S} \tag{57}$$

$$C^{conv} \geq \lambda^{conv} \cdot P_s^{conv}, \qquad \forall s \in \mathbf{S} \tag{58}$$

$$V_{STK1} \geq \frac{DT_s^c}{(1-\epsilon^{stk})} \cdot \sum_k \frac{F_{1,k,s}}{\rho_k}\,, \forall s \in \mathbf{S} \tag{59}$$

$$V_{STK2} \geq \frac{DT_s^c}{(1-\epsilon^{stk})} \cdot \sum_k \frac{F_{2,k,s}}{\rho_k}\,, \forall s \in \mathbf{S} \tag{60}$$

$$V_{GTK} \geq \frac{F_{11,\mathrm{C},s} \cdot DT_s^C}{\rho_{\mathrm{C}}} \tag{61}$$

$$T_{10} = T_{16}, T_{12} = T_{15} \tag{62}$$

$$QS_s = F_{11,k.s} \cdot DT_s^c \cdot \left(\phi^C + Cp_k \cdot (T_{13} - T^{eq})\right), \forall\, k = C, s \in \mathbf{S} \tag{63}$$

$$P_s^{comp} = 2 \cdot F_{11,k,s} \cdot \phi^{comp}, \forall k = C, s \in \mathbf{S} \tag{64}$$

$$C^{sen} \geq \lambda^{sen} \cdot QS_s, \forall s \in \mathbf{S} \tag{65}$$

$$C^{comp} \geq \lambda^{comp} \cdot P_s^{comp}, \forall s \in \mathbf{S} \tag{66}$$

$$C^{E1} \geq \lambda^{E1} \cdot A^{E1} \tag{67}$$

$$M^{sm} \geq \sum_k F_{2,k,s} \cdot (SRT_{R1,s} + DT_s^c) + F_{11,k,s} \cdot SRT_{R2,s} \tag{68}$$

$$C^{TCES} = \lambda^{reactor} \cdot \textstyle\sum_{i \in \mathbf{I^R}} A_i^r + \lambda^{stk} \cdot (V_{STK1} + V_{STK2}) + \lambda^{stk} \cdot V_{GTK} + C^{conv} + \lambda^{sm} \cdot M^{sm} + C^{sen} + C^{comp} + C^{E1} \tag{69}$$

$$CAPEX = [\lambda^{col} \cdot A^{col} + \lambda^{rec} \cdot \theta^{rec,ref} \cdot \left(\frac{QT^{rec}}{\theta^{rec,ref}}\right)^{\beta^{rec}} + C^{TCES} + \frac{\lambda^p \cdot \theta^{rate}}{\eta^{bop}}] \cdot (1 + \lambda^{indirect}) \cdot (1 + \lambda^{cont}) \tag{70}$$

$$OPEX = \lambda^{om,fix} \cdot \theta^{rate} + \lambda^{om,vary} \cdot W^{ele} \tag{71}$$

$$W_s^{day} = (\theta^{rate} - P_s^{conv}) \cdot DT_s^c, \forall s \in \mathbf{S} \tag{72}$$

$$W_s^{night} = \theta^{rate} \cdot NT_s^d, \forall s \in \mathbf{S} \tag{73}$$

$$W^{ele} = 365 \cdot \sum_s \pi_s \cdot (W_s^{day} + W_s^{night}) \tag{74}$$

$$LCOE = (CAPEX \cdot CRF + OPEX)/W^{ele} \tag{75}$$

Eq. (1) sets the flow of the reaction components in the utility streams to 0. Eq. (2) states that the component flow rates of stream 7 are equal to the sum of streams 1 and 5. Eq. (3) sets the temperature of streams 1 and 5 to be the same. Eq. (4) indicates that the temperature of the stream exiting the receiver should be at least 100 K higher than the temperature of the inlet stream. Eq. (5) is the component mass balance on the streams entering the receiver. Eq. (6-9) specify the difference between pinch and stream temperatures for the heat transfer to occur in the reactors. Eq. (10) states that the enthalpy of mixing is 0. Eq. (11) relates the receiver efficiency with the temperature. Eq. (12) states that the mass of utility entering the unit E1 and reactor units equals the mass exiting. Eqs. (13) and (14) determine the heat duty of the receiver and E1, respectively. Eqs. (15) and (16) set the temperature difference between the streams entering and exiting E1 for heat transfer to occur. Eq. (17) and (18) define the heat duty and average mean temperature difference (AMTD), respectively. Eq. (19) relates the heat exchange area, heat transfer coefficient, and AMTD with the heat duty of E1.

Eqs. (20-23) models the mass balance of the reaction components and utilities in the reactors. Eqs. (24) and (25) compute the heat exchanged in the reactors. Eq. (26) relates the heat exchange area in the reactors, heat transfer coefficient, and AMTD with the heat exchanged. Eq. (27) relates the reactor volume with the heat exchange area of the reactors. Eq. (28) defines the AMTD of the streams associated with the reactors. The overall heat transfer coefficient between solids and HTF/WF is estimated using Eqs. (29-33). Eqs. (34) and (35) relate the reactor volume with the residence time. Eqs. (36) and (37) estimate the flow rate of C and HT/WF in the reactors with the respective flow rates. Eqs. (38) and (39) specify the relationship between the average temperature of the tube surface and the inlet and outlet process stream temperatures. Eqs. (40) and (41) relate the pinch temperature with the heat exchanged in the reactors.

Eqs. (42) and (43) set the minimum temperature difference between the stream for heat transfer. Eqs. (44) and (45) relate the efficiency of the power block to temperature. Eq. (46) specifies the relationship between the inlet and outlet WF temperature of E2 and R2. Eq. (47) estimates the heat exchanged in E2 and the corresponding power produced in given by eq. (48). Eqs. (49) and (50) relate the charging and discharging duration with sun and night hours, respectively. Eqs (51) and (52) are the mass balance equations on TK1 and TK2.

Eq. (53) relates the heat exchanged in R2 with the power produced. Eq. (54) states that the heat transferred to HTF during charging is the sum of heat transferred to R1 and E2. Eq. (55) estimates the receiver size based on the heat exchanged. Eq. (56) states that the energy the collector receives is equal to the sum of heat exchanged in the receiver and curtailed. Eq. (57) estimates the power needed by the conveyor to transport solids and eq. (58) computes the capital cost of the conveyor. Eqs. (59-61) relate the volume of storage tanks with the discharging time, flow rates, density, and void fraction. Eq. (62) states that the temperature of the solids entering the storage tanks equals that of the solids exiting. Eq. (63) estimates the sensible heat stored by gas C. Eq. (64) estimates the power consumed by the compressor. Eq. (65), (66), and (67) compute the capital costs of sensible heat storage unit, compressor, and heat exchanger E1, respectively.

Eq. (68) estimates the total material required. Eq. (69) states that the total cost of thermochemical energy storage is the sum of reactor, storage tanks, conveyor, material, sensible heat storage, compressor, and heat exchanger costs. Eqs. (70) and (71) estimate the total capital expenditure and operating costs. Eq. (72) and (73) compute the total electricity produced during day and night, respectively. Eq. (74) estimates the total electricity produced in a year. Eq. (75) relates LCOE with the annual costs and the total electricity produced.

Table S3. Parameter values [2–5].

Parameter	Values	Parameter	Values
δ^{e}	0.034	λ^{cont}	0.07
δ^{in}	0.049	θ^{rate}	100
δ^{dc}	0.118	$\theta^{rec,ref}$	670
$\lambda^{indirect}$	0.26	δ^{T}	10
κ_s^{day}	s1: 3.9, s2: 5.2, s3: 6.8, s4: 7.8, s5: 9.6, s6: 11.1	ϵ^{r}	0.7
ϵ^{stk}	0.5	ϕ^{comp}	0.36
ζ^{t}	18.6	β^{rec}	0.7
ζ_k^{f}	s-CO_2: 0.075, CO_2: 0.092	η^{col}	0.6
μ_k	s-CO_2: 4.3×10^{-5}, CO_2: 4×10^{-5}	η^{bop}	0.9
σ	5.7×10^{-8}	λ^{col}	150
ξ	10	λ^{conv}	10^6
ξ^{HTC}	50	λ^{E1}	10^3
ψ^{t}	0.9	λ^{comp}	10^6
ψ^{b}	0.9	λ^{sens}	3×10^4
ϕ^{col}	1200	λ^{rec}	1.75×10^5
α^{rec}	0.95	λ^{p}	1.2×10^6
ψ^{rec}	0.85	$\lambda^{reactor}$	500
λ^{CRF}	0.1	λ^{stk}	1800
υ_s	s1: 0.27, s2: 0.6, s3: 0.74, s4: 0.89, s5: 0.94, s6: 0.97	π_s	s1: 0.04, s2: 0.08, s3: 0.11, s4: 0.24, s5: 0.3, s6: 0.22
θ^{conv}	0.0504	$\lambda^{om,fix}$	6.5×10^4
λ^{gtk}	100	$\lambda^{om,vary}$	3.5

S5 Solution strategy

The process model is nonlinear consisting of non-convex terms and the existing solvers (e.g., BARON [6], ANTIGONE [7], etc.) could not solve it to global optimality. Accordingly, we develop a solution strategy, which is based on the observation that by fixing the temperature of streams 1 (T_1) and 16 (T_{16}) in Figure S3, the model could be solved quickly to global optimality using BARON. The lower and upper bounds of T_1, denoted as T_1^L and T_1^U, respectively, are determined using:

$$T_1^L = T^{eq} + 10, T_1^U = \min\{1750, T_A^m, T_B^m\}$$

The lower and upper bounds of T_{16} are determined using:

$$T_{16}^L = T^{eq} - 500, T_{16}^U = T^{eq} - 10$$

Thus, we discretize the range of the two variables to generate grid points (Figure S4A) and solve the model at all the grid points (Figure S4B). The solution of the model corresponds to the grid point for which the minimum LCOE is attained.

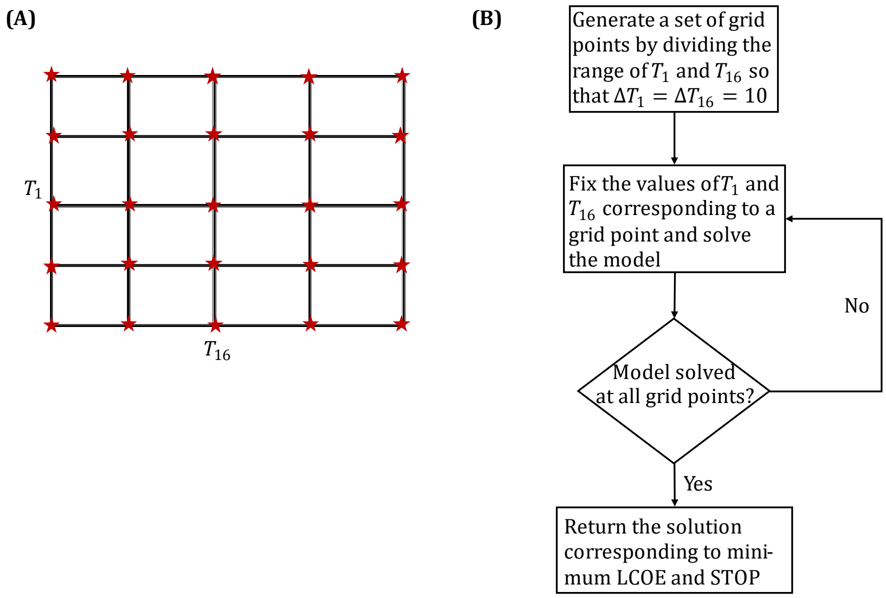

Figure S4. (A) Illustration of the grid points generated by discretizing the range of T_1 and T_{16}. (B) Solution strategy developed to solve the model to global optimality.

S6 Derivation of empirical relationships for material property targeting

The properties that are of interest are: reaction enthalpy and entropy, equilibrium temperature, density, heat capacity, and molar weight of the materials involved in the reaction. We begin with stating the Neumann-Kopp rule [8]:

$$Cp_A^m = Cp_B^m + \left(\frac{x-y}{2}\right) \cdot Cp_{O_2}^m \tag{76}$$

where Cp_A^m, Cp_B^m, and $Cp_{O_2}^m$ are the molar heat capacities of A, B, and O_2, respectively. The entropy of component k, denoted by S_k, is given by:

$$S_k = S_k^\circ + \int_{298}^{T} \frac{Cp_k^m}{T} dT \,, k \in \{A, B\} \tag{77}$$

where S_k° is the entropy of component k at standard conditions. Using Eqs. (75) and (76), the reaction entropy (ΔS^r) is:

$$\Delta S^r = S_B^\circ - S_A^\circ + \left(\frac{x-y}{2}\right) \cdot S_{O_2}^\circ \tag{78}$$

Using similar arguments, the reaction enthalpy (ΔH^r) is given by:

$$\Delta H^r = H_B^\circ - H_A^\circ + \left(\frac{x-y}{2}\right) \cdot H_{O_2}^\circ \tag{79}$$

where H_B°, H_A°, and $H_{O_2}^\circ$ are the formation enthalpies of B, A, and O_2, respectively at standard conditions. Glasser and Jenkins [9,10] related molecular volumes (MV_k) with heat capacity, standard entropy, and density as follows:

$$Cp_k = \kappa_{Cp} \cdot MV_k + \gamma_{Cp}, \forall\, k \in \{A, B\} \tag{80}$$

$$S_k^{\circ} = \kappa_S \cdot MV_k + \gamma_S, \forall k \in \{A, B\} \tag{81}$$

$$\rho_k = \frac{\omega_k}{602.2 \cdot MV_k}, \forall k \in \{A, B\} \tag{82}$$

By relating a single variable (molecular volume) with heat capacity, standard entropy, and density, the correlations between the properties are established. The bounds on the property values are imposed and they correspond to the minimum and maximum values of the properties of existing materials. Equations for molar weight balance and the stoichiometry coefficient for gas C are as follows:

$$\omega_A = \omega_B + \nu_C \cdot \omega_C \tag{83}$$

$$\nu_c = \frac{x - y}{2} \tag{84}$$

The optimal material properties, design, and operating conditions are obtained by solving the optimization model formed by including Eqs. 1-75 and Eqs. 78-84.

S7 Optimization results for Fe_2O_3/Fe_3O_4 system

The solution of the optimization model yields the design and operational decisions that lead to minimum LCOE. In this section, we present the results for the Fe_2O_3/Fe_3O_4 system. The optimal design decisions are given in Table S4. The values of operating variables are given in Table S5-S6. The detailed energy flows are shown in Figure S5.

Table S4. Optimal design decisions for Fe_2O_3/Fe_3O_4 system.

Heliostat	Receiver	R1 Volume	R2 Volume	R1 Heat Exchange area	R2 Heat Exchange area	Tank TK1	Tank TK2	Sensible storage for C
1.33 km^2	752 MW	316 m^3	424 m^3	3539 m^2	4759 m^2	4952 m^3	4903 m^3	127 MWh

Table S5. Stream temperatures (K) for Fe_2O_3/Fe_3O_4 system based on flowsheet in Figure S3.

Day		Night	
$T_1 = T_5$	1675	T_{13}	298
T_2	1360	T_{14}	1342
T_3	1665	T_{16}	1233
T_4	1350	T_{17}	1332
T_6	1605	T_{18}	1060
T_7	1553		
$T_8 = T_{11} = T_{12} = T_{15}$	1623		
$T_9 = T_{10}$	1245		

Table S6. Storage charging and discharging hours in the six scenarios for Fe_2O_3/Fe_3O_4 system.

Storage charging (h)						Storage discharging (h)					
1	2	3	4	5	6	1	2	3	4	5	6
3.9	5.3	6.8	7.8	9.6	11.1	0	1.0	5.3	10.4	14.4	12.9

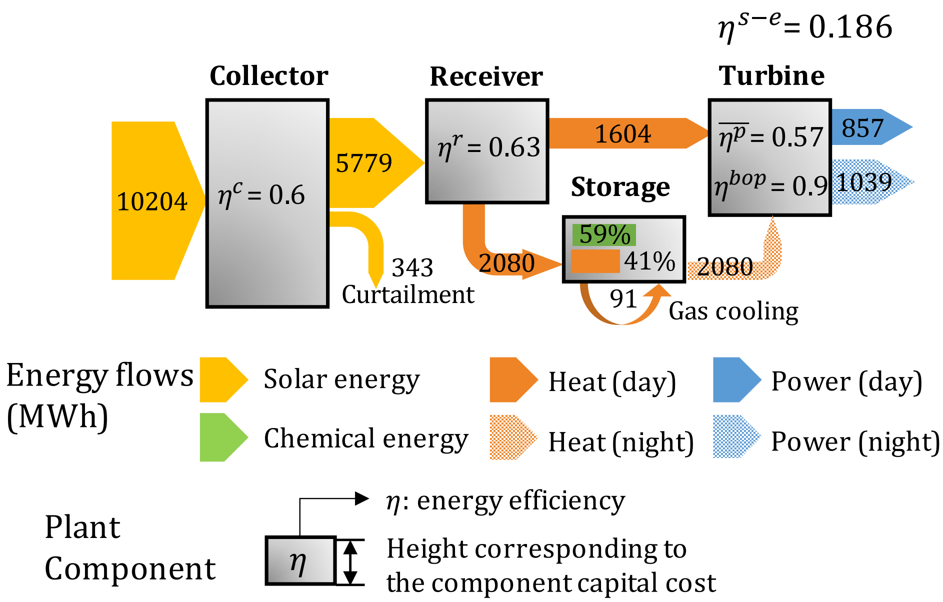

Figure S5. Energy flows and energy efficiencies of CSP-TCES system employing Fe_2O_3/Fe_3O_4 system. Daily energy flows are scenario-weighted averages. The storage efficiency is assumed to be 100%. The percentages of chemical and sensible energy storage are shown in the storage block.

S8 Heat transfer process

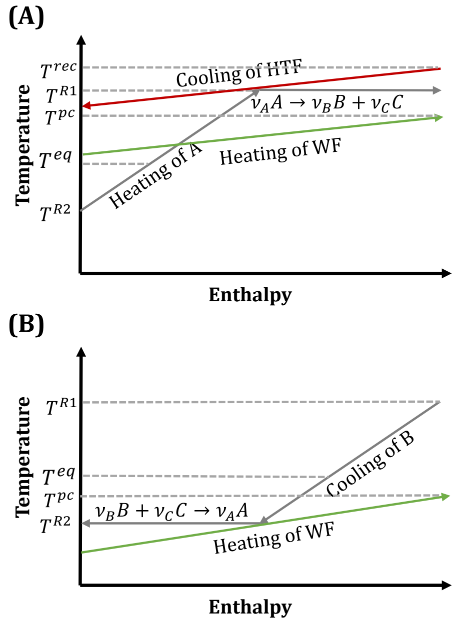

Figure S6. Illustration of heat transfer process during (A) day and (B) night operation.

For the overall system efficiency to be high, it is critical that T^{rec} should be low, T^{pc} should be high, and the difference between T^{rec} and T^{pc} should be small. The temperature-enthalpy diagram shown in Figure S6 illustrates the heat transfer process and highlights that $T^{rec} > T^{pc}$ so that the second law of thermodynamics is satisfied. Secondly, a finite difference in T^{rec} and T^{pc} will always exist due to heat transfer limitations.

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