B.1 Gaseous Feed Reducer

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Introduction

The primary component of natural gas is methane, so it is used to represent natural gas in the cocurrent chemical looping reducer reactor for syngas production. The oxygen carrier is an iron-aluminum composite metal oxide (IACMO). Modeling of IACMO in Aspen Plus® is discussed in detail in Section 6.4.1 while Section 6.5 provides process simulation results. The main reaction in the reducer can be described by Reaction (B.1.1).

$$CH_4+Fe_2O_3+2Al_2O_3 \rightarrow CO+2H_2+2FeAl_2O_4 \quad (B.1.1)$$

In the presence of an excess amount of IACMO, syngas, comprised of CO and H_2, can further react with the IACMO, as shown in Reaction (B.1.2) and (B.1.3). The over-oxidation of CO, Reaction (B.1.2), and H_2, Reaction (B.1.3), result in the production of CO_2 and H_2O, respectively, both of which are undesired products during syngas generation.

$$CO+Fe_2O_3+2Al_2O_3 \rightarrow CO_2+2FeAl_2O_4 \quad (B.1.2)$$
$$H_2+Fe_2O_3+2Al_2O_3 \rightarrow H_2O+2FeAl_2O_4 \quad (B.1.3)$$

However, it is also possible for the reducer reactor to be deficient in IACMO, in which methane pyrolysis, Reaction (B.1.4), would occur. This would result in the formation of carbon deposition, which has several negative effects that is discussed throughout Chapter 4.

$$CH_4 \rightarrow C+2H_2 \quad (B.1.4)$$

The Fe_2O_3:CH_4 ratio, therefore, must be maintained within a specific range where syngas production is favored over the formation of combustion products and carbon deposition. The effect of this ratio along with that of steam injection on syngas purity is examined in this model. Steam is utilized to tailor the H_2:CO ratio towards H_2 production by promoting the water-gas shift reaction, Reaction (B.1.5). The main assumption when modeling the cocurrent moving bed reducer reactor is that phase and chemical equilibrium is attained.

$$H_2O+CO \leftrightarrow H_2+CO_2 \quad (B.1.5)$$

Model Setup

A single RGIBBS module is used to simulate the cocurrent moving bed reducer. The important variables affecting the syngas purity are reaction temperature, pressure, IACMO flow rate, and steam flow rate. The reducer reactor is operated under isothermal and isobaric conditions. The heat duty is automatically calculated based on the enthalpy of the reactant and product streams.

Components and Physical Properties

Table B.1 provides the components and physical property parameters involved in the simulation. The stream class is MIXCISLD. The databanks selected are COMBUST, SOLIDS, AQUEOUS, PURE27, and INORGANIC. The physical properties of the solid compounds are calculated based on the Barin equation. The model retrieves the coefficients for the heat capacity of the solid from the INORGANIC databank. Several parameters have been modified to improve the accuracy of the reactor model. The original values are given in Table B.2 and the modified values are given in Section 6.4.1. Section 6.4.1 also provides the variables and equations for which the modified values are applicable.

Table B.1 List of components

Type: Solid	
Hematite (Fe_2O_3)	Iron-dialuminum tetraoxide ($FeAl_2O_4$)
Magnetite (Fe_3O_4)	Carbon: Graphite (C)
Ferrous oxide (FeO)	Iron monosulfide (FeS)
Iron (Fe)	Iron disulfide: Pyrite (FeS_2)
Aluminum oxide: alpha-Corundum (Al_2O_3)	
Type: Conventional	
Methane (CH_4)	Hydrogen (H_2)
Ethane (C_2H_6)	Water (H_2O)
Propane (C_3H_8)	Oxygen (O_2)
n-Butane (C_4H_{10}-1)	Nitrogen (N_2)
Carbon monoxide (CO)	Argon (Ar)
Carbon dioxide (CO_2)	

Table B.2 Original parameters for CPSXP2

Component	FE3O4
Temperature unit	°C
T1	576.85
T2	1596.85
Property unit	J/kmol
a	-9.7E+08
b	527383.9
c	-50171.2
d	-35.9673
e	-6.02E-05
f	6.13E-09
g	-4.3E+10
h	5.47E+09

Operating Conditions

The operating conditions for the base case simulation of the reducer are presented in Table B.3.

Table B.3 Inlet component parameters

Species	CH_4	H_2O (steam)	Fe_2O_3	Al_2O_3
Flow Rate (kmol/hr)	1	0	1.2	3.2
Temperature (°C)	600	600	1125	1125
Pressure (bar)	10	10	10	10

Table B.4 Reactor parameters

Reactor	Reducer
Temperature (°C)	900
Pressure (bar)	10

Results and Discussion

By adjusting the IACMO:CH_4 mole ratio in the feed, the products of the reducer can be controlled to favor syngas generation. By fixing the CH_4 flow rate at 1 kmol/hr and varying the IACMO flow rate from 0.5 to 10 kmol/hr, performed in sensitivity block IACMO variable 1, the syngas composition at varying IACMO:CH_4 ratios are obtained. The results are given in Table B.5. From Table B.5, when the total IACMO flow rate is greater than 4, there is no carbon deposition. When the IACMO flow is further increased, syngas generation begins to decrease and products of full combustion begin to increase.

Another variable affecting syngas purity is the steam flow rate into the reducer. The steam flow rate is varied using sensitivity block STEAM variable 1. Increasing the steam flow rate increases the hydrogen generation while carbon monoxide decreases as the CO produced is oxidized to CO_2 by the steam, which is reduced to H_2 via the water-gas shift reaction, given in Reaction (B.1.5). The overall effect of steam addition is the generation of hydrogen, thereby increasing the H_2:CO ratio of the syngas. At a CH_4 and an IACMO flow rate of 1 and 4.4 kmol/hr, respectively, the steam injection rate was varied from 0.1 to 1 kmol/hr. Table B.6 summarizes the results.

Table B.5 Product distribution as function of IACMO:CH_4 mole ratio

OC	CO	H_2	CO_2	H_2O	H_2:CO	C
KMOL/HR	KMOL/HR	KMOL/HR	KMOL/HR	KMOL/HR		KMOL/HR
0.5	0.104	1.49	0.00156	0.0296	14.4	0.657
1	0.206	1.50	0.00578	0.0554	7.27	0.564
1.5	0.307	1.50	0.0121	0.0780	4.88	0.469
2	0.407	1.50	0.0202	0.0980	3.69	0.372
2.5	0.507	1.50	0.0297	0.116	2.97	0.273
3	0.605	1.50	0.0404	0.132	2.48	0.172
3.5	0.704	1.50	0.0521	0.147	2.14	0.070
4	0.779	1.52	0.0682	0.175	1.95	0
4.4	0.793	1.54	0.0893	0.228	1.94	0
4.5	0.795	1.54	0.0950	0.242	1.93	0
5	0.796	1.53	0.125	0.317	1.92	0
5.5	0.785	1.49	0.159	0.397	1.90	0
6	0.766	1.44	0.194	0.481	1.88	0
6.5	0.740	1.38	0.232	0.568	1.86	0
7	0.709	1.30	0.271	0.657	1.84	0
7.5	0.675	1.23	0.312	0.747	1.82	0
8	0.637	1.14	0.354	0.837	1.80	0
8.5	0.597	1.06	0.397	0.928	1.77	0
9	0.555	0.974	0.441	1.02	1.75	0
9.5	0.512	0.887	0.485	1.11	1.73	0
10	0.467	0.799	0.531	1.20	1.71	0

Table B.6 Effect of steam flow on syngas purity

STEAM	CO	H_2	CO_2	H_2O	H_2:CO	C
KMOL/HR	KMOL/HR	KMOL/HR	KMOL/HR	KMOL/HR		KMOL/HR
0	0.793	1.54	0.089	0.228	1.94	0
0.1	0.795	1.62	0.108	0.289	2.03	0
0.2	0.792	1.68	0.127	0.355	2.12	0
0.3	0.785	1.74	0.145	0.424	2.21	0
0.4	0.777	1.79	0.164	0.495	2.30	0
0.5	0.768	1.83	0.181	0.569	2.38	0
0.6	0.757	1.87	0.199	0.645	2.47	0
0.7	0.746	1.90	0.215	0.723	2.55	0
0.8	0.735	1.93	0.232	0.802	2.63	0
0.9	0.723	1.96	0.247	0.882	2.71	0
1	0.711	1.98	0.262	0.964	2.79	0

Conclusions

A single stage RGIBBS reactor was used to simulate a cocurrent moving bed reforming reducer using gaseous fuel (CH_4) in Aspen Plus®. Based on the Gibbs free energy minimization as well as assuming phase and chemical equilibrium is achieved, the product distribution is calculated under the specified conditions of the RGIBBS reactor.

The operating range where syngas production is favored over combustion products with no carbon deposition was identified through a sensitivity analysis. By observing the product distribution through a wide range of IACMO:CH_4 mole ratios, the demarcations where carbon deposition and combustion products form establishes the operating range for syngas generation. Through steam injection, the H_2:CO ratio of the syngas can be adjusted as necessary to obtain the appropriate ratio, which is product dependent. However, because the H_2:CO ratio is adjusted through the water-gas shift reaction, an increase in H_2:CO ratio correspondingly increases the CO_2 content in the syngas.

Appendix

The Aspen Plus file of the gaseous feed reducer simulation is given in the file titled, "B.1 Reducer with Gaseous Feed."