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Effect of natural gas catalytic reforming reaction kinetics on a pilot reformer design

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Abstract

One of the best methods for constructing a pilot plant of plug and packed bed flow reactor is to scale down the dimensions of an industrial one. In this regard, the first step is to simulate the reactions of the industrial equipment by employing proper kinetic equations and then scale down all the dimensions with different scaling factor in order to find out the smallest possible dimensions for the physical model. In this paper attempts were made to find out the proper dimensions of physical model, of a catalytic natural gas reformer pilot based on the industrial reformer which is currently operates at Ghadir Iron and Steel Company in Iran. .In this regard, the simulation of reforming, Water-gas shift and methanation reactions on the Ni/ Al_2O_3 catalyst, with the operational condition data was performed with Aspen-Hysys software. The results showed that since the reforming reactions are so fast, the kinetics of the reactions is not much dependent on the tube reactor dimensions and therefore the dimension of the physical model of the reformer is not an issue in designing a physical model.

Key words: Catalytic reforming, scale down, kinetics, reforming simulation

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Introduction

There are basically two ways in order to develop new process like a catalytic reaction. Scale up and scale down methods. The steps In Scale Up method, comprise of: Catalyst screening and development by using a small, laboratory reactor, Development of a conceptual process sequence, Scaling up the laboratory reactor to a pilot plant size with adding the other process steps to study the recycle effects and finally scaling up the pilot plant size to the commercial size[1]. On the other hand scaling down method includes other steps such as: Catalyst screening and development as mentioned above, Development of a kinetic model possibly by using another type of laboratory reactor, Development of a conceptual process design and simulation of the commercial scale process, Scaling down the commercial scale to the smallest possible pilot plant size, Determination or verification of design parameters by using the pilot plant data, and at last, Final design of the commercial plant by using the validated or updated parameters from the pilot plant results. [1, 2]

In the Scale Down method, the simulation of the commercial design exists even before the designing of the pilot plant. The pilot plant is then designed to improve the estimates of the most important, least well known parameters. These parameters are of two kinds, scale dependent and scale independent. Examples of the latter are physical properties of the fluids and their components as well as the properties of other materials. The scale dependent parameters usually arise due to the use of a simplified model for a complex process. Examples of the scale dependent parameters are axial and radial heat and mass dispersion coefficients that can be calculated by using the developed correlations in the literatures. Generally, despite the fact that the second method is more reliable, in many applications, the first one is used as a default [8]. Defining a correct sizing for the pilot plants is a critical decision in process development. Larger units provide more similarities to commercial-scale unit operations, but require more time and cost to implement, and will have greater challenges in risk abatement and safety matters. Smaller units may be deployed and modified more rapidly at lower cost, but unless properly designed, may not address key issues in design and scale up, or may not produce sufficient product to evaluate commercial unit[2].

Reactor scaling is typically dominated by transport phenomena, rather than chemical reactions. Slow, direct reaction of liquid or gas streams is a rare objective. Most typically, reactor design entails challenges in fast homogenous reactions, or catalytic reactions where transport to or from an active site, may be limited, and contacting of multiple phases (liquid-solid, gas-solid, gas-liquid) dominates the scaling problem. For the fast liquid- or gas-phase reactions, mixing is a key player. Scaling rules for catalytic, multiphase reactors are dominated by the characteristic size of the catalyst particles, or gas or liquid droplet formation. Characteristic dimensions for the fixed-bed catalyst particles, liquid droplets are typically on the order of 1 – 3 mm, such that many different reactor types ultimately result in similar minimum scales, where reactor diameter should approach at minimum 10 particle or droplet diameters, and length should approach 20 characteristic diameters to avoid entrance effects and minimize the impact of axial dispersion. The fixed-bed limit in particle size is set by commercial pressure drop considerations, while droplet size is set by minimum allowed and maximum sustainable droplet size, set by interfacial tension. Similar scaling considerations for these diverse systems mean that a 25-mm or 1-inch diameter reactor that is at least twice as long as wide, can be sufficient for wide range of reaction systems, from fixed-bed reactors with catalyst pellets, to multiphase gas-liquid reactors with finely divided slurry catalyst. [3]

In some cases by using more finely divided solid diluent in trickle bed reactors in order to achieve 10:1 average particle to fluid diameter we might be able to improve transport at a smaller scale . Care must be taken in scale down however to insure that maximum bubble diameter does not approach tube diameter, leading to a lab reactor flow regime (slug flow) which cannot be the Representative of commercial. If heat transfer is an important consideration for piloting, then the fact that heat transfer area per unit volume scales depends inversely to the diameter should be taken in to consideration especially in exothermic reactions [9]. Also, in the case that a single tube reactor is used as a pilot for a multitube reactor, as it is the case in natural gas reformers, uniformity of the catalyst bed and flow distribution will be the scale up challenge. [4,5]

As mentioned above, in this article, in order to find the proper dimension of a pilot reformer, first the most important reactions are simulated using a reliable kinetic model, in this way the dimensions of the reactor and operational process data of an industrial reformer of *Iranian Ghadir Iron and steel company* (IGISCO) which is producer of sponge iron by *MIDREX* technology were used. Then all the parameters were scaled down by different factors and then the reactors with new dimensions were simulated again. Then the results were compared and the smallest possible dimensions were selected for the pilot plant.

Process Description

The reference industrial unit in this research is a DRI plant (MIDREX unit). A general and simple schematic view of the MIDREX process plant is shown in Figure1. In this process, syngas is produced via an endothermic reaction between water and carbon dioxide with the natural gas on the bed surface of the Ni based catalysts. The rate of this reaction is strongly affected by heat transfer from furnace to the catalyst bed [6].

Process simulation:

As mentioned in introduction part, after the catalyst selection, the most important step in scaling down the industrial reformer is simulation of the reactions in operational process conditions and the first step in reaction simulation is to select the proper reaction kinetics on the selected catalyst bed. Many effort has been performed to study the mechanisms and kinetics of methane steam and dry reforming on many types of the catalysts since 1950 and many results have been reported in the literature[7], This process comprises not only the reactant and product transfer and diffusion between bulk and the catalyst surface, but also comprises some parallel and series reactions and any change in catalyst particle size distribution and also temperature and pressure range can have a dramatic change in reaction mechanism as well as kinetics. In this case one of the most reliable kinetics which is developed in 2001 by *Hou* and *Hughes* on the nickel catalyst with alumina support is used for simulations of the reactions [7,8].

In addition to this model compatibility with the industrial catalysts, it has an accurate prediction of the reactions in a vast range of temperature, pressure and species compositions. Kinetics equations as well as related coefficients and constants for three most reactions, reforming, water-gas shift and methanation, is present in table 1. These equations are based on the Langmuir Hinshelwood model and limitations [7].

$$r_1 = \frac{k_1\left(\frac{P_{CH_4}P_{H_2O}^{1.25}}{P_{H_2}^{1.25}}\right)\left(1-\left(\frac{P_{CO}P_{H_2}^{3}}{K_{P_1}P_{CH_4}P_{H_2O}}\right)\right)}{(DEN)^2} \quad (1)$$

$$r_2 = \frac{k_2\left(\frac{P_{CO}P_{H_2O}^{0.5}}{P_{H_2}^{0.5}}\right)\left(1-\left(\frac{P_{CO_2}P_{H_2}}{K_{P_2}P_{CO}P_{H_2O}}\right)\right)}{(DEN)^2} \quad (2)$$

$$r_3 = \frac{k_3\left(\frac{P_{CH_4}P_{H_2O}}{P_{H_2}^{1.75}}\right)\left(1-\left(\frac{P_{CO_2}P_{H_2}^{4}}{K_{P_3}P_{CH_4}P_{H_2O}^{2}}\right)\right)}{(DEN)^2} \quad (3)$$

$$DEN = 1 + K_{CO}P_{CO} + K_{H_2}P_{H_2}^{0.5} + K_{H_2O}\left(\frac{P_{H_2O}}{P_{H_2}}\right) \quad (4)$$

$$K_i = A_i \exp\left(\frac{-B_i}{T}\right) \quad (5)$$

Simulation of the reactions has been conducted by commercial software (Aspen-Hysys) at the operational process conditions of the IGISCO unit. These parameters as well as the catalyst properties are shown in the tables 1-2 and 2-2. The results of the simulation using the mentioned parameters with the outlet operational data from the control room are shown in the table 3.

The next step of the pilot design is to scaling down all the industrial dimensions in order to have the smallest size, so all the IGISCO reformer dimensions were scaled down by factor 4 to 40 and again simulated by using the aforementioned software. It should be noted that, for the mass flow, the velocity of gas in pipes are kept constant and the quantity of them were scaled down by square of the diameters. The outputs of the simulation for each sample are shown in table 4. In lined with the table above, the composition of each species in outlet stream in different scaling factor is shown in figure2. As it can be seen, the compositions become constant at factors above 6. It means that the reforming reaction is so fast that the kinetics of the reaction is not much relevant to the reactor dimensions and it will be reach to equilibrium instantly. In other words, kinetics is not a constraint and other transfer phenomenon is more important.

Conclusion

In this research, Different methods of the pilot unit design were studied, selecting one of the methods, the reactor simulation of an industrial unit was performed, and then by scaling down the dimensions regarding to their proportional importance, the smallest possible dimensions, which was fit to the pilot construction purposes were selected. Effects of the different dimensions of IGISCO catalytic reformers tube on the outlet species composition were studied. The results showed that the reforming reactions are so fast that the reach to equilibrium at once and the kinetics is not much relevant to the reactor dimensions. So, the kinetic factor is not the limiting case and heat transfer and diffusion are more important in reaction part in designing the reactor.

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Table 1. coefficient of the kinetic model [1,4].

Kinetic parameters	Quantity	Unit
A_1	5.92×10^{8}	$(Kmol/Kg\ cat\ s)(KPa)^{0.25}$
B_1	25162	K
A_2	6.03×10^{-4}	(Kmol/Kg cat s)(KPa)
B_2	1852.37	K
A_3	1.09×10^{3}	$(Kmol/Kg\ cat\ s)(KPa)^{0.25}$
B_3	13158	K
A_{p1}	1.19×10^{17}	$(KPa)^2$
B_{p1}	26830	K
A_{p2}	1.77×10^{-2}	(KPa)
B_{p2}	-4400	K
A_{p3}	2.12×10^{15}	$(KPa)^{0.25}$
B_{p3}	22430	K
A_{CO}	5.13×10^{-13}	$(KPa)^{-1}$
B_{CO}	-16839	K
A_{H2}	5.68×10^{-10}	$(KPa)^{0.5}$
B_{H2}	-11234	K
A_{H2O}	9.25	(KPa)
B_{H2O}	1912	K

Table 2-1. dimensions of the IGISCO reforming unit.

Parameter	Tube inside diameter (mm)	Tube wall thickness (mm)	Tube no.	Tube length (mm)
Quantity	200	11.2	468	9550

Table 2-2. Catalyst properties of IGISCO unit.

Parameter	Catalyst shape	Particle size (mm)	Porosity	sphericity	Equal diameter (mm)	Tortuosity	Particle density (kg/m3)	Bed density (kg/m3)	Bed porosity
Quantity	Raschig ring	16×6×16	0.52	0.656	17.41	2.74	2390	1362	0.6

Table3. Comparison of simulation output and IGISCO operational output.

Items		IGISCO input data	Simulation output	IGISCO Output data
Parameter	Unit			
Temperature	(K)	500	925	925
Pressure	(bar)	1.74	1.375	1.74
Mass flow	(Kg/hr)	88900	88900	88900
CO Composition	%	1.74	0.3729	0.372
CO_2 Composition	%	0.152	0.00025	0.0034
H_2 Composition	%	0.311	0.5419	0.5428
H_2O Composition	%	0.139	0.0641	0.0632
CH_4 Composition	%	0.198	0	0.018
N_2 Composition	%	0.026	0.0186	0.0186

Table4. result of simulation for the scaled samples.

Factor / Item	1	4	5	6	10	15
Tube length(mm)	9550	2387.5	1910	1591.66	955	636.66
Tube ID (mm)	200	50	40	33.334	20	13.334
Mass flow(kg/hr)	88900	5557	3556	2470	889	396
Temperature©	925	925	925	925	925	925
Pressure (Bar)	2.37	2.37	2.37	2.37	2.37	2.37
CH_4 %	0.3729	~0	~0	~0	~0	~0
CO %	0.0002	0.4251	0.4188	0.3967	0.3825	0.3663
CO_2 %	0.5419	0.0059	0.0138	0.005686	0.0536	0.072
H_2 %	0.0641	0.5108	0.5128	0.5451	0.5233	0.5282
H_2O %	~0	0.0372	0.0345	0.0609	0.0201	0.0135
N_2 %	0.0186	~0	0.0201	0.01862	0.0205	0.0203

Table 4. Result of simulation for the scaled samples(continued).

Factor / Item	20	25	30	35	40
Tube length(mm)	477.5	382.1	318.3	272.8	238.7
Tube ID (mm)	10	8	6.6	5.7	5
Mass flow(kg/hr)	222.25	142.25	98.78	72.58	55.57
Temperature C	925	925	925	925	925
Pressure (Bar)	2.37	2.37	2.37	2.37	2.37
CH4 %	~0	~0	~0	~0	~0
CO %	0.3576	0.3522	0.3486	0.3456	0.3434
CO_2 %	0.0815	0.0874	0.0916	0.0949	0.0974
H_2 %	0.5307	0.5323	0.5333	0.5342	0.5349
H_2O %	0.0101	0.0079	0.0064	0.0052	0.0043
N_2 %	0.0202	0.0202	0.0201	0.0201	0.0201

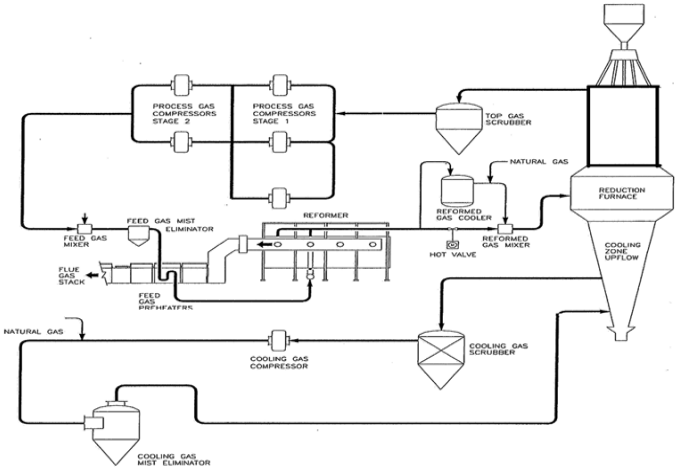

Figure 1. General and schematic view of a MIDREX plant [6].

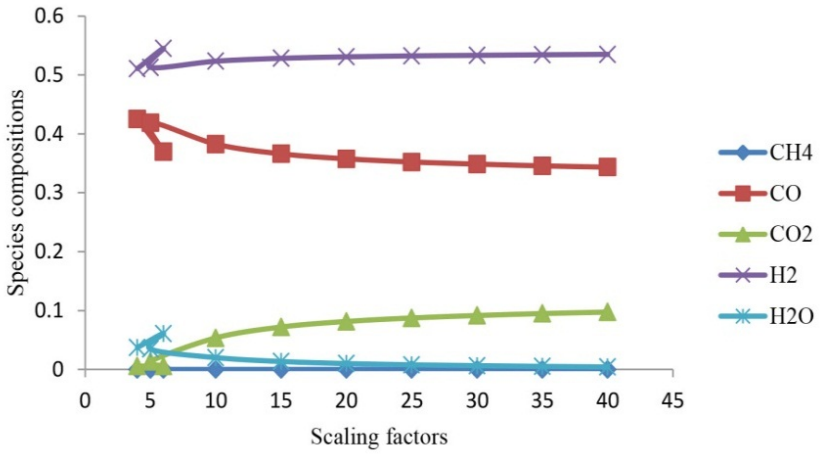

Figure 2. Species composition vs. scaling factor.