Kinetic Model of Nitric Oxide Reduction on CuFe/SUZ-4 Catalyst in Packed Bed Column

P. Worathanakul, T. Layakul, and P. Juengsura

***Abstract*—Model was predicted for suitable condition to achieve the maximum nitric oxide (NO) conversion for using with even-CuFe/SUZ-4 zeolite catalyst in packed-bed reactor in NO reduction. Comsol Multiphysics and Reaction Engineering Lab3.5a based on Computional Fluid Dynamics (CFD) were used to evaluate performance of the reactor. The simulation results were according to the experiments in different sequence of Cu and Fe loadings on SUZ-4 zeolite with impregnation method. Volume flow rate, preheat temperature, and reactor temperature of gas feed rate were used as variables for finding the maximum NO reduction. The results show that the maximum NO conversion of CuFe/SUZ-4 catalyst can achieve at 500 ℃ reaction temperature with 250 ppm of 250 ℃ preheat temperature gas feed rate. To increase NO conversion, decreasing of gas feed flow rate is the main effect than decreasing of preheat temperature. Moreover, the simulation results were closed to the experiments with only 0.12-1.55 % of error.**

***Index Terms*—CuFe/SUZ-4 zeolite, nitric oxide, kinetic model, catalyst.**

I. Introduction

In general, oxides of nitrogen (NO_x), this means the nitric oxide (NO) and nitrogen dioxide (NO_2). Nitric oxide as a substrate cause to toxic gas ozone (O_3) and nitrogen dioxide can be nitric acid that causes acid rain, smog and destroy ozone layer with an impact on the environment. Moreover, the NO_x cause to diseases of the respiratory system and cancer.

Oxides of nitrogen occur from the thermal reaction of nitrogen when oxidized in air at high temperature. To reduce the amount of toxic gas, technology has been developed using a catalyst (Selective Catalytic Reduction, SCR Process) and using ammonia as a reducing agent to reduce emissions from engines [1], [2]. For these reasons, NO_x emissions can be controlled, using catalytic technologies for the abatement of emission nitrogen oxides into the atmosphere. The selective catalytic reduction (SCR) using ammonia (NH_3) as a reductant (NH_3-SCR) has been used for a long time. This is mainly applied for emission reduction of coal and oil-fired power plants [3]. However, this process suffers from many disadvantages due to the use of an additional gaseous reducing agent such as ammonia slip, device corrosion, danger in transportation and storage of ammonia [4].

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Study of the transition metal ion exchange with in the zeolite will help the positive effect the catalytic properties in reducing NO_x such as metal copper (Cu) on the support value changes NO_x well during low temperature (150 ℃) for combustion of diesel engine under normal conditions, but Cu was born of oxidation reaction with ammonia (NH_3) increased at high temperature (>300 ℃) which will affect the overall performance in reducing NO_x. Therefore, Fe and Cu loading as a catalyst was selected because of the combustion temperature range of iron are high. (> 450 ℃) [5] and combination of metal copper (Cu) and iron (Fe) on SUZ-4 supporter catalyst was suitable to improve the efficiency in reducing NO_x better [6]. Ammonia and hydrocarbons are considered to be the best reducing agents in this process but hydrogen has also been reported to be a very effective reducing agent [7]. Hydrogen is one of the exhaust gases emitted by automobiles and can easily be generated by an on-board compact reformer used in a fuel cell system [8], [9].

At present, the effective scientific technologies are used for nitric oxide (NO) reduction processing with catalysts, but the cost of experiments in the laboratory to evaluate the efficiency of reduction rather high. Moreover, many researches on simulation model and kinetic mechanism using with catalytic reduction process to reduce the nitric oxide does not demonstrate CuFe/SUZ-4 zeolite and hydrogen as reducing agent on packed bed reactor for nitric oxide removal [10]-[15].

Therefore, this research was aimed to simulate the model and study the factors that affected on the process efficiency for CuFe/SUZ-4 zeolite. Hydrogen was used as reducer in packed-bed reactor. The simulation model was used to demonstrate and reduce the operation cost. The optimum conditions were determined by using the computer program including Aspen plus user interface V7.3, Comsol Multiphysics and Reaction Engineering Lab 3.5A. The model can increase the efficiency of nitric oxide reduction. Furthermore, this research was aimed to develop and apply knowledge in industrial for reducing of pollution and maintaining the organisms and environments.

II. Procedure for Model Simulation

The methodology for model simulation based on setting the chemical reactions, predict fluid flow patterns within the packed-bed reactor, solved the problems from the assumptions set up.

A. Reaction and Physical of Reactor Conditions

This research paper was simulated based on the reaction according to equations (1) to (3) [10]

$$2NO + 2H_2 \rightarrow N_2 + 2H_2O \quad (1)$$

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$$2NO + H_2 \rightarrow N_2O + H_2O \quad (2)$$

$$H_2 + 0.5\, O_2 \rightarrow H_2O \quad (3)$$

From the experimental reduction of nitric oxide (NO) in the laboratory by loading 2.3% Cu 1% Fe SUZ-4 zeolite on the support simultaneously (2.3%Cu1%Fe/SUZ-4 catalyst), the results of study were found that nitric oxide conversion was high efficiency than other condition loadings [16], [17]. This study was used packed bed column with CuFe/SUZ-4 catalyst for NO reduction. Mixed gas of NO: O2: H2: He ratios in 0.025: 1: 10: 88.975 by volume was fed into mixer at temperature 25˚C in gas phase at 1 atm and temperature was increased in the heater. Reacted NO was then reduced in plug flow reactor. Size of packed bed reactor was with 0.7752 cm diameter and 5 cm length and CuFe/SUZ-4 catalyst loading was 4 cm length as shown in Fig. 1.

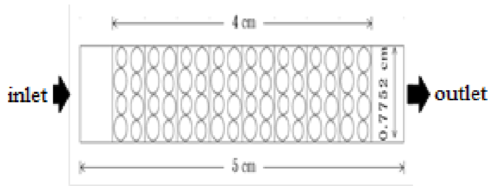

Fig. 1. Creating model of packed bed reactor with catalyst.

B. *The Model Simulation*

The first part of this study was matched the model with experiments data. The model simulation was compared the results with the experiment of different sequence of copper and iron loadings on SUZ-4 zeolite with impregnation method for NO reduction. Next part was finding suitable condition for NO reduction by varying parameters; reactor temperature, volume flow rate of gas feed, and preheats temperature. Aspen plus was used to find the density, viscosity, velocity of gas feed, inlet gas concentration, heat duty of heater and reactor, residence time, and of the molar of gas feed. Molar of gas feed and velocity of gas feed was used in the Comsol reaction. After the suitable condition of NO reduction was obtained, density, viscosity velocity of gas feed, and inlet gas concentration from Aspen plus was used to input in Comsol Multiphysics in order to analyze velocity profile and pressure profile of gas feed according to the distance of the reactor and creating reactor model.

The studies of the flow characteristics of the reactor (momentum transfer), assumptions for momentum transfer were set with these conditions:

1) The system was steady state flow
2) Inlet gas was laminar flow
3) The system was incompressible flow, so that the density of the fluid was constant or a small change was ignored.
4) The fluid mixed perfectly round cross-section of the flow channel.
5) The inlet temperature of the reactant fed was 300 ˚C.
6) The physical properties of fluids were averaged by taking at the inlet and outlet temperatures of the channel.

Governing equation was used solving the Navier-Stokes'equations with hydrodynamics of the reactor for the nonlinear momentum and the continuity equations as in (4) and (5):

$$p\frac{\partial u}{\partial t} - \nabla \cdot \eta(\nabla u + (\nabla u)^T) + pu \cdot \nabla u + \nabla p = 0 \quad (4)$$

$$\nabla \cdot u = 0 \quad (5)$$

The boundary condition as in (6) at the inlet for initial condition was a specified normal velocity, namely

$$u = u_0 \quad (6)$$

The inlet gas velocity as in (7) was defined via the inlet flow rate of 0.09 m/s as:

$$u_0 = v\_av \quad (7)$$

The outflow boundary condition as in (8) at the outlet of the reactor was the pressure, no viscous stress as:

$$p = p_0 = p\_ref \quad (8)$$

The boundary condition as in (9) at the Interior boundary is continuity flow in eq.

$$n(\eta_1(\nabla u_1 + (\nabla u_1)^T) - p_1 I - \eta_2(\nabla u_2 + (\nabla u_2)^T) + p_2 I = 0 \quad (9)$$

The no slip boundary condition at the wall with any velocity components at a boundary was applied to the reactor wall, as in (10)

$$u = 0 \quad (10)$$

The slip symmetry condition as in (7) was applied to the catalyst surfaces corresponding to the absence of viscous effects in the continuum equations in accord with the underdeveloped boundary layer on the catalyst surfaces. This condition allowed the tangential velocity is different from zero.

To get optimum conditions for nitric oxide reduction with zeolite in packed-bed reactor, the steps were determined by using the computer program as follows;

Step 1: Finding suitable reactor temperature condition

1) Using volume flow rate of gas feed before enter to mixer 200 ml/min and preheat temperature at 300 ˚C
2) Varying reactor temperature at 300 ˚C, 400 ˚C, 500 ˚C and 600 ˚C

Step 2: Finding suitable volume flow rate of gas feed before enter to mixer

1) Using reactor temperature from step 1 and preheat temperature at 300 ˚C
2) Varying volume flow rate of gas feed before entering to mixer

Step 3: Finding suitable preheat temperature

1) Using reactor temperature from step 1 and volume flow rate of gas feed before entering to mixer from step 2
2) Varying preheat temperature

III. Results and Discussion

A. *Step 1: Finding Suitable Reactor Temperature Condition*

The NO reduction with different reactor temperature between the model and the experiment were carried out at volume flow rate of gas feed with 200 ml/min and preheat temperature at 300˚C. The higher reactor temperature gets the higher of the percentage NO conversion. However, NO conversion at 600 ˚C will decrease may be due to structure of the catalyst was changed and affected to NO reduction conversion. The results were found that the highest NO reduction was 86.2% at 500 ˚C as shown in the Table I.

TABLE I: COMPARING OF NITRIC OXIDE CONVERSION OF MODEL WITH EXPERIMENTAL DATA

Reactor temperature (˚C)	% NO conversion		% Error
	Experiment	Model	
300	58.0	58.9	1.55
400	57.0	57.1	0.23
500	86.2	86.2	0.12
600	59.0	58.9	0.19

B. Step 2: Finding Suitable Volume Flow Rate of Gas Feed before Enter to Mixer

From Step 1, the suitable reactor temperature was chosen to find volume flow rate of gas feed before entering to mixer to get the maximum percent NO conversion. The volume flow rate was varied with 10-600 ml/min. Decreasing of volume flow rate caused to decrease average gas velocity and affect to increase the residence time of reaction in the reactor. Therefore, % NO conversion will increase and get 100% NO conversion with the volume flow rate of gas feed 10 ml/min and gave the minimum heat duty of heater and reactor. It is resulted to energy cost saving in the system.

C. Step 3: Finding Suitable Preheat Temperature

The suitable volume flow rate and reactor temperature were already solved from Step 1 and 2. Step 3 was then used to find pre-heat temperature with the balance condition of thermal load of heater and reactor. The results from Table II showed that decreasing of pre-heat temperature bring to average gas velocity before enter to reactor decreased. At 100 ˚C, 250 ˚C and 300 ˚C pre-heat temperature, NO conversion was achieve at 100%, while the condition was at 500 ˚C, the NO conversion decreased to 97%. However, changing of pre-heat temperature did not affect to total heat duty and residence time of reactor. It was still 7.09 ×10-5 kW heat duty and 4.37 seconds residence time, respectively.

TABLE II: EFFECT OF PRE-HEAT TEMPERATURE AT 500 ˚ C REACTOR TEMPERATURE AND VOLUME FLOW RATE OF GAS FEED 10 ML / MIN

Pre-heat temperature (˚C)	NO conversion (%)	Average gas velocity (10^{-4} m/s)	Heat duty of heater (10^{-5} kW)	Heat duty of reactor (10^{-5} kW)	Total Heat duty (10^{-6} kW)
100	100	44.20	1.111	5.986	70.973
250	100	61.96	3.344	3.754	70.973
300	100	67.88	4.091	3.006	70.973
500	97.06	91.56	7.097	0.000	70.973

The results were shown that pre-heat temperature was increased, heat duty of reactor decreased. Therefore, the pre-heat temperature at balance load point of heater and reactor was found from the intersection point between heat duty of heater and reactor. From the simulation model, the suitable condition of pre-heat temperature for nitric oxide reduction was at 250 ˚C with 500 ˚C reactor temperature and 10 ml/min of volume gas feed flow rate before enter to the mixer.

D. Characteristics and Velocity and Pressure Profile of Gas

Studying of gas flow through packed bed reactor in axial symmetry, dimension of reactor in Step 2 is important to monitor the potential of the designed reactor; mass transfer, heat transfer, and chemical reactions occurring. The uniform distribution of gas in the reactor can help transferring of gas to the surface of catalyst are thoroughly. Moreover, energy transfer can reduce hot spot and cold spot phenomena in the endothermic and exothermic reaction type and also prolong the catalyst life time. This research was presented the velocity profiles to distance of reactor. Fig. 2 show mixed gas flow through the catalyst surface in the reactor with uniform appearance flow according to bed of catalyst arrangement. As a result, it can be analyzed that the arrangement type of catalyst affected to direction and velocity of gas flow. While gas flow through gaps between the surface of the catalysts, the velocity of gas feed are raised up due to changing within a bed surface area of catalysts.

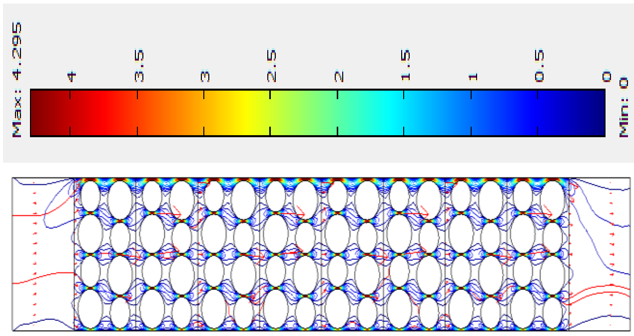

Fig. 2. Characteristic and contour line of gas flow through catalyst surface.

The correlation between velocity of gas feed in reactor and distances of reactor was shown in Fig. 3. Gas velocity for reactor inlet is 0.004 m/s. After gas flow through bed of catalysts, velocity will increase immediately because of changing of cross sectional area between reactor and catalyst.

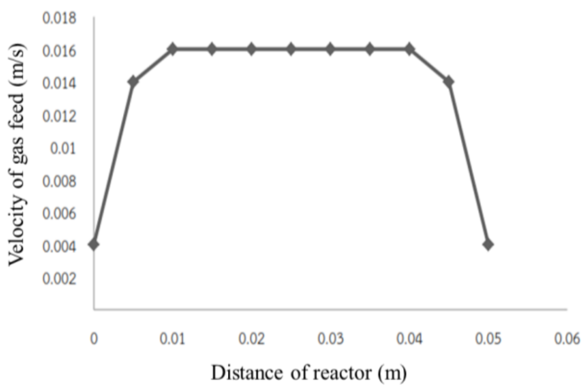

Fig. 3. Velocity profile of feed gas.

Maximum velocity is constantly held at 0.016 m/s with the assumption of uniform arrangement of the catalyst in the model. At the exit of reactor, gas velocity is decreased immediately because of changing of cross sectional area between reactor and catalyst again to 0.004 m/s.

However, studying pressure and pressure drop in packed bed reactor are important for considering the efficiency of reactor. The characteristic of reactor and arrangement of catalyst pellet will result in the pressure distribution and pressure drop which confirm ability and suitability between designed. The pressure profile of this research was shown as in Fig. 4.

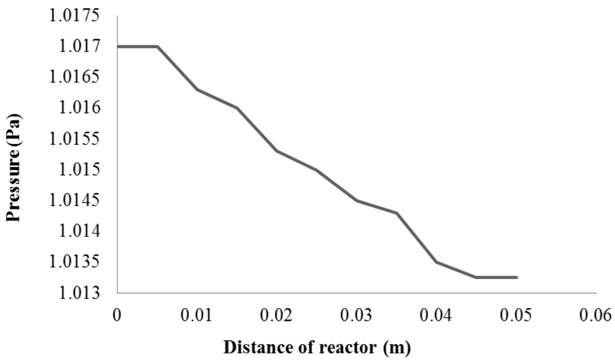

Fig. 4. Pressure profile of gas feed.

From Fig. 4 at inlet of the reactor, pressure profile of gas has indicated that a maximum pressure is at 101.732 kPa. Pressure was decreased continually along the distance of bed length when the gas flows through the bed of catalyst. At the end of reactor have a minimum pressure at atmospheric pressure 101.325 kPa. The relationship between the pressure and the distance along the length of reactor found that, pressure was reduced when gas flow through the bed which pressure drop is 0.407 kPa. These results due to the friction loss structure of catalysts.

IV. Conclusion

The optimal conditions for nitric oxide reduction in packed bed reactor with CuFe/SUZ-4 catalyst was used hydrogen as a reducing agent, reactor size 1.89 cm^3 and diameter of reactor 7.75 mm. Reactor temperature was used at 500˚ C and preheats temperature at 250˚C to continue for varying volume flow rate of gas feed. The results were concluded that at 10 ml/min is the maximum volume flow rate of gas feed with average gas velocity 0.0062 m/s, residence time 4.37 seconds, and total heat duty 7.09×10^{-5} kW. The maximum NO reduction was 100%. This is due to decreasing volume flow rate of gas feed and resulted in increasing residence time of gas feed in reactor. This research was successful the optimization condition for NO reduction of CuFe/SUZ-4 catalyst by adjusting the volume flow rate. The factor of gas feed can increase efficiency of nitric oxide reduction more than adjusting the preheat temperature. However, the optimum conditions from simulation model should further confirm the results with laboratory.

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