Modeling and simulation of photoreactor for photocatalytic conversion of CO_2 into methanol

A. Asadi [1], A. Larimi [2*], A. Naderifar [1]
[1] *Department of Chemical Engineering, Amirkabir University of Technology, Tehran, Iran*
[2] *Department of Chemical and Process Engineering, Niroo Research Institute, Tehran, Iran*
alarimi@nri.ac.ir

Abstract
Photocatalytic conversion of CO_2 to value-added products like methanol has been recognized as a reliable solution in reducing greenhouse gas emission as well as clean fuel supply by renewable fuel production. Reactor design plays an important role in increasing reactor efficiency and production. This is an important factor in moving us toward reactor modeling and simulation. This paper investigates the computational fluid dynamics in a three-phase slurry photoreactor. The intensity of light source and its effect on the concentration of the methanol product was investigated and reliable answers were obtained after using appropriate modules, hydrodynamic and kinetic studies in COMSOL Multiphysics software.

Keywords: CO_2 photoreduction, slurry photoreactor, multi-phase flow, modeling and simulation

1. Introduction
Sustainable development depends directly on the availability of sufficient energy resources, consumption/restoration ratio and environmental effects. Combustion of fossil fuels generates greenhouse gases especially carbon dioxide (CO_2), the main cause of global warming [1]. Converting CO_2 into renewable fuels by simultaneously reducing atmospheric CO_2 levels and using renewable solar energy to drive photocatalytic reactions could provide a viable solution [2].
The photoreactor design is of great importance in the photocatalytic CO_2 reduction. One type of photoreactor used for this purpose is a slurry type of which a little research has been done on the modeling and simulation [1, 3-5]. This led us to develop and investigate these types of reactors.
In this study, modeling and simulation of slurry photoreactors has been done by COMSOL Multiphysics software. This research is of great importance for investigating the photoreactor performance as well as parametric study while reducing laboratory costs and being time-saving.
The following equation was used to show the photoreduction of carbon dioxide to methanol as the main reaction [6]:

$$CO_2 + 2H_2O \xrightarrow{catalyst+hv} CH_3OH + \frac{3}{2}O_2 \quad (1)$$

2. *Experimental*

To validate the present investigation, the data obtained from the laboratory system available at Niroo Research Institute has been used. This set up has been developed and tested by Larimi and co-workers [7].

3. *Theoretical Method*

To simulate the laboratory system, fluid dynamics, reaction kinetics and radiation must be modeled simultaneously by employing the following modules of COMSOL Multiphysics:

- Euler – Euler, Turbulent model $k-\varepsilon$
- Transport of Diluted Species

The following assumptions have been used to simplify the modeling process:

1. The reaction is carried out at a constant temperature of 35 °C.
2. The photocatalyst particles, bubbles and water are considered homogeneous and the light radiates equally on the surfaces of the photocatalysts.
3. In all reaction sites, turbulent flow is predominant.
4. The photocatalytic reaction occurs only at the surface of the photocatalytic particles.

These assumptions cause the reaction mechanism to be spent and the reaction rate to be the target of this study.

3.1. Euler – Euler, Turbulent model $k-\varepsilon$

To simulate the hydrodynamic of photocatalytic reactors, two methods can be used for multiphase flow: Euler-Euler and Euler-Lagrange. Due to the larger scale usability and lower computational requirement needed for Euler – Euler method compared to the Euler – Lagrange, Euler – Euler method is employed for solving equations as follows [8, 9]:

- This model requires the resolution of two sets of Navier-Stokes equations, one for each phase, to calculate the velocity fields.
- The dispersed particles and bubbles are much smaller than the grid size.

The RANS turbulence flow model is used to simulate the mixing phenomena. The standard $k-\varepsilon$ model is the most adopted turbulence model due to its simplicity and less computational requirement [10].

For the *k*th phase, the volume-average continuity equation is given by [8]:

$$\frac{\partial\left(\varepsilon_k \rho_k\right)}{\partial t}+\nabla.\left(\varepsilon_k \rho_k U_k\right)=\sum_{\substack{p=1 \\ p\neq k}}^{n} m_{pk} \tag{2}$$

While the corresponding momentum equation can be expressed as follows:

$$\frac{\partial\left(\varepsilon_k \rho_k U_k\right)}{\partial t}=-\nabla.\left(\varepsilon_k \rho_k U_k U_k\right)-\varepsilon_k \nabla p-\nabla.\left(\varepsilon_k \tau_k\right)+\varepsilon_k \rho_k g+F_k \tag{3}$$

3.2. Transport of Diluted Species

The transport of diluted species module is used to model the mass transfer and reaction in the COMSOL Multiphysics simulator software.

3.2.1. Reaction rate

Equation 4 is used to model the kinetics in the slurry reactor. In this equation, k is a function of temperature, radiation, catalyst loading and concentration of pollutants [6].

$$-r_P = k\left(f\ [P]\right) \tag{4}$$

3.2.2. Two – Film theory

Two-film theory is used to study the mass transfer between the bubble (dispersed phase) and the mixture of water and photocatalyst (continuous phase).

4. Numerical Simulation

4.1. Geometry

A two-dimensional design domain is considered, a rectangle with a width of 5 cm and a length of 14 cm with a lamp in the top center. A symmetric physics is used. To blow CO_2 to the reaction medium, spargers with a diameter of 1 mm are provided at the bottom of the reactor.

4.2. Boundary conditions

For the gas inlet as the dispersed phase, the velocity boundary condition was considered. Because of the pressure drop, the gas outlet on the top was assigned as pressure outlet.

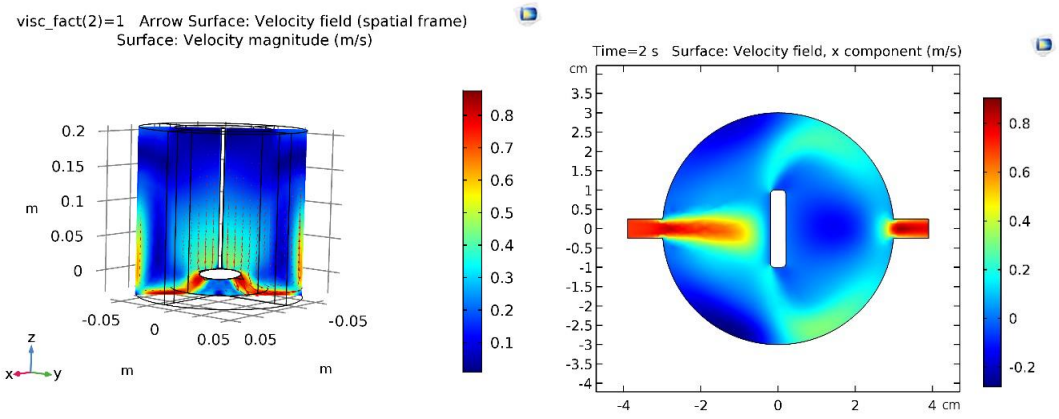
5. Results and discussion

5.1. Multiphase modeling

For the hydrodynamic modeling of photocatalytic reactors, a two-phase Euler – Euler flow interface is used. Here, the flow is first modeled and then simulated and the results are used for kinetics. Because it is not possible to use two modules including multi-phase flow and kinetic directly and coupling them together.

5.1.1. Magnetic stirrer

A magnetic stirrer is used to create the turbulent, homogeneous flow and also the same light impact on the photocatalytic surfaces inside the reactor. As can be seen in Figure 1, this magnetic stirrer has caused mixing and turbulency in the entire reactor.



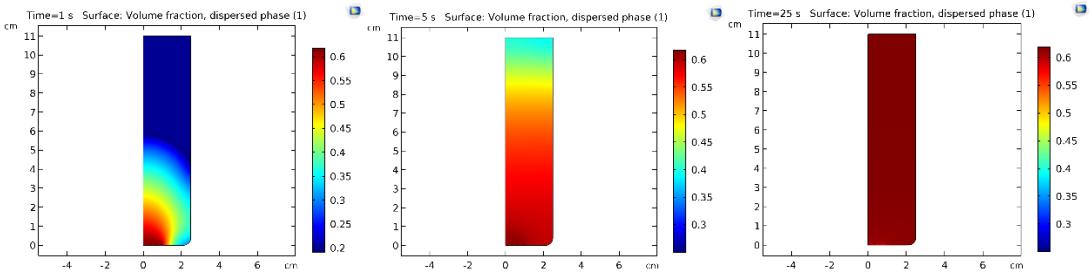
(a) (b)

Figure 1. Hydrodynamic simulation and investigation of velocity alterations during reactor, gas flow rate = 5 1/min (a) Arrow lines of liquid velocity alterations due to mixing between bubbles and water by magnetic stirrer at 100rpm of revolution in 3D at the last time (b) Liquid velocity alterations from the top view after 2s from the beginning.

According to Equations (2) and (3), as can be seen in Figure 1, the mixing inside the reactor is well done.

5.1.2. Volume fraction

To create a bubble inside the reactor, three spargers were designed in the middle of the bottom of the reactor. As the bubble moves upward and the lamp irradiates on the photocatalyst, the redox reaction takes place. Figure 2 illustrates how the bubble is pervasive inside the reactor.



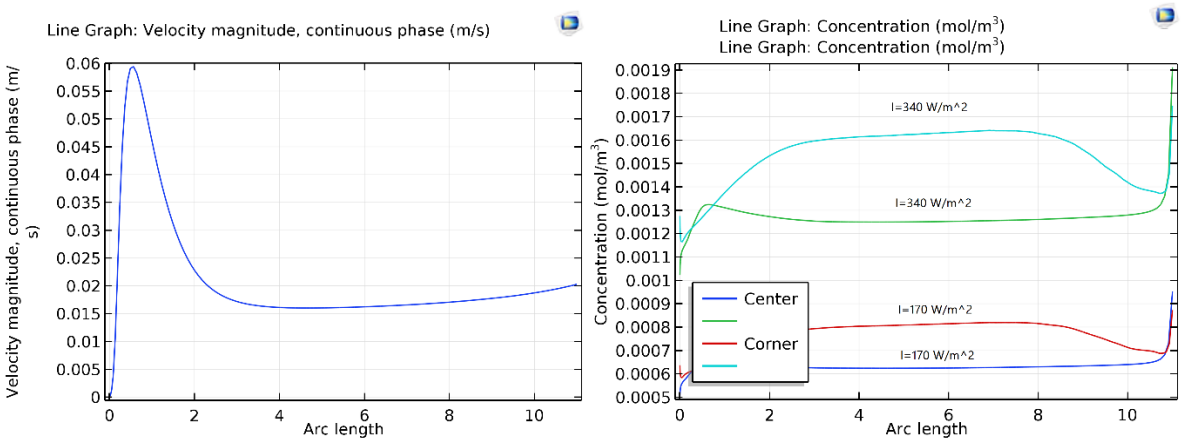
(a) (b) (c)

Figure 2. Blowing the bubble into the reactor and making it uniform by magnetic stirrer, initial volume fraction = 0.2. (a) 1 second after the bubbles were blown by the spargers. (b) 5 seconds after being blown (bubbles are becoming pervasive due to the mixer and inlet gas velocity). (c) 25 seconds after being blown (bubbles are pervasive in the whole reactor).

5.2. Concentration and reaction rate

Using the hydrodynamic results, the kinetics has been simulated. The mass transfer equation is called from the Euler – Euler interface and the concentration in the transport of diluted species interface is used to generate the reaction equation for the slurry reactor. According to the stoichiometry, the reaction rate was defined for each of the reactants and the producers. Figure 3(a) shows the alterations of velocity along the reactor. It can be seen that at the point

where the stirrer is located the velocity is maximum and as moving along the reactor, the velocity becomes uniform. Besides, the changes in concentration along the reactor in different light intensities can be observed in Figure 3(b).



(a) (b)

Figure 3. (a) The alterations of velocity along the reactor. (b) The concentration alterations at different light intensities (I = 170 W/m^2 and I = 340 W/m^2).

When the light intensity doubles, the product concentration increases. However, this increase should be based on the principles and considerations of the amount of energy consumed. Because the cost and capability of the lamp should be taken into account.

6. Conclusions

In this study, the photocatalytic slurry reactor was investigated. Since a few studies have been performed on the hydrodynamics of these types of reactors, the study was performed, modeled and simulated by COMSOL Multiphysics software. The intensity of different light and its effect on the methanol concentration was investigated. The highest concentration of methanol in the product was $13\times10^{-4}\ mol/m^3$. This study is innovative in the simultaneous use of magnetic stirrer and multi-spargers. These spargers have clear and equal spacing and have the same diameter. Creating a complete mix of water, bubble and photocatalyst is a key point in this study. This has led to advantages such as increased mass transfer coefficient, useful simplification and less computational requirement.

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