

## CFD Simulation of Catalytic Combustion of Benzene

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### Abstract

*This paper reports the result of CFD simulation of catalytic oxidation of benzene on monolithic catalyst. The geometries of the catalyst and reactor were designed in Gambit software and simulation of catalytic oxidation was carried out in fluent 6.2. Results of simulation showed excellent agreement with the experimental data. This study confirmed the accuracy of the used model in this simulation (Mars van Krevelen). Furthermore, CFD made it possible to obtain a more accurate view of heat transfer and fluid flow. This study confirmed CFD is the best tool for study of fluid regime and heat transfer and especially, concentration of species, and surface deposition along the reactor in the chemical process.*

**Keywords:** CFD, Gas phase catalytic Oxidation, Simulation, Volatile organic compounds

### 1- Introduction

One of the major parts of air pollutant components are volatile organic compounds (VOCs) which are emitted from many industrial processes and transportation activities [1]. For the elimination of these substances, catalytic combustion is considered an effective method due to its low energy requirement [2].

Simulation of chemical process is an

appropriate tool and easy way to study and predict the effect of influencing parameter on a process. Computational fluid dynamics (CFD) is a theoretical way to investigate and predict the performance of processes involved with fluid, heat and mass transfer. This tool is useful to impose our knowledge about increasing the separation performance without recourse to further experimental works, especially in complex geometries

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modules [3]. Simulations of chemical process equipment, chemical reactors and a variety of industrial combustion devices using CFD tools have obtained increasing popularity in the industry and at universities during the last decade. The commercial CFD codes, normally used in the industry, have been expected to manage the modeling of chemical reactions within a wide spectrum of reacting systems. Nevertheless, the codes have typically limited, if any, capabilities for modeling chemistry with the detailed chemical-kinetic mechanisms relevant to e.g. combustion processes. Therefore, development of reliable methods to combine detailed chemical-kinetic models and CFD is an essential requirement. The design of a catalytic reactor for the catalytic oxidation of VOCs is hampered by the lack of an accurate mathematical model for the process; as a result, some semi-empirical correlations are sometimes applied. The prediction of the flow field and temperature distribution in a reactor is in a more advanced stage of development and involves the use of CFD analysis, although further validation data is still required [4]

Rodrigo et al.[5] reported the use of CFD in the catalytic oxidation of vanillinic acid in a trickle bed reactor. In addition, CFD modeling the high – temperature catalytic partial oxidation of methane over platinum gauze has been reported by Deutschmann and Quiceno [6]. Their study shows that today's CFD tools allow the implementation of detailed homogeneous reaction scheme, even for complex catalytic geometries. Jiang and Khadilkar [7] used CFD simulation for modeling of multiphase flow distribution in

catalytic packed bed reactor under steady state and unsteady state condition in bench – scale cylindrical and rectangular packed bed reactors. The porosity distribution in the packed bed was implemented into CFD simulation by pseudo-randomly assigned cell phase holdup distribution. Zakharov and Zolotarski [8] studied gas flows and mass transfer in a two-stage catalytic system applied in ammonia oxidation at nitric acid plants by simulation of gauze pad-honeycomb catalytic system.

CFD simulation of gas phase catalytic oxidation of VOCs has not been studied until now. Furthermore, most of the studies are two-dimension (2D). In this work we used three-dimension (3D) CFD for simulation of gas phase catalytic oxidation of benzene (as VOCs). This process was simulated by CFD and experimental conditions were applied in this simulation. The objectives of this simulation are to evaluate the Mars van Krevelen model for catalytic oxidation of benzene and to use CFD ability in studying the thermal and fluid regimes of surface reactions in detail during catalytic oxidation. In this paper, at first, the experimental setup is explained. Then, CFD simulation of benzene catalytic oxidation and the kinetic model used for gas phase catalytic oxidation of benzene are described. Finally, the results of the simulation are compared with the experimental results and the performance of fluent in the simulation of the catalytic oxidation process is evaluated.

## **2- Characterization of Experimental setup**

A laboratory-scale tubular reactor, along with peripheral feed and product analysis

equipment, was used for all experiments and is shown in Fig. 1. The experimental apparatus consisted of a gas and liquid feeding system, an insulated tubular reactor and an analytical system utilizing off-line Shimadzu 2010 GC. The inlet to the reactor consisted of a stream containing nitrogen, oxygen and Benzene. Inlet feed to reactor was a gaseous mixture containing benzene (1298 ppm, mol/mol), oxygen (12724 ppm, mol/mol), argon and helium.

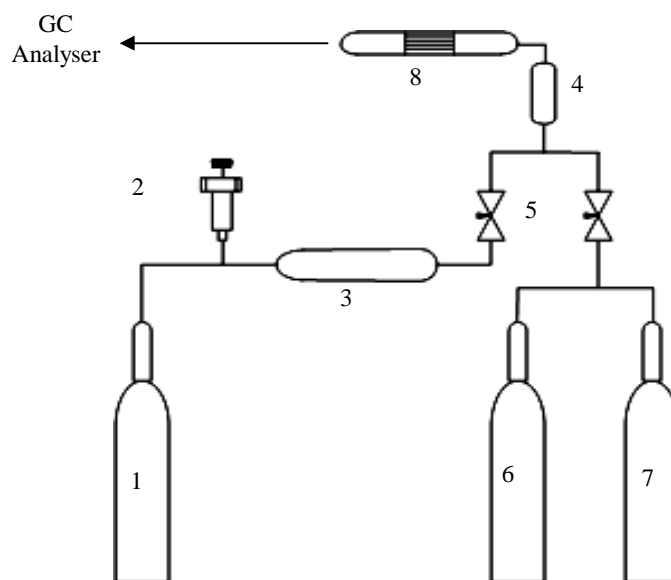
The gas streams were heated using pre-heaters. The reactor was made of a  $7.5 \times 10^{-5}$  L SS316 pressure vessel modified with a flange to allow the opening of the vessel to replace the catalyst. The reactor was heated in such a fashion as to achieve almost isothermal conditions across the catalyst bed and a consistent heating profile. The temperature of the gas entering and leaving the catalyst bed

was measured using thermocouples, placed about 15 mm from the catalyst surface. The temperature difference between the two thermocouples was found to be less than 3-5 K.

The catalyst was placed about 0.08 m away from the reactor inlet to minimize any flow entrance effects. The reactor has been operated continuously at atmospheric pressure. The temperature range was from 348 to 523 K for benzene.

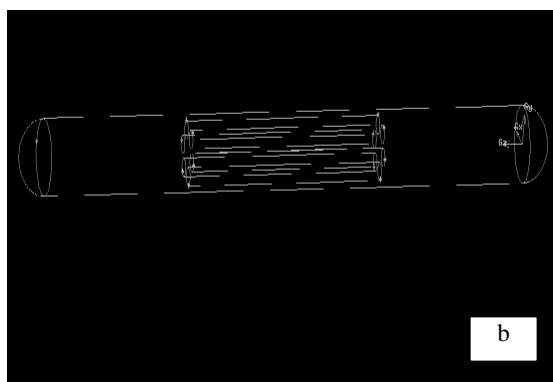
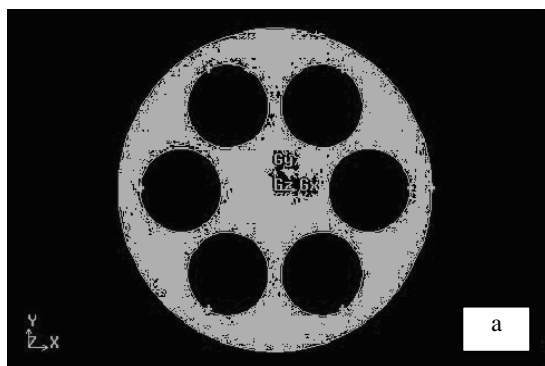
### 3- Simulation of catalytic oxidation

CFD is a well-established tool for several areas of reaction engineering. In this work, the catalytic combustion process of benzene over monolithic catalyst was simulated. Since the catalytic reactions occur on monolith catalyst surface, the monolith was considered as reactor.



**Figure 1.** Schematic of experimental setup Helium gas cylinder(1), Injection syringe (2), Mixing chamber(3), preheater (4), Needle Valve(5), O<sub>2</sub> cylinder(6), N<sub>2</sub> cylinder (7), monolith catalyst (8)

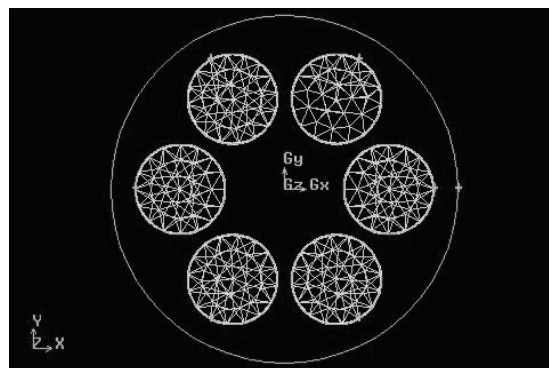
The first step of simulation was the creation of a representative geometric model of the desired flow situation. The geometry of monolith catalyst was designed by Gambit software. For the present work, the CFD code was used in three-dimensional (3D). The physical system of monolith catalyst and reactor designed in Gambit software is shown in Fig. 2. The cylinders of monolith catalyst were meshed (Tet/Hybrid-TGrid). The grid used for the system is shown in Fig.3. The boundaries of the reactor such as inlet, outlet and walls were determined in this software.



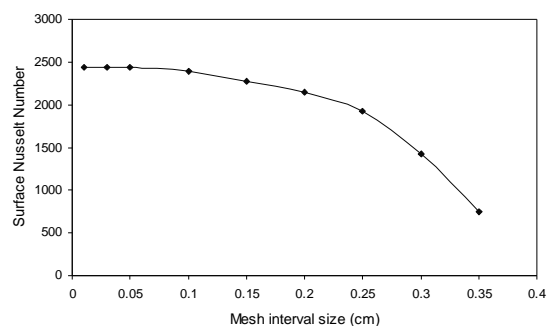
**Figure 2.** Physical scheme of monolith catalyst designed by Gambit software, Monolith catalyst (a), catalytic reactor (b)

Simulation of catalytic oxidation process was carried out in Fluent 6.2. In order to

determine the grid independency, we simulated the process in different mesh interval sizes of monolith catalyst and calculated the surface Nusselt number ( $T=400\text{K}$ ). Nusselt number is a non-dimensional heat transfer coefficient that relates convective and conductive heat transfer. We concluded that the interval sizes less than 0.05 cm do not affect the Nusselt number and thus we select an interval size of 0.05 cm in the next studies (Fig. 4).



**Figure 3.** Grid used for monolith catalyst



**Figure 4.** Surface Nusselt numbers vs. mesh interval sizes at catalytic combustion of benzene ( $T=400\text{K}$ )

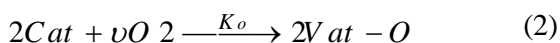
The experimental conditions were applied for boundary conditions in this simulation. The laminar flow model; segregated solver and Simple algorithm were applied for this simulation. The regime of fluid, reaction,

kinetic and thermodynamics constants of reactions, type of reactions (volumetric or surface), etc were inserted. All reactions were supposed surface type. All simulations were run on a computer with 2.8 GH intel and DDR RAM 512MB. The model used for catalytic oxidation was the Mars van Krevelen model. This model assumes reaction occurs when the reactant molecule interacts with an oxygen-rich portion of the catalyst. The form of the oxygen in the catalyst could be either chemisorbed or lattice oxygen [9-10]. A particular portion of the catalyst surface is alternately reduced and oxidized. This model postulates two redox steps:

(i) Reduction of the oxidized catalyst by the VOC (V):



Oxidation of the catalyst by oxygen from the gas phase:

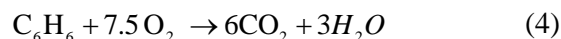


In steady-state operation, the rates of the oxidation and reduction steps must be equal, considering the overall stoichiometry of the reaction ( $\nu$ ). This model is the most frequently reported redox model for catalytic combustion of VOC. According to this model, the reaction rate ( $-r_v$ ) is expressed as follows:

$$(-r_v) = \frac{k_o k_v P_o P_v}{k_o P_o + \nu k_v P_v} \quad (3)$$

Where  $P_0$  is partial pressure of oxygen.  $P_v$  is

the partial pressure of VOC (benzene),  $\nu$  is the stoichiometric constant coefficient for the total combustion reaction (mol  $O_2$ / mol of hydrocarbon),  $K_o$  the kinetic constant for the non- equilibrium dissociative adsorption of oxygen on the catalyst surface, and  $k_r$  kinetic constant for the reaction between chemisorbed oxygen and the hydrocarbon. In this simulation, the Mars Van Krevelen Model was used to describe the catalytic combustion of benzene. Catalytic Oxidation of benzene can be represented as follows:



Kinetic constants used in the model for catalytic combustion of benzene were as follows:

$$K_o = k_{oo} \exp(-E_o/RT)$$

$$K_r = k_{or} \exp(-E_r/RT)$$

the values of these parameters are shown in Table 1.

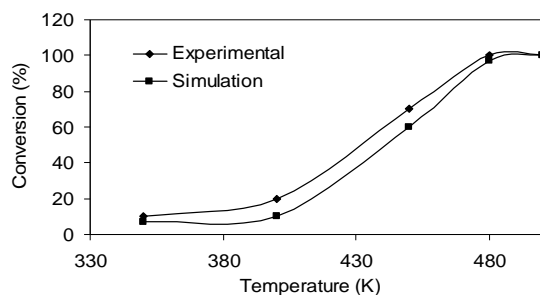
**Table 1.** Kinetic parameters for oxidation of benzene

compound	$K_{oo}$ (mol seg <sup>-1</sup> kg <sup>-1</sup> Pa <sup>-1</sup> )	$E_o$ (kJ/mol)	$k_{or}$ (mol seg <sup>-1</sup> kg <sup>-1</sup> Pa <sup>-1</sup> )	$E_r$ (kJ/mol)
Benzene	130750	97.4	$1.77 \times 10^8$	101

#### 4- Result and Discussion

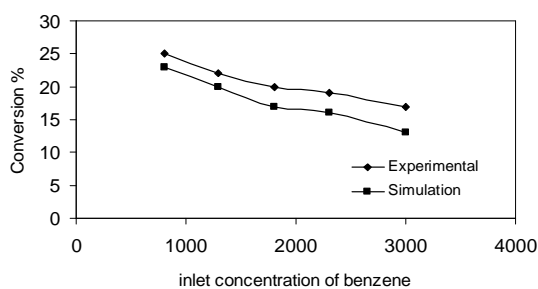
The CFD simulation was performed for catalytic combustion of benzene in a catalytic reactor. Fig. 5 shows Light-off curve for conversion of benzene by experimental and simulation. There is an excellent agreement between these results. The conversion of

benzene increases with increasing of temperature. It can be seen that the conversion of benzene at temperatures above 480 K is 100%.



**Figure 5.** Conversion of C<sub>6</sub>H<sub>6</sub> at different temperatures

In order to be more certain about the conformance between the simulation result and the experimental data, the effect of concentration of benzene at inlet feed on conversion efficiency at a temperature of 400 K was studied. Light-off curve of simulation and experimental are compared in Fig. 6.

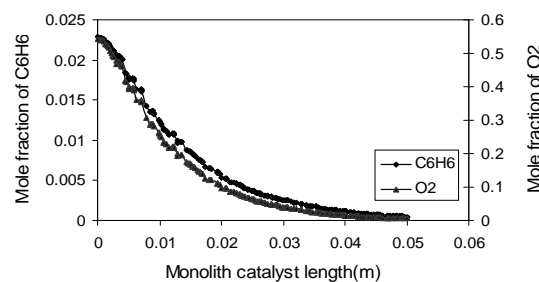


**Figure 6.** Influence of inlet concentration of benzene on its conversion (%)

This study also confirmed a good agreement between simulation and experimental results. This study confirmed the ability of CFD as a good tool for simulation of catalytic combustion of VOCs. Furthermore, it is concluded that the used model (Mars Van

Krevelen) was a suitable model for the description of the gas phase catalytic oxidation of VOCs.

For greater study, and to obtain a greater view of the fluid flow, heat transfer, and prediction of the species reactor along the catalyst, we used the abilities of CFD simulation. The changes of benzene and oxygen mole fractions along the reactor have been shown in Fig. 7. As can be seen in this figure, the conversion of benzene and oxygen increases with an increasing reactor position that reaches 100 at the end of the monolith at the higher temperatures. In addition, the conversion of products versus catalyst length has been shown in Fig. 8. The contours of reactants and products and surface deposition of oxygen during catalyst oxidation, and temperature contribution along the monolithic reactor have been predicted by simulation.



**Figure 7.** Mole fraction of reactants along the monolith catalyst

The contours of benzene, oxygen and carbon dioxide mole fractions, relative humidity and surface deposition rate of oxygen during catalyst oxidation have been shown in Figs. 9-14 respectively. The simulation predicts that the mole fraction of benzene decreases along the catalyst, which has a compatibility

with the expected results. Furthermore, the resulted contours for oxygen and carbon dioxide mole fractions by simulation have an excellent agreement with the experimental results shown in Figs. 8 and 9 respectively. The second stage of the Mars-van Krevelen model is adsorption of oxygen on the catalyst and the oxidation of the catalyst. Fig.13 shows the contour of the oxygen surface deposition rate over catalyst. Velocity vector of fluid inside the monolith catalyst is shown in Fig. 14. The Velocity vectors of gaseous fluid have been presented in Fig. 13.

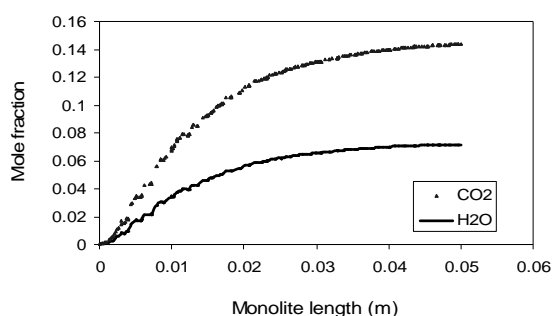


Figure 8. Mole fraction of products along the monolith catalyst

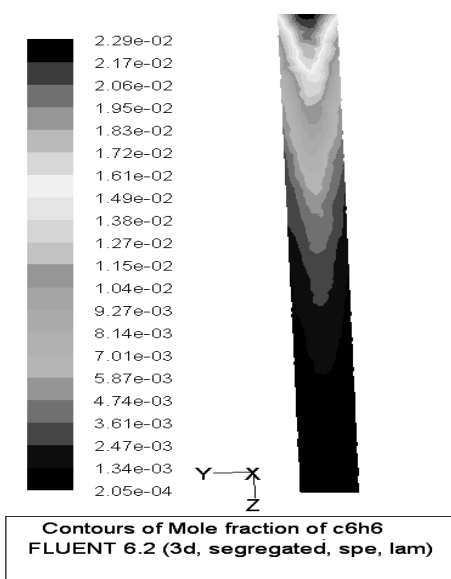


Figure 9. Contours of Mole fraction of C<sub>6</sub>H<sub>6</sub>

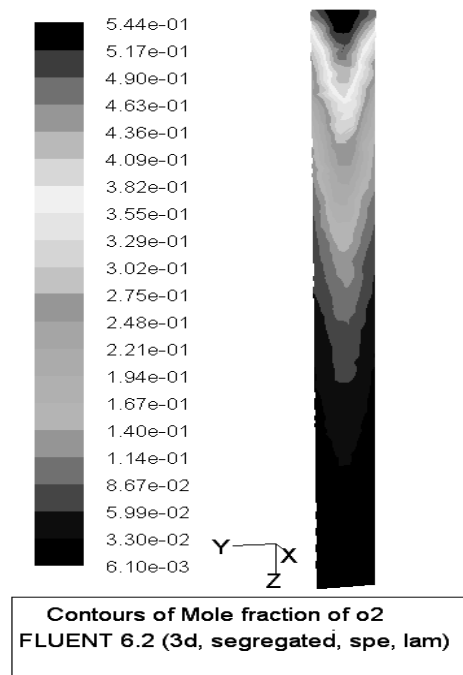


Figure 10. Contours of Mole fraction of O<sub>2</sub>

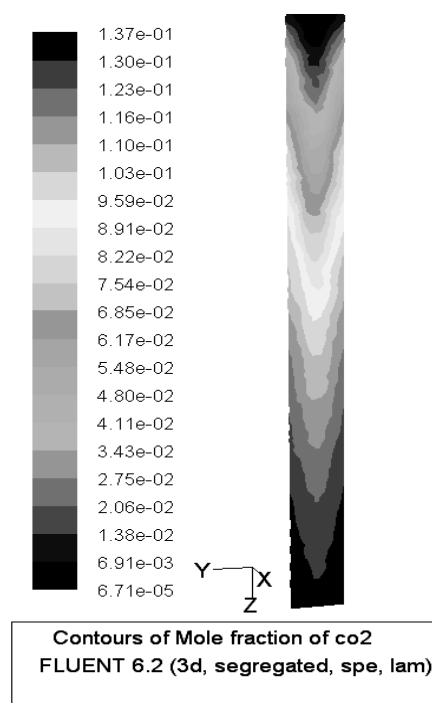
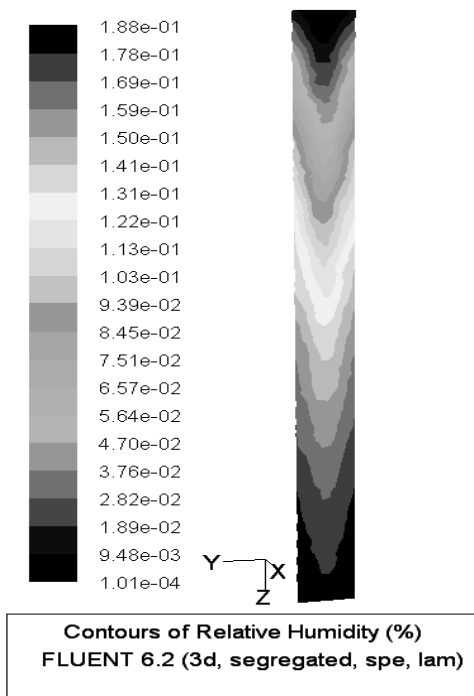
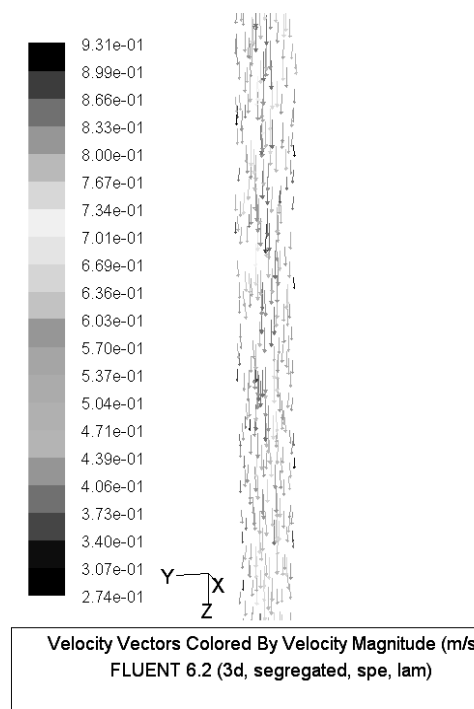


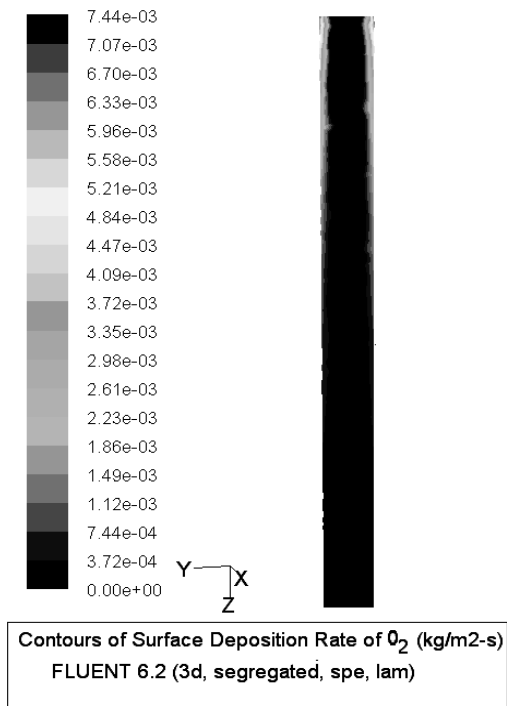
Figure 11. Contours of Mole fraction of CO<sub>2</sub>



**Figure 12.** Contours of Mole fraction of Relative Humidity



**Figure 14.** Velocity vector of gaseous fluid in reactor



**Figure 13.** Contours of surface deposition of O<sub>2</sub> over Catalyst

The velocity of fluid at wall sections is less than in the middle of the tube. The velocity of fluid shown in this figure corresponds to a bed section passing through monolith in the y-z plane. This section clearly shows the velocity of fluid at the middle section of the monolith is higher than next to the walls. The main product of complete combustion of VOCs is carbon dioxide. It has been revealed that the yield of production of carbon dioxide resulted from the combustion of VOC increases with increasing temperature. According to the equation 3, the yield of production of carbon dioxide can be stated as follows:

$$Y_{CO_2} = \frac{F_{CO_2}}{6F_{CO_2}} \quad (5)$$



Where F is molar flow. The yield of production of carbon dioxide at different temperatures was predicted using simulation. The result has been presented in Table 2.

**Table 2.** Yield of carbon dioxide production at different temperatures

Temperature (K)	Yield of CO <sub>2</sub> (%)
350	6
380	8
400	38
430	59
480	98
500	98

## 5- Conclusion

The results of CFD simulation showed an excellent agreement with the experimental results. This study confirmed that the Mars van Krevelen model is a suitable model for gas phase catalytic oxidation of VOCs. Furthermore, this study also confirmed that CFD could be used as an appropriate tool for the study of the chemical process, especially catalytic combustion. It is concluded that CFD is the best software to study surface reactions and related phenomena such as oxygen deposition rate on catalyst during catalyst reaction.

## Nomenclature

CFD Computational Fluid Dynamics  
 VOCs volatile organic compounds  
 SS stainless steel  
 K<sub>o</sub> kinetic constant for non-equilibrium dissociative adsorption of oxygen, Pa<sup>-1</sup>

K<sub>r</sub> kinetic constant for the reaction between chemisorbed oxygen and the hydrocarbon, Pa<sup>-1</sup>  
 P<sub>o</sub> partial pressure of oxygen, Pa  
 P<sub>v</sub> partial pressure of VOC, Pa  
 E<sub>o</sub> Activation energy for non-equilibrium dissociative adsorption of oxygen, kJ/mol  
 E<sub>r</sub> Activation energy for the reaction between chemisorbed oxygen and the hydrocarbon, kJ/mol  
 v overall stoichiometry of the reaction  
 T Temperature, Kelvin  
 (-r<sub>v</sub>) rate of reaction, mol/s. g<sub>cat</sub>

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