Computational Fluid Dynamics (CFD) Analysis of Phthalic Anhydride's Yield Using Lab Synthesized and Commercially Available (V₂O₅/TiO₂) Catalyst

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Abstract—**V_2O_5/TiO_2 is an important catalyst used in many industrial reactions like selective oxidation of o-xylene to phthalic anhydride, selective catalytic reduction of NO_x, selective oxidation of alkanes, etc. The partial oxidation of o-xylene to synthesize phthalic anhydride is an exothermic reaction and leaves hot spots on the catalyst's surface. The yield of phthalic anhydride strongly depends on the activity and stability of the catalyst. In this work, a computational fluid dynamics (CFD) analysis has been conducted to compare the yield of lab prepared catalyst with the commercially used catalyst. This work is first attempt to simulate V_2O_5/TiO_2 catalyst for cracking heavy hydrocarbons in the petrochemical industry using k- ε turbulence and species transport models in CFD. The results obtained are in the form of scaled residuals, area-weighted average, and contours of pressure and temperature. Simulation results of lab synthesized and commercially used catalysts, applying finite volume method (FVM) are compared, which emphasize the scope of CFD modeling in the catalytic cracking process of petrochemical industry.**

Keywords-V_2O_5/TiO_2; computational fluid dynamics; CFD; hydrocarbon cracking; hydrodynamics; k-ε turbulence model; o-xylene; phthalic anhydride

I. INTRODUCTION

Catalytic cracking is one of the fundamental processes in petrochemical industries. Heavy hydrocarbons are cracked catalytically to give valuable products. For example, the partial oxidation of o-xylene with air is carried out in fixed bed reactor to produce phthalic anhydride. The reaction takes place in the gas phase in which the reactor is filled with catalyst V_2O_5/TiO_2. It is a selective oxidation process in which the ratio of o-xylene to air is set below the explosive limit [1]. As o-xylene reacts with air, the reaction becomes highly exothermic leaving hot

spots on catalyst pellets which deactivate the catalyst. The industrial reactor is designed on low ratio of the tube to particle diameter to remove the heat of reaction instantly and to avoid catalyst hot spots and deactivation [1]. Due to inefficient oxidation and rise in reaction temperature from (245ºC to 480ºC) the yield of phthalic anhydride decreases. Consequently, series of byproducts like methyl maleic anhydride, benzoic acid, maleic anhydride, o-toluic acid, carbon dioxide, carbon monoxide and water are produced. Phthalic anhydride is the intermediate product for the manufacturing of many chemicals. It acts as a plasticizer for the production of flexible polyvinyl chloride, polyester resins and is used as modifier for rubbers and polymers [1-7].

An attempt was made to develop V_2O_5/TiO_2 catalyst on lab scale with improved chemical and physical properties. Through the sol-gel method, the nanosize catalyst was synthesized using vanadyl acetylacetonate and titanium isopropoxide. A controlled number of sulfates was introduced into the sample which provides acidic nature of the solid catalyst. The addition of sulfates enhanced the redox properties of the catalyst. The crystalline structure and morphological analysis of lab prepared catalyst have been done by using X-Ray diffraction (XRD) and scanning electron microscopy (SEM). Computational fluid dynamics (CFD) analysis has been conducted to compare the activity of the commercially used catalyst and lab prepared catalyst. A three-dimensional reactor grid having triangular meshing and ceramics monolith substrate for catalyst support has been constructed in Ansys Fluent. The ceramics monolith substrate was made to control the heat transfer. The monolithic structures work more efficiently than random packing of catalyst [8]. In this research work, three-dimensional hydrodynamics and reaction study have been done using Ansys Fluent to compare the yield of phthalic anhydride and

convergence of reactants. Through reactor grids, comprehensive study of species transport, reaction mechanism, and hydrodynamics in term of scaled residuals, static pressure, static temperature, and area weighted average, has been conducted. The simulation results showed complete conversion of o-xylene to phthalic anhydride, without any byproduct formation. The temperature profile and hydrodynamics in the reactor are evaluated by applying industrial conditions. To our knowledge, this is the first attempt to model heavy hydrocarbon cracking in the presence of V_2O_5/TiO_2 using CFD with Finite Volume Method (FVM) by implemented suitable governing equations and boundary conditions.

II. CFD MODELING

CFD helps to design, model, and analyze industrial applications. Simulation of ceramics monolith substrate reactor has been conducted to study the partial oxidation of o-xylene with air to produce phthalic anhydride. This research may be considered as a meager contribution to better understanding of the interaction between gas phase reactants in the presence of a catalyst. The objectives of this CFD modeling are 1) to compare the yield of phthalic anhydride obtained from commercially used catalyst and lab prepared catalyst, 2) to understand reaction chemistry and heat transport in the reactor, 3) to optimize operating conditions of the reactor to maximize the yield of phthalic anhydride [9].

A. Turbulance Model

The model equations for k and ε in realizable k- ε model have already been presented in [10-12]

$$\frac{\partial}{\partial t}(\rho k) + \frac{\partial}{\partial x_j}(\rho k u_j) = \frac{\partial}{\partial x_j}[(\mu + \frac{\mu_t}{\sigma_k})\frac{\partial k}{\partial x_j}] + G_k + G_b - \rho\varepsilon - Y_M + S_k \quad (1)$$

and

$$\frac{\partial}{\partial t}(\rho\varepsilon) + \frac{\partial}{\partial x_j}(\rho\varepsilon u_j) = \frac{\partial}{\partial x_j}[(\mu + \frac{\mu_t}{\sigma_\varepsilon})\frac{\partial\varepsilon}{\partial x_j}] + \rho C_1 S_\varepsilon - \rho C_2\frac{\varepsilon^2}{k+\sqrt{v\varepsilon}} + C_{1\varepsilon}\frac{\varepsilon}{k}C_{3\varepsilon}G_b + S_\varepsilon \quad (2)$$

Where

$$C_1 = \max[0.43, \frac{\eta}{\eta+5}], \quad \eta = S\frac{k}{\varepsilon}, \quad S = \sqrt{2S_{ij}S_{ij}} \quad (3)$$

As in other k-ε models, the eddy viscosity is computed from

$$\mu_t = \rho C_\mu \frac{k^2}{\varepsilon} \quad (4)$$

The difference between the realizable k-ε model and the standard RNG k-ε models is that C_μ is no longer a constant. It is computed from

$$C_\mu = \frac{1}{A_o + A_s\dfrac{kU^*}{\varepsilon}} \quad (5)$$

where

$$U^* \equiv \sqrt{S_{ij}S_{ij} + \Omega_{ij}\Omega_{ij}} \quad (6)$$

and

$$\tilde{\Omega}_{ij} = \Omega_{ij} - 2\varepsilon_{ijk}\omega_k \quad (7)$$

$$\Omega_{ij} = \overline{\Omega}_{ij} - \varepsilon_{ijk}\omega_k \quad (8)$$

Here, $\overline{\Omega}_{ij}$ is the mean rate-of-rotation tensor viewed in a rotating reference frame with the angular velocity ω_k. The model constants A_o and A_s are given by

$$A_o = 4.04, \quad A_s = \sqrt{6}\cos\varphi \quad (9)$$

where

$$\varphi = \frac{1}{3}\cos^{-1}(\sqrt{6}W), \ W = \frac{S_{ij}S_{jk}S_{ki}}{\tilde{S}^3}, \ \tilde{S} = \sqrt{S_{ij}S_{ij}}, \ S_{ij} = \frac{1}{2}(\frac{\partial u_j}{\partial x_i} + \frac{\partial u_i}{\partial x_j}) \ (10)$$

B. Species Transport Model

A particle undergoing an exothermic reaction in the gas phase is shown schematically in Figure 1 where T_p and T_∞ are the temperatures while $C_{d,b}$, $C_{d,s}$, and C_k are the concentrations [12-18]. Ansys Fluent uses the following equation to describe the rate of reaction r of a particle surface species j and the gas phase species η. The reaction stoichiometry of reaction r, in this case, is described by

Particle species j(s) + gas phase species $\eta \rightarrow$ products N_r

$$\overline{R}_{j,r} = A_p\eta_r Y_j R_{j,r} \quad (11)$$

The effectiveness factor η_r is related to the surface area and can be used in each reaction in the case of multiple reactions. $D_{o,r}$ is given by

$$D_{o,r} = C_{1,r}\frac{[T_p + T_\infty / 2]^{0.75}}{d_p} \quad (12)$$

The kinetic rate of reaction r is defined as

$$R_{kin,r} = A_r T^{\beta_r} e^{-(E_r/RT)} \quad (14)$$

The rate of depletion of particle surface species for the reaction order $N_r = 1$ is given as,

$$\overline{R}_{j,r} = A_p\eta_r Y_j p_n \frac{R_{kin,r}D_{o,t}}{D_{o,r} + R_{kin,r}} \quad (15)$$

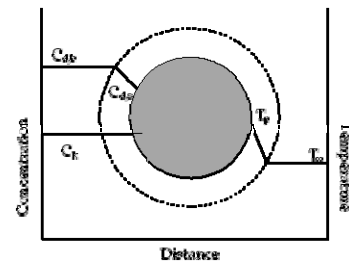For reaction order $N_r = 0$, equation (15) gives (11)

Fig. 1.   A reacting particle in the multiple surface reactions model [12]

The model equations required two important characteristics of the catalyst: 1) inertial resistance 2) viscous resistance. The inertial resistance of a catalyst is the built-in inertia which

enables the catalyst to enhance the rate of reactants convergence into products but never gets consumed in a chemical reaction. It is observed that if a nanoscale catalyst is used in the reaction, the convergence of o-xylene to phthalic anhydride is increased.

C. Boundary Conditions

Gambit^{TM} pre-processor is used to construct the 3D geometry of the system. The geometry of ceramic monolith substrate has been discretized using 125772 cells, 271496 faces, and 33608 nodes. Grid size analysis has been carried out using three different mesh intervals. The simulation results from different geometries did not show any significant difference. Triangular grids are used in the geometry of fixed bed reactor as shown in Figures 2 and 3. The geometry dimensions are x=0.31m, y=0.128m, z=0.028m. O-xylene and air entered with a uniform velocity of 50m/s, pass through a ceramic monolith substrate of square-shaped channels and then exit through the outlet. The substrate is impermeable in Y and Z directions, which has been modeled by specifying loss coefficients three orders higher than in X direction. The properties of species, gases, and catalyst bed are mentioned in Tables I and II.
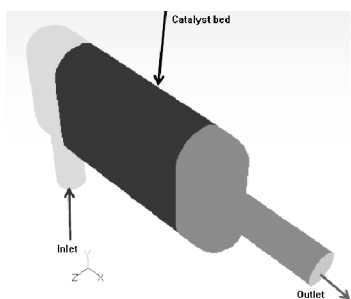

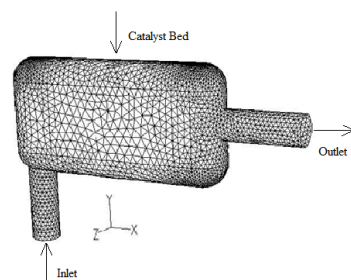Fig. 2.   Schematic diagram of fixed bed reactor

Fig. 3.   Grids of fixed bed reactor

TABLE I.   PROPERTIES OF SPECIES [19]

Reaction Type	Surface of catalyst
Number of Reactants	2
Species	C_8H_{10}, O_2
Stoichiometric Coefficient	1, 3
Rate Exponent	1, 0.5
Arrhenius Rate	27000 J/Kg mole
Pre-Exponential Factor	4.12×10^{11}
Number of products	2
Species	$C_8H_4O_3$, H_2O
Stoichiometric Co-efficient	1, 3
Rate Exponent	0, 0

TABLE II.   PROPERTIES OF REACTANTS, PRODUCTS AND CATALYSTS [22]

Properties (Units)	O-xylene	Phthalic Anhydride	Industrial Catalyst	Lab Synthesized Catalyst
Density (Kg/m^3)	880	1530	5067	5067
Temp. (K)	298.15	367	630	780
Cp (J/Kg.K)	132.5	160	721.89	721.89
Thermal Conductivity (W/m.K)	0.131	Kinetic Theory	46.3	46.3
Viscosity (Kg/m.s)	0.760	0.00064	Kinetic Theory	Kinetic Theory
Molecular Weight (Kg/Kmole)	106.16	148	281.9	261.6
Standard State Enthalpy (J/mole)	19000	-3259.4	-880	-880

D. Assumptions

1) The ideal gas law is assumed to hold while calculating the pressure-velocity variations on account of convergence and molar expansion due to heavy hydrocarbon cracking and gas phase temperature [20]. 2) Catalyst particles are fixed as a cluster of a bed to account for the observed velocity of the gas [20]. 3) Mass and heat resistance are assumed as negligible Assuming plug flow conditions for both phases hence back mixing of multi-phases is neglected [20-21].

E. Simulation Setup

Ansys Fluent worked for 100 iterations on an Intel Core i5 CPU with the 32-bit operating system and 4GB RAM. The simulation steps are shown in Figure 4. Ansys Fluent shows remarkable convergence while solving problems. There is no rule to predict convergence because scaled residue for one type of model doesn't mean it's same for another. Therefore, it is important to examine and monitor the results through Drag's law and heat transfer coefficient. For all equations, the criteria of scaled residue must decrease to 10^{-3} except for radiations, energy and combustion reactions which are 10^{-6}. For this work, scaled residuals decrease for both lab catalyst and commercial catalyst up to 10^{-6} [12].

III.   RESULTS AND DISCUSSION

Simulations of lab prepared catalyst and commercial catalyst in the fixed bed reactor were run for 2 hours. Constant catalytic performance was observed because of strong adhesion of lab V_2O_5/TiO_2 particles on monolith ceramics substrate. Lab synthesized V_2O_5/TiO_2 (anatase) indicated the stability in catalytic behavior after the reaction. The lab catalyst showed significantly higher conversion of o-xylene to phthalic anhydride due to better catalyst activity as shown in Figure 5. The comparison of the convergence of o-xylene for lab catalyst and commercially used catalyst is shown in Figures 5-6. The lower selectivity of phthalic anhydride in the case of commercial catalyst is due to lower surface area of the catalyst which leads to the formation of intermediates and byproducts

like CO_x. The percentage yield of commercial catalyst and lab-prepared catalyst has been calculated as 66.7% and 80% respectively. Table III shows the yield comparison among other models and the results obtained in this work. It is seen that maximum yield of phthalic anhydride can be achieved through lab synthesized catalyst.
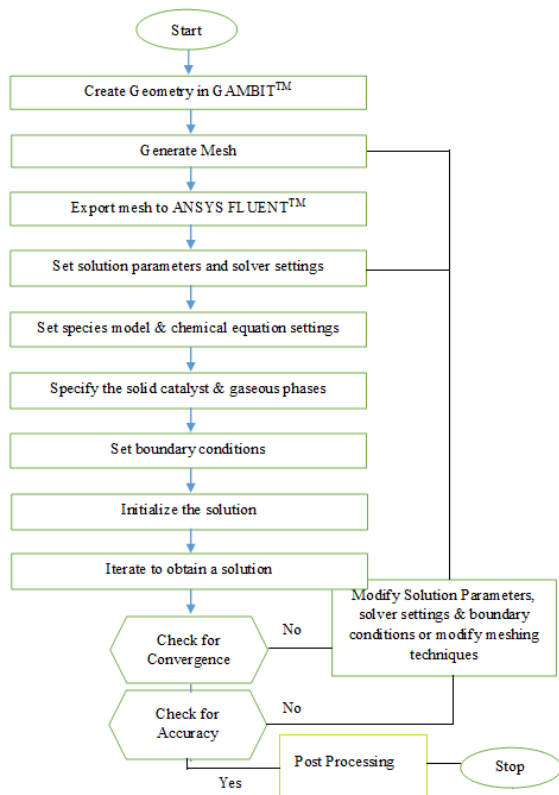

Fig. 4.   Block diagram of simulation steps

TABLE III.   THE YIELDS OF PHTHALIC ANHYDRIDE (PA) COMPARISON CALCULATED FROM THIS MODEL WITH OTHER MODELS AND INDUSTRY DATA [1, 13].

Comparison 1	Yield of PA (This work)	Yield of PA [13]	Error
Commercial Catalyst	66.7 %	67 %	0.44 %
Lab prepared Catalyst	80 %		19.40 %
Comparison 2		**Yield of PA [1]**	
Commercial Catalyst	66.7 %	79.5 % (With Industrial Values)	16.10 %
Lab prepared Catalyst	80 %		0.62 %
Comparison 3		**Yield of PA [1]**	
Commercial Catalyst	66.7 %	80.6 % (Under optimum conditions)	17.24 %
Lab prepared Catalyst	80 %		0.74 %

This work also predicts the temperature and conversion profiles in case of lab prepared and commercially used catalysts. For combustion reactions, energy and heavy hydrocarbon cracking scaled residuals must reach to 10^{-6}. Figures 5 and 6 show the rate of conversion from o-xylene to

phthalic anhydride, in which equation of continuity, species transport model, and turbulence model was applied. Three-dimensional velocity profile of catalysts, energy and thermal conductivity were calculated. Both commercial and lab-prepared catalysts showed 10^{-6} convergence in 2hrs with 90 and 100 iterations respectively. The lab prepared catalyst showed a sudden drop when it reached 80 iterations in residuals which may be because of composition change [10]. The temperature and concentration were recorded at every point of the reactor. It helped in determining the optimum operating conditions to avoid deactivation of catalyst and side reactions. The temperature profile was obtained with time by solving the model equations.
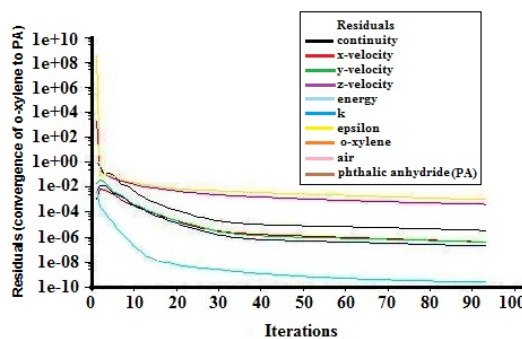

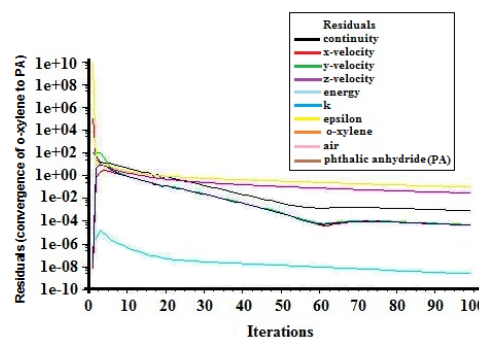Fig. 5.   Scaled residuals of commercial catalyst

Fig. 6.   Scaled residuals of lab prepared catalyst

In Figures 7-8, the contours show the temperature regimes of both commercially used and lab-prepared catalysts in radial and axial directions. Due to the highly exothermic reaction, heat dispersion has been observed in the radial direction, which may be attributed to radiation from solid to solid, from gas to solids or to a combination of both mechanisms. Unlike the commercially used catalyst, the lab prepared nanoscale V_2O_5/TiO_2 showed remarkably better temperature profiles. The temperature profile of lab prepared catalyst showed constant increment while the change in commercial catalyst varies. The results of lab synthesized nanocatalyst showed the best reaction temperature profile in order to get maximum yield of phthalic anhydride. Due to low activity of the commercial catalyst, the reaction temperature reached the upper limit, as a result of which hot spots were formed on the catalyst surface which caused the deactivation of the commercial catalyst. Furthermore, high catalytic temperature makes the small

crystallites of active phase to agglomerate, generally termed as thermal sintering. The difference in the results of both catalysts may be linked to variations in size, catalyst shape and the bed porosity of. The porosity of bed effects the rate of turbulence which leads to variations in heat transport [2, 18, 23].
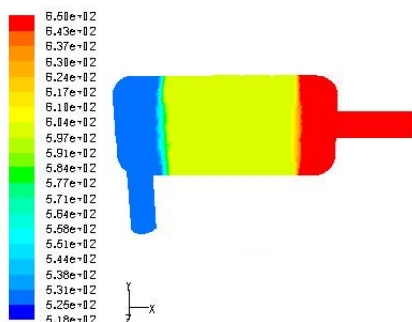

Fig. 7.   Temperature contours of commercial catalyst (K)
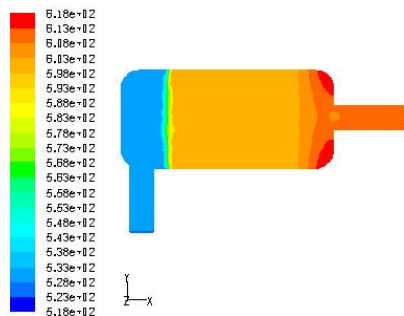

Fig. 8.   Temperature contours of lab prepared catalyst (K)

The CFD modeling done in this work provided point to point temperature and conversion by specifying the following conditions: a) inlet and outlet temperatures b) inlet composition of feed gas c) reactor surface temperature d) gas mass flow rate e) reactor size f) type of reaction g) size of catalyst [10, 11]. The study of this type of reactor and reaction system is highly sensitive to even a small variation in temperature, which can directly affect the concentrations of the reactants and inlet gas temperature. Pressure-velocity coupling model was used to find the inlet pressure of gases for fixed bed reactor. Two-phase flow regions require averaging of the fluid properties. These properties can lead to large errors due to the difference in magnitude order. An area-weighted average can lead to a significant improvement in the result quality and indicates suitable reaction mechanism and conditions. In the case of a micron-sized (commercially used) catalyst, high static pressure and high temperature are required to produce phthalic anhydride. An area-weighted average of the static pressure of commercially used and lab-prepared catalysts is shown in Figures 9 and 10 respectively. The results of commercial catalyst showed that it requires high pressure to achieve reaction condition. At 260KPa the reaction starts which requires high energy. The lab prepared catalyst having nano particle size (strong adhesion with ceramics monolith substrate) showed remarkably controlled pressure conditions. The

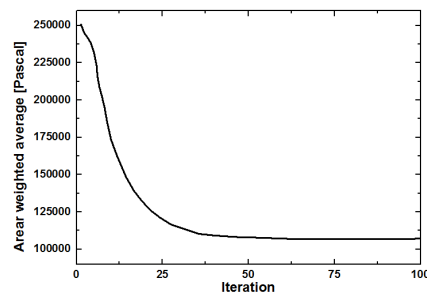difference in particle size has a noticeable influence on the convergence values in Figures 9-10.

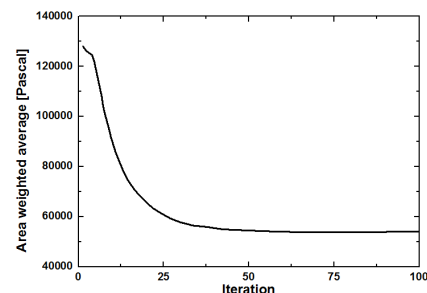Fig. 9.   Convergence history of pressure of commercial catalyst

Fig. 10.   Convergence history of pressure of lab prepared catalyst

IV. CONCLUSION

A CFD analysis has been done for nanoscale and commercially available V_2O_5/TiO_2 catalyst for the partial oxidation of o-xylene to phthalic anhydride. A three-dimensional multiphase flow reaction model for fixed bed reactor was developed by using finite-volume method solver, Ansys Fluent. Scaled residuals, temperature profile, contours of pressure and area weighted average are predicted by applying species transport and k-ε turbulence models. In this work, CFD simulations have been performed to predict the conversion of o-xylene to phthalic anhydride using V_2O_5/TiO_2 as a catalyst. The results of lab prepared catalyst showed better catalyst activity compared to the commercially used catalyst. FVM efficiently solved many model equations both for solid and gas phases. The nanoscale lab prepared catalyst showed better temperature profiles which favors the increase in catalyst's life and phthalic anhydride's yield. The proposed model is applicable for different simulation studies of fixed bed reactor.

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