Developing A 2D CFD Model of A Fixed Bed Reactor For Fischer Tropsch Synthesis On A Promoted Iron Catalyst

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Abstract - A two-dimensional fixed bed Fischer Tropsch reactor with a promoted iron (Fe) catalyst was modeled using computational fluid dynamics (CFD). Syngas ratio of 0.87, temperature of 515K and a pressure of 1.6 MPa were defined as the feed conditions. A two dimensional reactor geometry with dimensions of 0.1m by 1m was built and coupled with FTS chemical reaction, mass transport, momentum transport and transport of species to predict the behavior and concentration of species in the fixed bed reactor. A stationary plug flow without the effect of heat transfer was assumed in this model. The results obtained show higher conversion of H_2 of about 70% which agrees with experimental data from the literature. High conversion rates were also obtained for C_3, C_4 and C_5 through the reactor length. The model further predicted that the highest conversion of the species takes place at the catalytic bed within around 10 to 20 seconds of the reaction.

Keywords - Fischer Tropsch synthesis, fixed bed reactor, mathematical modeling, CFD simulation.

I. INTRODUCTION

Estimates show that global energy demand will continue to rise because of both increasing population and transport activities [1]. Conventional fuels from fossil crude oil are currently the dominating supplier of world's liquid fuels market. However, due to the limited and uneven distribution of these reserves, fossil fuel supplies will be depleted in the near future. These challenges have stimulated the search for alternative ways to produce liquid fuels from locally available sources of energy in order to meet the demand. As a result, production of liquid fuels through the Fischer Tropsch synthesis (FTS) has received attention as a substitute to produce synthetic fuels from abundant coal reserves, natural gas, biomass and other feedstocks.

Fischer Tropsch synthesis is a chemical process of converting syngas ($CO+H_2$) which is a composition of hydrogen and carbon monoxide to liquid fuels in a catalytic bed. The process was first discovered by Franz Fischer and Hans Tropsch in 1923 by converting a mixture of carbon monoxide and hydrogen to hydrocarbons using an iron catalyst [2].

Fischer Tropsch synthesis is categorized as one of the most effective processes of indirectly converting coal to liquid fuels (Indirect coal liquefaction). It employs gasification as a first step, which essentially uses oxygen as activator to convert the carbon in the coal into carbon monoxide and hydrogen. The syngas can then be cleaned to remove all the hetero-atoms apart from oxygen and thereby allow the subsequent synthesis of a clean liquid product. Clean syngas reacts over FTS catalysts to produce liquid fuels. Fuels from FTS usually exhibit quality in terms of hydrogen content, molecule uniformity, freeze point, combustion characteristics, and low aromatic contents [3]. Fischer Tropsch synthesis is a polymerization process made up of the following main reactions [4]: formation of paraffin, olefin formation reactions and water - gas shift (WGS) reaction, as shown correspondingly in Equations 1– 3:

Paraffin formation

$$(2n+1)\,H_2 + nCO \rightarrow C_nH_{2n+2} + nH_2O, \qquad (1)$$

Olefin formation

$$2nH_2 + nCO \rightarrow C_nH_{2n} + nH_2O, \qquad (2)$$

Water Gas Shift

$$H_2O + CO \leftrightarrow CO_2 + H_2 \qquad (3)$$

where *n* is the carbon number

There are two main types of FTS that are industrially available, namely; high temperature Fischer–Tropsch (HTFT) and low temperature Fischer–Tropsch (LTFT). In addition to this distinction there are many different catalyst formulations and reactor technologies available [5].

Reactor type, operation sequence and the type of catalyst used are the governing factors in the control of product yield during the process. The main challenge in FTS reactor design is the efficient and rapid removal of the large heat of reaction as the process is exothermic. High temperatures in the reactor can lead to excessive methane

yields, carbon deposition and catalyst deactivation. Therefore proper and efficient reactors should be designed and used in order to achieve high product yield from the process. There are four main reactor design technologies that have been commercially used for FTS, which are the Multi-Tubular Fixed Bed, Circulating Fluidized Bed reactor, Fixed Bed Tubular reactor, and Slurry Bubble Column reactor [4]. Multi-Tubular Fixed bed reactors are the most favorable reactor technology because of their ability to allow for high catalyst loading and reactor volume which leads to higher yields. The only challenge in the design of Multi Fixed Bed reactors is insufficient heat removal during the reaction process which may lower the conversion of higher carbon species leading to production of undesirable methane and water.

Various catalysts have been used to the FTS which includes: Fe, Co, Ni, Ru, and Rh. Due to economic considerations and product selectivity Fe seems to be the most appropriate catalyst. The only disadvantage of Fe is that it causes the water-gas-shift reaction to take place, which can consequently yield high volumes of methane instead of gasoline and diesel. To promote the yield and selectivity of middle distillate di-functional catalysts have been introduced to the FTS synthesis. Schulz et al [6] studied the selectivity of gasoline on a promoted iron zeolite catalyst (Fe/ HZSM5). Iron Zeolite is a composition of Fe with 5.4% Cu, 7% K_2O and 21% SiO_2 used as promoters. The results of the study depicted that promoted catalysts enhanced product yield during the FTS synthesis.

FTS research has and still is one of the most interesting studies in the field of energy because of the complexity of the processes involved. In recent years, high computational power has led to prominent ways of solving complex problems such as the FTS through CFD. Jess and Kern [7] used a two-dimensional pseudo-homogeneous model without axial mixing for simulating the FTS over both Fe and Co catalysts. Min-Sol Shin et al [8] devised a CFD model for the FTS reaction on a multichannel reactor with micro-channel heat exchangers. The model was used to evaluate the effect of reactor design and operating conditions on the overall performance of the reactor. Simulation results showed satisfactory conversion in the catalytic bed.

Wang et al [9] developed a one dimensional heterogeneous model to simulate a fixed bed Fischer Tropsch reactor. Results of the study showed that increase in reactor pressure has a significant effect on the increase in conversion of CO and the yield of C_{5+} species. Irani et al [10] developed a 2D CFD model with fluid flow, chemical reaction, heat and mass transfer in a fixed bed reactor to investigate the effect of reactor temperature on the yield of C_{5+} species. Their model was in good agreement with the experimental data. Mehdi et al [11] developed intrinsic rate equation and parameters for the FTS reaction over a promoted Fe catalyst.

II MATHEMATICAL MODELING OF THE REACTOR

A two-dimensional CFD model which couples multi-physics and chemical engineering of a FTS on a multi-tubular fixed bed reactor was developed. Finite volume method was used to discretize and solve the governing equations of mass conservation, momentum and species transport within the 2D model. The solution was achieved by first solving chemical reaction only at zero space dimension, followed by a 2D geometry coupled with all the transport equations until convergence was achieved.

Reaction Network during the FTS

Ten chemical species were considered to be involved during the FTS in this study, and these are: CO, H_2 as reactants and CO_2, H_2O, CH_4, C_2H_4 C_2H_6, C_3H_8, C_4H_{10}, n-C_4H_{10} as products. Below is the reaction network:

$$2CO + 3H_2 \xrightarrow{R_1} CH_4 + H_2O \quad (4)$$

$$2CO + 4H_2 \xrightarrow{R_2} C_2H_4 + 2H_2O \quad (5)$$

$$2CO + 5H_2 \xrightarrow{R_3} C_2H_6 + 2H_2O \quad (6)$$

$$3CO + 7H_2 \xrightarrow{R_4} C_3H_8 + 3H_2O \quad (7)$$

$$4CO + 9H_2 \xrightarrow{R_5} C_4H_{10} + 4H_2O \quad (8)$$

$$4CO + 9H_2 \xrightarrow{R_6} n - C_4H_{10} + 4H_2O \quad (9)$$

$$CO + H_2O \xrightarrow{R_7} CO_2 + H_2 \quad (10)$$

The general rate equations and rate parameters for equations 4-10 was obtained from Mehdi et al. [11].

General rate equation is expressed as:

$$R_n = k_n exp\left(\frac{E_n}{R_g T_b}\right) * P_{CO}^{m_n} P_{H2}^{n_n} \quad (11)$$

where:n *=1, 2, 3……7*

R_n is the general rate, E_n is the activation energy, $R_g$is the ideal gas constant, $T_b$is the temperature, P_{CO} , $P_{H2}$are partial pressure for carbon monoxide and hydrogen while m_n and n_n are the powers for CO and H_2 partial pressures respectively. Values of the kinetic parameters are presented in table 1.

Table 1: Fischer Tropsch kinetic parameters [12]

Reaction	m_n	n_n	k_n	E_n[J/mol]
1	-1.0889	1.5662	142583.8	83423.9
2	0.7622	0.0728	51.556	65018
3	-0.5645	1.3155	24.717	49782
4	0.4051	0.6635	0.4632	34885.5
5	0.4728	1.1389	0.00474	27728.9
6	0.8204	0.5026	0.00832	25730.1
7	0.5742	0.7100	410.667	58826.3

Geometry and Governing Transport Equations:

A two-dimensional schematic diagram shown in figure 1 represents a single tube within a fixed bed reactor. The 1m by 0.1m tube was divided into two free flow sections (Top which is the feed inlet for syngas ($CO+H_2$) and the bottom sections where the product is being collected). The middle third section is the porous zone that represents the catalyst pellet.

Mass Conservation Equation:

Mass conservation principle is represented by equation 12.

$$\nabla.(u^{\rightarrow}\rho) = 0 \qquad (12)$$

where: $u^{\rightarrow}$is the velocity vector and ρ is the density of the gas mixture.

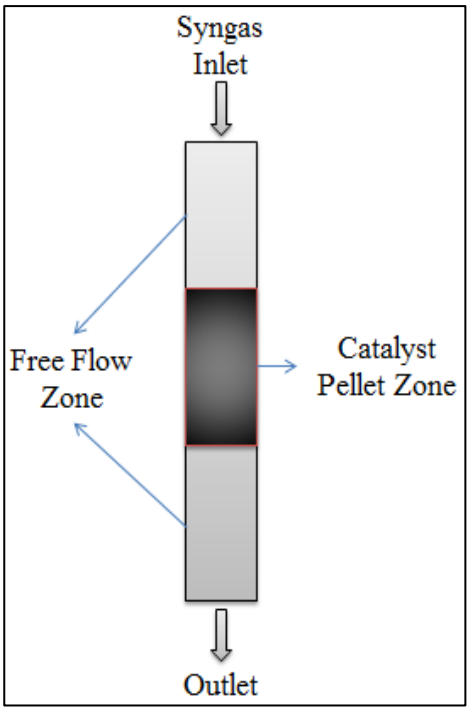

Figure 1: 2D Schematic of a fixed bed reactor tube

Momentum Equation:

Stationary plug flow Navier Stokes equation was used to describe fluid flow in the free flow zones.

$$\rho(\boldsymbol{u}\nabla)\boldsymbol{u} = \nabla.[-p\mathbf{I} + \mu(\nabla u + (\nabla u)^{\boldsymbol{T}}) \qquad (13)$$

The Brinkman equation for porous media was applied to describe the flow in the catalyst pellet zone.

$$\frac{\rho}{\varepsilon_p}\left(\frac{\partial u}{\partial t} + (u\nabla)\frac{u}{\varepsilon_p}\right)\nabla\left[-pI + \frac{\mu}{\varepsilon_p}(\nabla u) + (\nabla u)^T\right) - 2\mu 3\varepsilon P\nabla.uI - \mu K - 1u \qquad (14)$$

where ε_p is the porosity of the bed, μ is the dynamic viscosity of the mixture and *K* is the permeability of the porous matrix.

Species Transport Equation:

Conservation of transport species was described by equation 15 below:

$$\frac{\partial C_n}{\partial t} + \nabla.(-D_n\nabla c_n) + \mathrm{u}\cdot\nabla c_n = R_n \qquad (15)$$

where, Rn is the reaction rate for the production of species *n* from the chemical reaction network; c_n is the concentration of species *n* while D_n is the diffusivity coefficient of species *n*.

From equation 15 we obtain the overall flux that can be described by equation 16.

$$\boldsymbol{N}_n = -D_n\nabla c_n + uc_n \qquad (16)$$

Syngas is assumed to be entering as clean gas without traces of any liquid at inlet and walls, which means that there will be no flux across the boundaries as shown in equation 17.

$$-\boldsymbol{N}\cdot n = 0 \qquad (17)$$

Species concentration is assumed constant across the exit boundary; therefore the general equation for the species reduces to equation 18.

$$-\boldsymbol{n}(D_n\nabla c_n) = 0 \qquad (18)$$

The Fe/ HZSM5 catalyst section was modeled as a reactive pellet bed with the bed porosity (ϵ_b) calculated from the bed density (ρ_b) and pellet density (ρ_{pe}) as shown in equation 19.

$$\epsilon_b = 1 - \frac{\rho_b}{\rho_{pe}} \qquad (19)$$

A uniform size distribution was assumed for the catalyst pellet with a radius (r_c) and a bed porosity (ε_{pe}) [13]. The estimated operating parameters are given in Table 2.

Table 2: Operating Parameters

Parameter	Value
Tube Dimensions (m)	1mx0.1m
Molar Ratio (CO/H2)	0.78
Feed Temperature (K)	515
Reactor Pressure (Pa)	1.6e6
Inlet Mole Flow H_2 (mol/m^3)	18
Inlet Mole Flow CO (mol/m^3)	14
Velocity (m/s)	5
Bed Density (kg/m^3)	730
Pellet Density (kg/m^3)	1290
Bed Porosity	0.38
Radius of catalyst (m)	1.92e-3
Dynamic Viscosity (Pa.s)	1.83e-5
Permeability (m^2)	1e-11

III RESULTS AND DISCUSSION

An optimized physics controlled mesh with 20738 elements was generated using ANSYS Workbench version 16.0. A stationary plug flow of the entire model was assumed to solve the governing equations of the entire model in COMSOL Multi-physics version 5.1. Results from the simulation shows that during the FTS fixed bed reactor, H_2 is being consumed completely in 100 seconds while carbon monoxide reaches a conversion of 71% in 100 seconds as shown in figure 2.

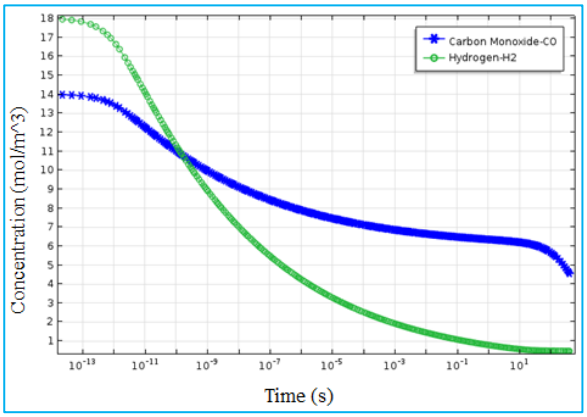

Figure 2: Consumption of concentration of CO and H_2

Production of species C_4H_{10} (n-butane), $C_4\_H_{10}$ (butane) is higher at the start of the experiment. The production of H_20 (water) is high at the beginning of the reaction and at around 10s the concentration begins to decrease as a result of the water-gas-shift reaction to form more H_2 and CO_2 as depicted in figure 3. The model exhibits that the start of the FTS reaction can be approximated at reactor volumes between 1e-5m and 1e-4m as shown in figure 4.

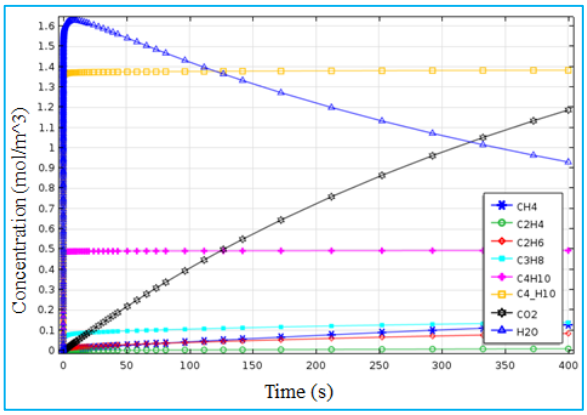

Figure 3: Production of methane, ethylene, ethane, n-butane, butane, carbon dioxide and water in the reactor.

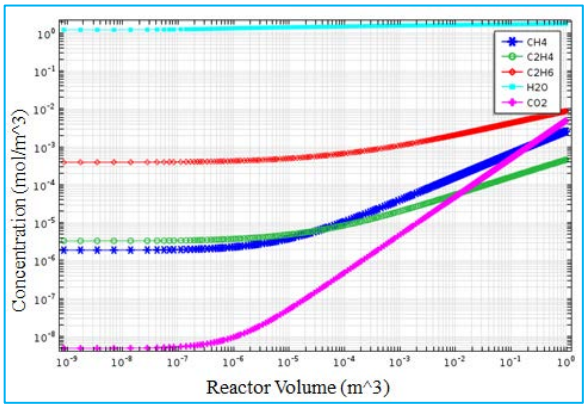

Figure 4: Concentration of species CH_4, C_2H_4, C_2H_6, H_20 and CO_2 against reactor volume.

Concentration contours of species along the reactor length are presented in figures 5 to 7. Figure 5 shows that the concentration of carbon monoxide and hydrogen start to reduce at the porous bed (0.4m of the reactor length) that is, where most of the reactions are taking place. The level of these species are very low at the reactor outlet which indicates that CO and H_2 are being consumed within the reactor bed. The level of H_2O is lower at the inlet part of the reactor and gradually increases beyond the catalyst bed at around 0.6m of the reactor length. Figure 6 shows that the production of methane (CH_4) and ethylene (C_2H_4) is higher at the inlet and the species begin to be consumed throughout the length of the reactor.

Figure 7 indicates that as the reaction progresses in the fixed bed reactor the production of C_3H_8, C_4H_{10} and n-C_4H_{10} increases greatly with the reactor length. C_4H_{10} has very high cncentrations of 10 mol/m^3 near the exit of the reactor. The model predicts that an increase in the partial pressure of hydrogen will result in a decrease in the production of CH_4, $C2H_4$, C_3H_8, C_4H_{10} and C_{5+} species as shown in figure 8.

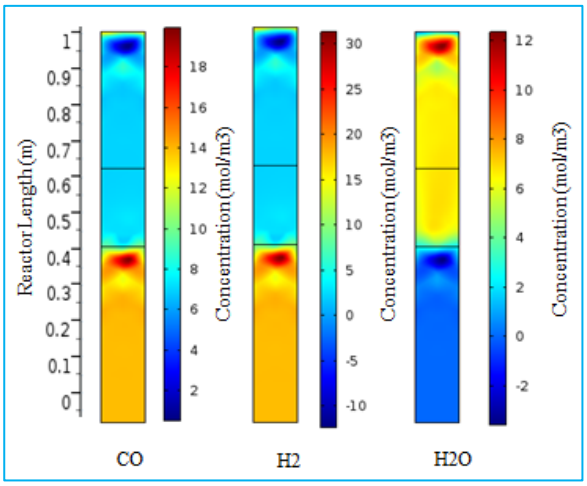

Figure 5: Concentration contour of species CO, H_2 and H_2O

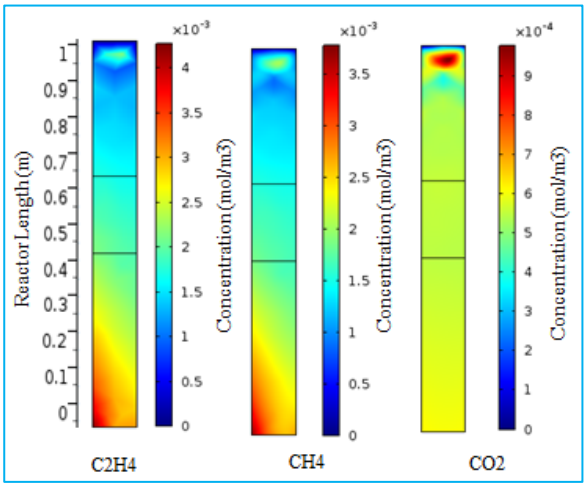

Figure 6: Concentration contour of species C_2H_4, CH_4 and CO_2

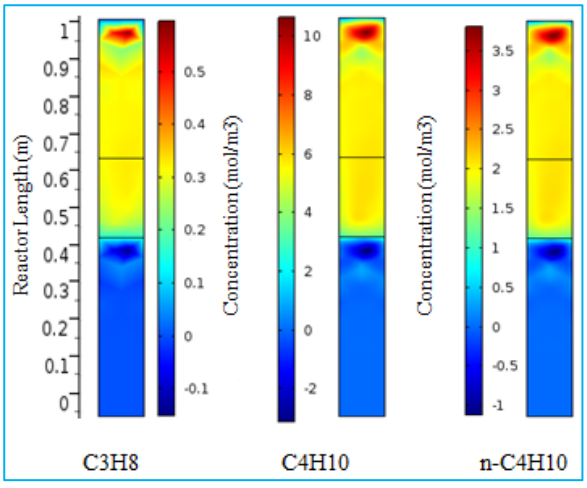

Figure 7: Concentration contour of species C_3H_8, C_4H_{10} and n-C_4H_{10}

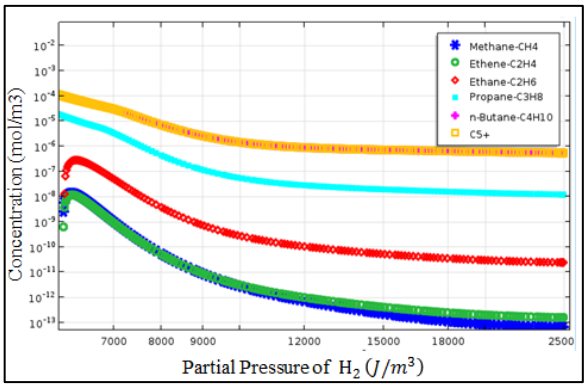

Figure 8: Effect of hydrogen partial pressure on the production of CH_4, $C2H_4$, C_3H_8, C_4H_{10} and C_{5+} species.

The results predicted by the model were validated against those reported by Mohammad Iran [13] as shown in Table 3. Figure 2 shows that at the end of the reaction, the composition of CO is 4.5mol/m^3 from an initial concentration of 14mol/m^3 (this reflects about 67.85% conversion of CO). The current model predictions are in good agreement with the results obtained by Mohammad Iran [13] as; there is a slight difference of less than 10% conversion of CO species in both the experiment and Mohammad Iran's model.

Further validation was done against the work of Srinivas et al [14] who carried out a similar study but on a micro reactor of 1.27cm by 20cm. As can be observed in figure 9, concentration distribution of species CO, H2, C2H6 and C3H8 species within the length of a reactor follow a similar contour pattern with the results obtained in the current model.

Table 3: Model Validation data

	Current Model	Model [13]	Experimental [13]
CO Conversion	67.85	58.59	60.7
Error (%)		-9.26	-7.15

IV CONCLUSION

A numerical 2D fixed bed model of the FTS was modeled on a promoted Fe catalyst. The results of the model show that high concentrations of C_4 and C_{5+} are achieved at the prescribed initial conditions of temperature and pressure. The model shows that about 70% conversions of H_2 occurred within the fixed bed reactor. The overall behavior of species in this model is consistent with data available in the literature for fixed bed reactor with improved iron catalyst. This confirms that the CFD models can be used for reactor optimization by varying feed parameters. Work is still ongoing to refine the model, which can be done by capturing the effect of heat transfer in the free flow and catalytic bed regimes.

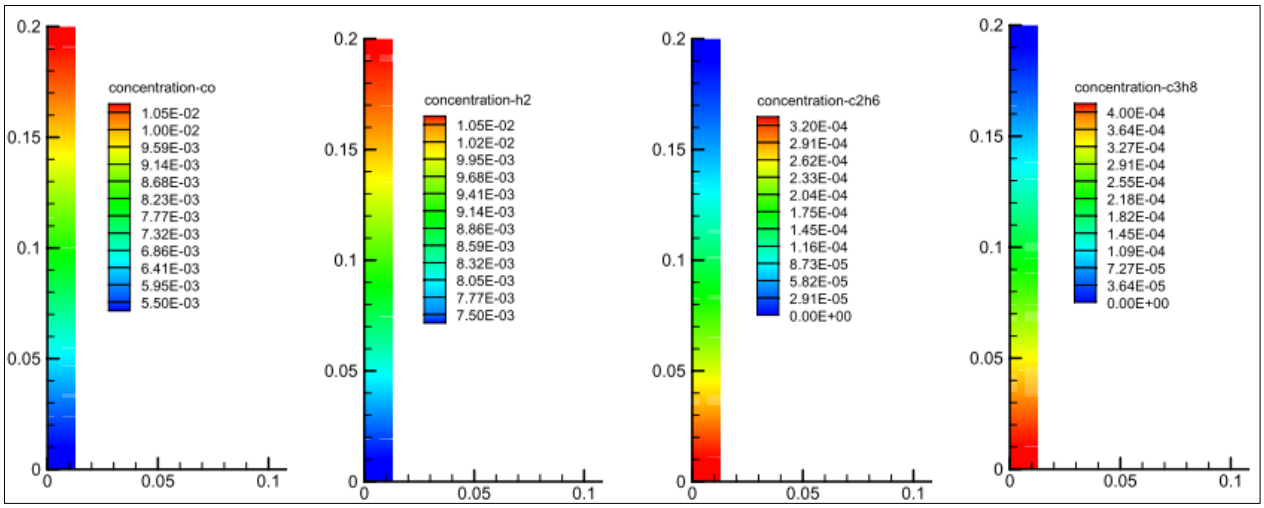

Figure 9: Concentration contour of CO, H2, C2H6 and C3H8 species within a reactor, from the work of Srinivas et al [14].

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NOMENCLATURE

C_n	Concentration of Species i [mol/m^3]
D_n	Diffusivity Coefficient [m^2/s]
E_n	Activation Energy [Jol/mol]
g	Gravitational Acceleration
k_n	Rate constant [mol/h.g(catalyst)]
m_n	Power for CO partial pressure
n_n	Power for H2 partial pressure
n	Reaction number

P	Reactor Pressure [Pa]
P_{CO}	Partial pressure of carbon monoxide [Pa]
P_{H2}	Partial pressure of hydrogen [Pa]
R_g	Universal gas constant [Jol/mol. K]
R_n	Reaction rate [mol/h.g.$_{cat}$]
T_b	Reactor Temperature [K]
V	Volume [m^3]

Greek Letters

v	*Velocity [m/s]*
ρ	*Density [kg/m^3]*
κ	*Permeability [m^2]*
μ	*Viscosity [kg/m.s]*
ε_{pe}	*Bed Porosity*
ρ_{pe}	*Pellet Density [kg/m^3]*
ρ_b	*Bed Density [kg/m^3]*