Hydrodynamics Simulation of Nanocatalyst Configuration for One-Step Urea Synthesis

by

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Bachelor of Engineering (Hons)
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CERTIFICATION OF APPROVAL

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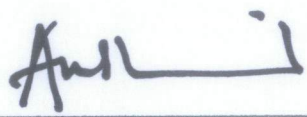
Approved by,



(DR. ANIS SUHAILA BINTI SHUIB)

UNIVERSITI TEKNOLOGI PETRONAS

TRONOH, PERAK

January 2014

CERTIFICATION OF ORIGINALITY

This is to certify that I am responsible for the work submitted in this project, that the original work is my own except as specified in the references and acknowledgements, and that the original work contained herein have not been undertaken or done by unspecified sources or persons.

NUR IDAYU BINTI BAHARI

ABSTRACT

Approximately 48% of global ammonia demand goes to urea production which is used as fertilizer. Currently the method used in urea production involves two steps. The first step is Haber-Bosch process to produce ammonia by reacting hydrogen (H_2) and nitrogen (N_2) at high temperature and pressure and the second step is to produce urea by reacting NH_3 and carbon dioxide (CO_2). The current method used in urea production consumes high cost and energy; hence one-step-urea synthesis method is introduced. The patent of one-step-urea synthesis is constructed based on the method's potential to bypass ammonia step by reacting H_2, N_2 and CO_2 directly at ambient temperature and pressure. Presently, the design of microreactor used in one-step-urea synthesis is not available; hence this study will focus on investigating the optimum nanowire arrangement for the microreactor. In this paper, the fluid flow and the molecular motion in the mixing gases for urea synthesis is simulated by using Computational Fluid Dynamics (CFD) approach. In the microchannel where the scale is between micrometer to nanometer, the ability of mixing the gases can be achieved by varying the configuration of nanowire and flow rate of the fluid. The optimal nanowire orientation and flow rate of fluid will be based on degree of mixing and pressure.

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My sincere thanks and appreciation goes to Mr. Reza Nurrahman for his endless effort in tutoring me on ANSYS software and the project itself throughout the completion of the project.

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CHAPTER 1

INTRODUCTION

1.1 Background Study

Ammonia (NH_3) synthesis has reached it 100 years by this year since its first production in 1913. Strong agricultural fundamentals are expected to drive ammonia growth as fertilizer uses account for approximately 80 percent of global ammonia demand with 48% of ammonia production going to produce urea (PotashCorp, 2013). Despite of the high demand, ammonia production can be costly and energy consuming. The formation of ammonia that involves an exothermic reaction between nitrogen and hydrogen ($N_2 + 3H_2 \leftrightarrow 2NH_3$) required the operational condition to be at 400 - 500°C and at pressure of 150 – 200 bar (Modak, 2002). This has been a challenge for the production company to seek for more advance technology in order to satisfy the world ammonia demand at lower cost.

The establishment of Yttrium iron garnet (YIG) and α-Fe_2O_3 as the new nanocatalyst in ammonia synthesis (Yahya & Hussain, 2011) has led to the new method in urea production called one-step urea synthesis. These nanocatalysts make it possible for the ammonia to be synthesized at room temperature (28°C) and ambient pressure which greatly cut the production cost on energy consumption. Moreover, in one-step urea process, urea can be produced by surpassing the reaction between nitrogen and hydrogen by reacting $N_2 + H_2 + CO_2 \rightarrow NH_2COONH_4$ then $NH_2COONH_4 \rightarrow H_2O + NH_2CONH_2$, hence reduce the cost to produce ammonia.

Microreactor has been designed with the target to increase the urea production at lower cost succeeding the existence of one-step urea synthesis. A microreactor is a device in which chemical reaction take place in a confinement with typical lateral dimensions below 1 mm; where the most typical form of such confinement are microchannel (Watts & Wiles, 2007). Compared to vessel, microreactor has the ability to remove heat efficiently besides being able to conduct a safe critical reaction at high temperatures (Roberge, Ducry,Bieler, Cretton, & Zimmermann, 2005). In order to decrease the energy used as well as urea production cost, the microreactor has been proposed to have such a good micromixing. Nevertheless, in the case of straight microchannel structure, the incoming fluid flow will act as laminar flow. Longer mixing channel is required to satisfy mixing result (Chen & Chang, 2008), consequently leading to pressure increment inside the channel.

1.2 Problem Statement

Despite the ability of microreactor to operate at low temperature and pressure, it turns into less cost-effective device when featuring straight microchannel configuration. This is because the straight structure of microchannel will induce laminar flow instead of turbulent, leading to poor fluid mixing process. Hence longer microchannel is proposed to ensure the fluids are well-mixed. Consequently, longer microchannel requires more energy to assist the fluid to flow along the channel in order to counter the increasing pressure result from the selection of longer microchannel. Yet, the production of ammonia and urea in microreactor as for the researcher knowledge is concerned is still not available.

Inside the microchannel, there are nanocatalysts embedded within many nanowires, a tight nano-structure being attached to the surface of microreactor. As for the straight configuration of microchannel, the fluid will flow in the middle path of the channel, avoiding direct contact with the nanowires thereby causing a low interaction between molecular flow and nanocatalyst. The arrangement of the microwire for efficient mixing is not yet reported. Therefore, the effectiveness of the molecular and nanocatalyst

interaction, the arrangement of the nanowires will be investigated and measured using ANSYS.

1.3 Objective

1. To develop a numerical simulation of one-step urea synthesis to predict the hydrodynamics interaction between molecular flow and nanocatalyst.
2. To investigate the effect of different nanowires arrangement on fluid flow mixing efficiency.
3. To study the effect of fluid velocity on mixing efficiency.

1.4 Scope of study

This study will discuss on the topic of hydrodynamics simulation of gas flow in urea synthesis (N_2, H_2 and CO_2) in microchannel by using ANSYS software. Chemical reaction is not taken into account in investigating hydrodynamics interaction of molecular flow with nanocatalyst. The parameters considered in this study include mixing efficiency, pressure drop and fluid flow rate which will be used to identify the best design for microchannel structure.

CHAPTER 2

LITERATURE REVIEW

2.1 Synthesis of Ammonia

Approximately 50% of the synthesized ammonia in the world is being used in urea production. Besides, ammonia is also used as the raw material in various industries such as fertilizer manufacture, cleaner products and fermentation.

2.1.1 Conventional Method of Ammonia Synthesis via Haber – Bosch Method

Ammonia production involves an exothermic reaction between N_2 and H_2 ($N_2 + 3H_2 \rightarrow 2NH_3$) at operating condition of 400 - 500°C and a pressure between 150 – 200 bar, assisted by iron-based catalyst (Modak, 2002). The method was first developed by Fritz Haber in 1909 and later scaled up by Carl Bosch for commercial production. By applying high temperature and pressure to the process, it contributes to the high cost production since the operational condition consumed a lot of energy and fuel.

2.1.2 Synthesis of Ammonia via Magnetic Induction Method

Yttrium Iron Garnet (YIG) and α-Fe_2O_3 have recently been used as the nanocatalyst in ammonia synthesis. For this purpose, the nanocatalyst is embedded within permanent magnetic field inside microreactor. In the application of magnetic induction method, nanocatalysts are able to assist the reaction to operate at ambient condition (28°C and 1 atm) (Modak, 2002) as well as enhancing the yield of ammonia up to 78% (Yahya, 2011).

2.1.3 Synthesis of Urea via Basaroff Exothermic Liquid Reaction

In this conventional process, ammonia and carbon dioxide are reacted at high temperature and pressure. This method comprises of two steps of reaction; Basaroff exothermic reaction $2NH_3 + CO_2 \rightarrow NH_2COONH_4$ and endothermic reaction $NH_2COONH_4 \rightarrow H_2O + NH_2CONH_2$ (Meessen, 2012). Figure 2-1 below shows the reaction to produce urea.

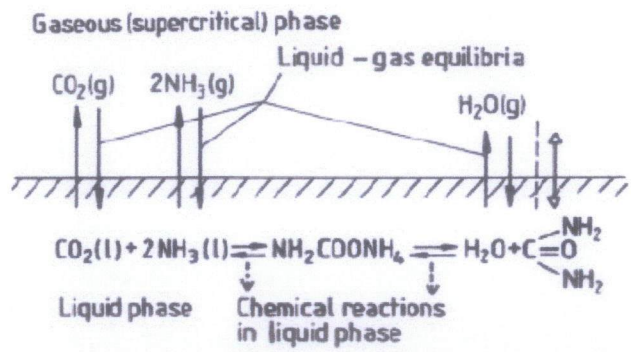


Figure 2-1 Chemical and Physical equilibria urea production (Meessen, 2012).

2.1.4 Synthesis of Urea via One-Step Urea Synthesis

One-step urea synthesis takes place inside a microreactor with high density magnetic flux. The reaction between three gases reactants which is N_2, H_2 and CO_2 will be assisted by new catalyst support system in order to produce molten urea (Yahya & Hussain, 2011). Compared to the current conventional method, this process is found to be un-complicated.

2.2 Hydrogen, nitrogen, and carbon dioxide as ideal gas

Most real gases act like ideal gas in the typical temperature and pressure. Ideal gas is assumed to be non-interacting particles that move constant and randomly in their container. In this paper, hydrogen, noble gases including heavier gases like carbon dioxide can be treated like ideal gases (Wilke, 1950).

Table 2-1 Properties of hydrogen, nitrogen and carbon dioxide

Gas	Symbol	Property	Value
H_2	ρ_{mH_2}	Density (kg/m^3)	0.08189
	m_{mH_2}	Molecular Weight (kg/kgmol)	2,01594
	μ_{mH_2}	Viscosity (kg/m.s)	8.411×10^{-6}
	D_{mH_2}	Molecular Diameter (nm)	0.289
N_2	ρ_{mN_2}	Density (kg/m^3)	1.138
	m_{mN_2}	Molecular Weight (kg/kgmol)	28.0134
	μ_{mN_2}	Viscosity (kg/m.s)	1.663×10^{-5}
	D_{mN_2}	Molecular Diameter (nm)	0.3681
CO_2	ρ_{mCO_2}	Density (kg/m^3)	1.7878
	m_{mCO_2}	Molecular Weight (kg/kgmol)	44.00995
	μ_{mCO_2}	Viscosity (kg/m.s)	1.37×10^{-5}
	D_{mCO_2}	Molecular Diameter (nm)	0.33

2.6 Microreactor and microchannel

Microreactor could serve as a reactor with a diameter dimension below 1mm (Watts & Wiles, 2007). The microreactor is capable in removing heat efficiently and able to maintain the operation carried out at high temperature (Roberge *et al.*, 2005). Microchannel inside the microreactor is a sub-unit of the device that acts both as reactor as well as a channel to mix the fluid.

2.7 Nanowire

Nanowire is a nano-scaled tube structure which grows on the internal wall of microchannel and helps to support nanocatalys. Research has found that nanowire with Hermatite (α-Fe_2O_3) embedded can have a dimension of diameter range of 20 nm and length of less than 3µm (Abd Razak, Sufian, Zilati, & Yahya, 2011). Nevertheless, another study reported that nanowire made from iron element can grow up to micro scale with diameter range of iron element of nanowire 10 – 40 nm (Chueh, Lai, Liang,

Chou, & Wang, 2006). Figure 2-2 shows the morphology of ZrO_2 nanotubes oxide while Figure 2-3 shows α-Fe_2O_3 nanowires grow on two different surfaces.

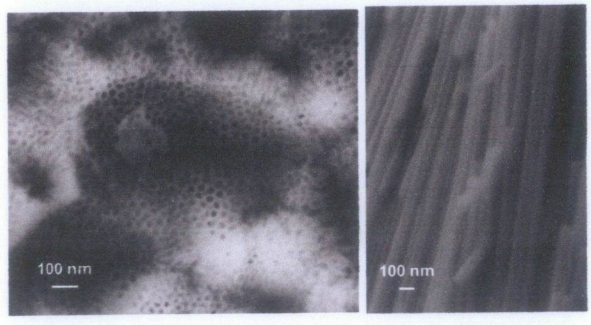


Figure 2-2 SEM images show morphology of ZrO_2 nanotubes oxide

(Lockman& Ismail, 2011)

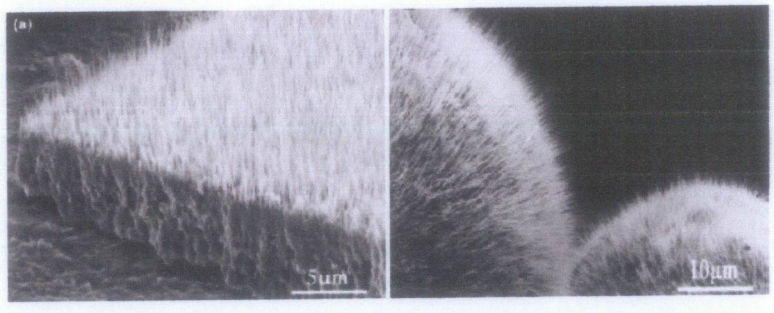


Figure 2-3 SEM images of as-synthesized α-Fe_2O_3

(a) α-Fe_2O_3 nanowires grow vertically from the substrate over a large flat area. (b) α-Fe_2O_3 nanowires grown on the spherical radial surfaces of iron particles (Fu *et al.*, 2003)

2.8 Mixing Efficiency and Pressure Drop in Microchannel

Data of Chen and Change (2008) shows that the fluid mixing efficiency in straight microchannel is at 20% hence the structure design needs to be modified to improve the mixing efficiency.

2.8.1 Mixing efficiency

Mixing efficiency is necessary to be at its optimum level in order to ensure high conversion and attain high urea production. Mixing efficiency can be written as follow (Hsieh & Huang, 2008):

$$m_{eff} = \left(1 - \frac{\int_0^w |V - V_\infty| dx}{\int_0^w |V_0 - V_\infty| dx}\right) x\ 100\% \quad (1)$$

where, m_{eff} is the mixing efficiency, V is the volume fraction distribution across the transverse direction at the outlet, V_∞ is the volume fraction of complete mixing, V_o is the initial distribution of the volume fraction before any mixing occurs, W is the width of the micro-mixers (diameter of microchannel)

2.8.2 Pressure Drop

Besides its function as microreactor, microchannel also has the role as a long tube that has probability to decrease the pressure. Pressure drop in pipe is indicates by friction factor (f) that is defined as (Schlinchting, 1979):

$$f = \frac{\Delta P\ x\ 2\ x\ D}{x\ x\ \rho\ x\ u^2} \quad (2)$$

Where, ΔP is Pressure drop along pipe length (Pa), x is the Length along of pipe (m), D is pipe diameter (m), u is average velocity in the pipe section ($m.s^{-1}$), ρ = fluid density ($kg.m^{-3}$)

2.9 Euler Equation

The fluid dynamics concept of Euler equation has always been referred to the conservation of mass, momentum and energy. The combination of these three conservations is called as the Euler equation. The conservation form of Euler equation is used to emphasis more on the physical interpretation of the equation by fixing volume value in space. Application of Euler equation can be applied over compressible and non-

compressible flow by assuming the corresponding flow velocity of divergence field is equal to zero.

$$\frac{\partial \rho}{\partial t} + \nabla.(\rho \mathbf{u}) = 0 \tag{6}$$

$$\frac{\partial \rho \mathbf{u}}{\partial t} + \nabla.(\mathbf{u} \otimes (\rho \mathbf{u})) + \nabla p = \mathbf{0} \tag{7}$$

$$\frac{\partial E}{\partial t} + \nabla.(\mathbf{u}E + p)) = 0 \tag{8}$$

Where, ρ is the fluid mass density, u is the fluid velocity vector, with components u, v, and w, $E = \rho\, e + ½\, \rho\, (u^2 + v^2 + w^2)$ is the total energy per unit volume, with e being the internal energy per unit mass for the fluid, p is the pressure, ⊗ denotes the tensor product, **0** being the zero vector.

2.10 Navier Stokes Equations

In performing CFD simulation, Navier Stokes Equations are essential to be understand since the equation is the fundamental to CFD problems. The general form of Navier Stokes equation is given as below:m

$$\rho\left(\frac{\partial \mathrm{v}}{\partial t} + \mathrm{v}.\nabla \mathrm{v}\right) = -\nabla p + \nabla.\mathbf{T} + \mathbf{f} \tag{5}$$

where, v is the flow velocity, ρ is the fluid density, p is the pressure, **T** is the (deviatoric) stress tensor, **f** represents body forces (per unit volume) acting on the fluid, ∇ is the del operator.

The left side of the equation is the term for acceleration and composed of time dependent (as well as the effects of non-inertial coordinates) while the right side of the equation describes the summation of body forces and divergence of stress.

CHAPTER 3

METHODOLOGY

3.1 Hydrodynamics Simulation

The flow of research method is shown in Figure 3-1. ANSYS Computational Fluid Dynamic (CFD) software was used to conduct hydrodynamics simulation in order to select the optimum design of microchannel and nanowire configuration with respect to the process specification. Prior to the simulation, several parameters are required to be determined which are nanowire arrangement and rate of fluid flow. In addition, this study is established only to consider the horizontal flow of gas inlet stream. The illustration of the microchannel and nanowires configuration were constructed in 2D.

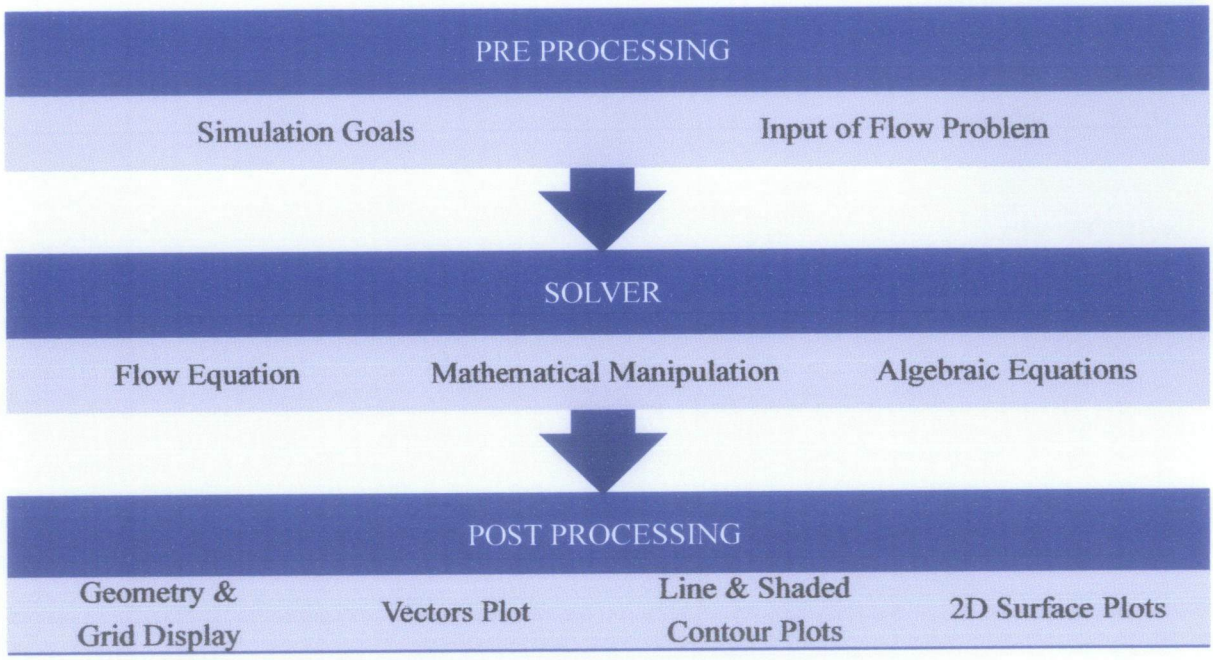


Figure 3-1 CFD simulation phases

3.1.1 Microchannel Model Construction using FLUENT

In FLUENT program of ANSYS, the microchannel was initially constructed for its geometry to serve as the base structure of the 2D drawing, where it was done in Design Modeller. Since the drawing was in 2D, the geometry drawing only involve XY plane. The geometry is then set according to the dimensions as shown in the Table 3-1.

Table 3-1 Configuration for hydrodynamics simulation

Item	Symbol	Property	Value
General	T	Ambient Temperature (^{o}K)	298.15^{o}
	P	Ambient Pressure (atm)	1
Microchannel	d	Diameter of Microchannel (μm)	5
	l	Length of Microchannel (μm)	50
Nanowire	-	Length section for molecular interaction analysis (μm)	8.075
	-	Gap length between nanowire (μm)	2.0
Nanocatalyst	-	Nanocatalyst diameter (μm)	0.015

3.1.1.1 Dimensions

A rectangular shape with total length of 50μm and 5μm height was drawn horizontally on the XY plane to represent the microchannel structure indicating the area of study. At the distance of 20μm from the inlet area, five pairs of rectangular shape with width of 0.015μm and various length arrangements are constructed vertically on the top and bottom of the inner side of microchannel surface. The sub-rectangular geometries with gap of 2μm width in between represent the nanowire structure which holds the catalyst at the tip of it within the microchannel. After the last pair of nanowire, another 21.985μm gap is left within the microchannel in order to create a space to illustrate the condition of the fluid after passing through the nanowires.

3.1.1.2 Nanowire Configuration

Currently, the published literature has not reported the optimum nanowire arrangement to be applied in microchannel, hence three different arrangements of nanowire were proposed in this study. The gap between two nanostructures was fixed to be 2μm. Table 3-2 shows the suggested

nanowire length for three different structures and Figure 3-2, 3-3 and 3-4 illustrate the configuration of different nanowire arrangement.

Table 3-2 Variation of nanowire length

Variation	**Structure type**	**Height name**	**Nanostructure**	**Distance between nanowires**
Variation 1	A	Homogenous	2 μm	2 μm
Variation 2	B	Low	1.5 μm	2 μm
		High	2 μm	2 μm
Variation 3	C	Low	1 μm	2 μm
		Medium	2 μm	2 μm
		High	3 μm	2 μm

Type A: Middle path gap = 1μm, Nanowire length = 2μm

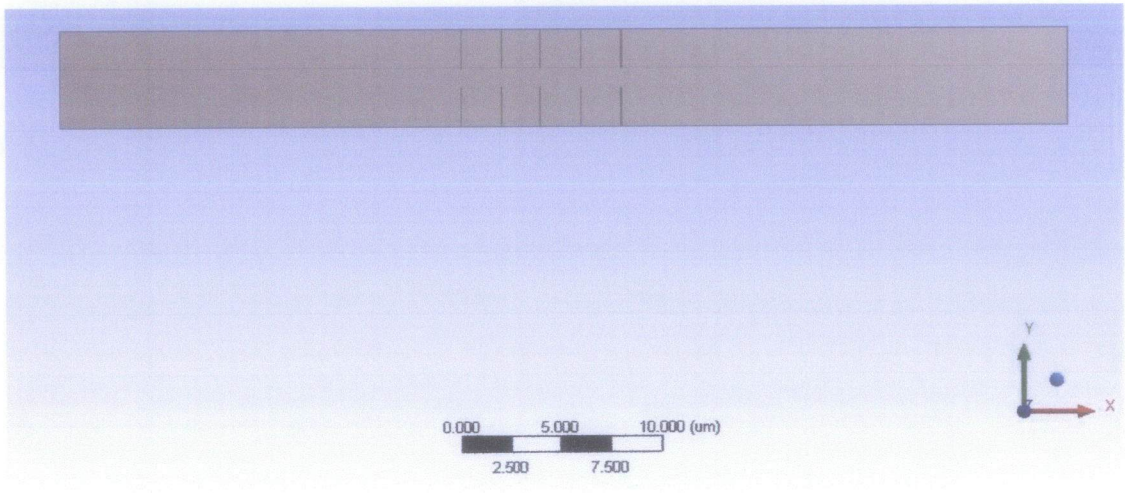


Figure 3-0-2 Type A nanowire arrangement geometry

Type B: Middle path gap = 1μm and 2μm, Nanowire length = 2μm and 1.5μm

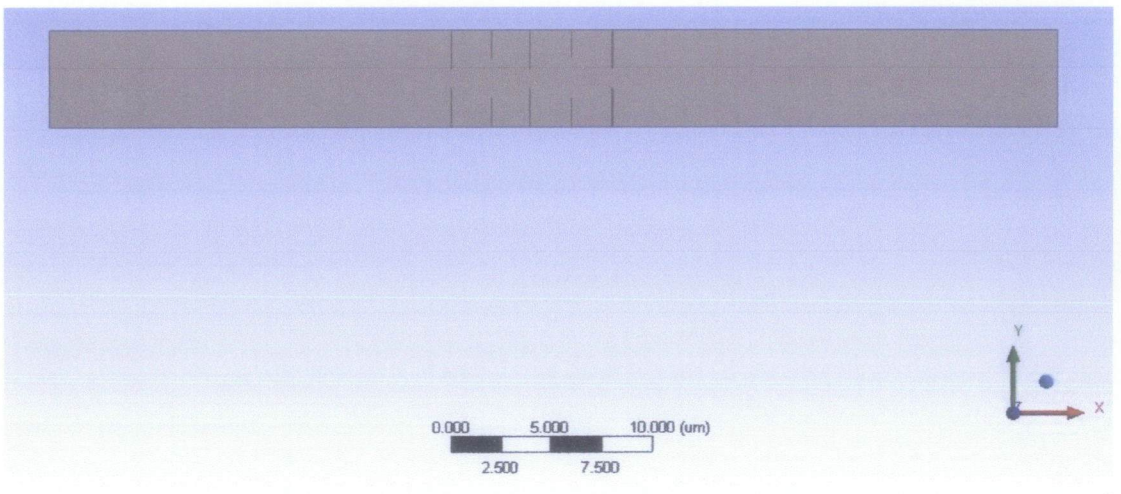


Figure 3-3 Type B nanowire arrangement geometry

Type C: Middle path gap = 1μm, Nanowire length = 2μm, 1μm and 3μm

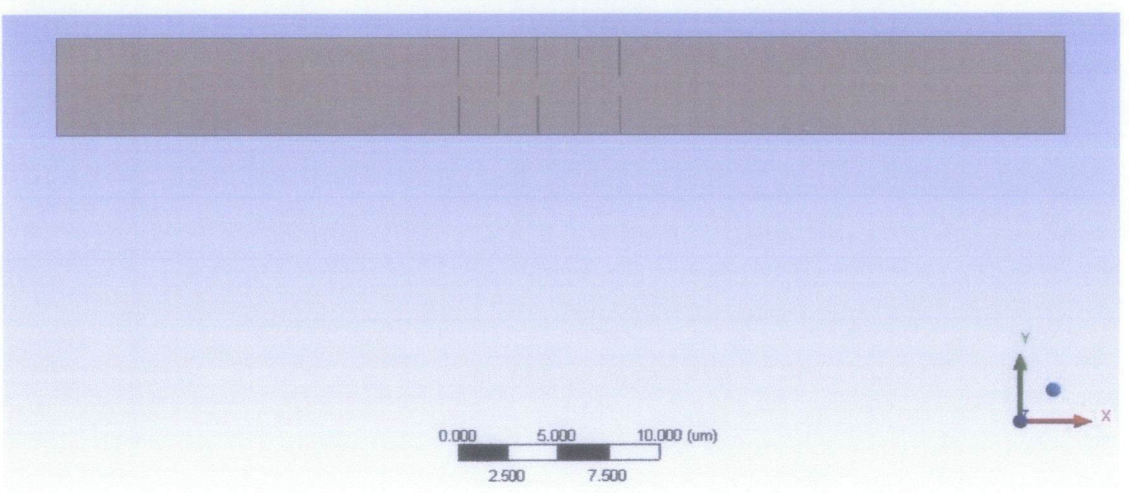


Figure 3-4 Type C nanowire arrangement geometry

The nanowire structures are then subtracted from the geometry by using *Boolean* properties in order to define the structure as wall. The blue colour of the geometry in Figure 3-5 shows the subtracted part the geometry that represents nanowire structure.

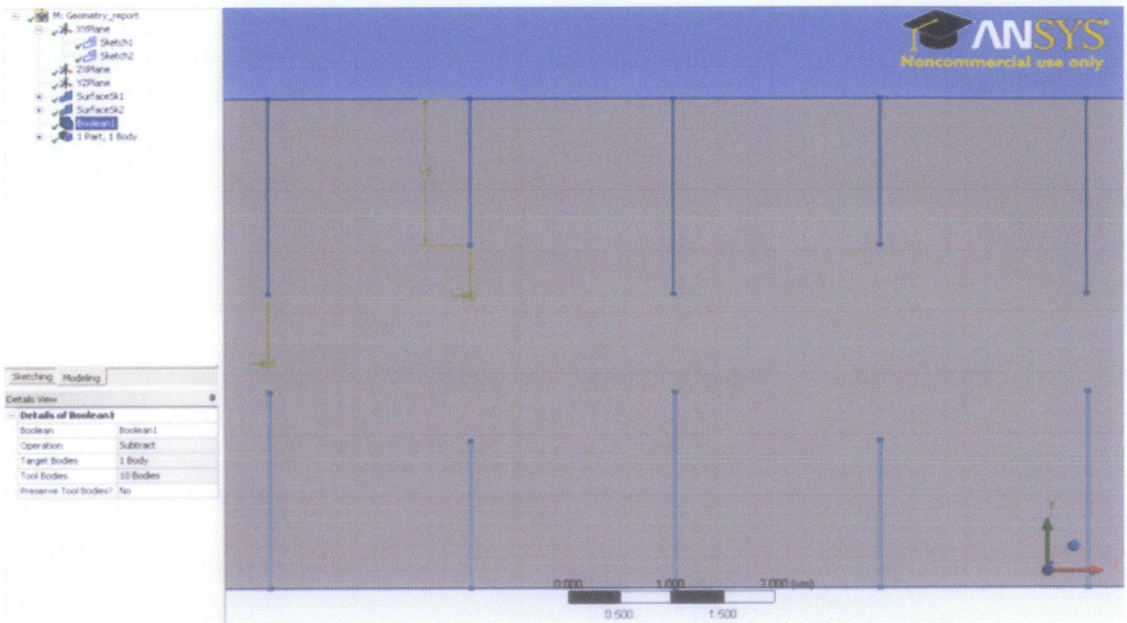


Figure 3-5 Subtraction of geometry using Boolean properties

3.1.2 Meshing

The geometry was then proceeded to meshing model phase in order to determine the area of study of the geometry such as the properties or condition of each wall face of the geometry structure. The significant of this phase is to inform the solver about certain condition of the model that need to be considered in solving the equation in solver stage. For this model, the flow of fluid is from the direction of x-axis, hence the inlet was specified at the left side of the geometry and outlet at the right side while tip of nanowire structures are specified as wall trap as shown in Figure 3-6.

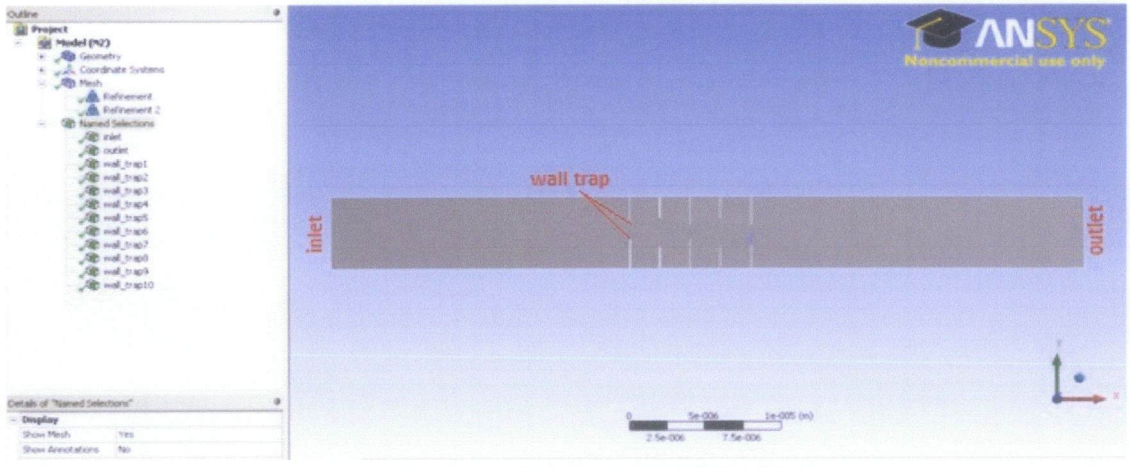
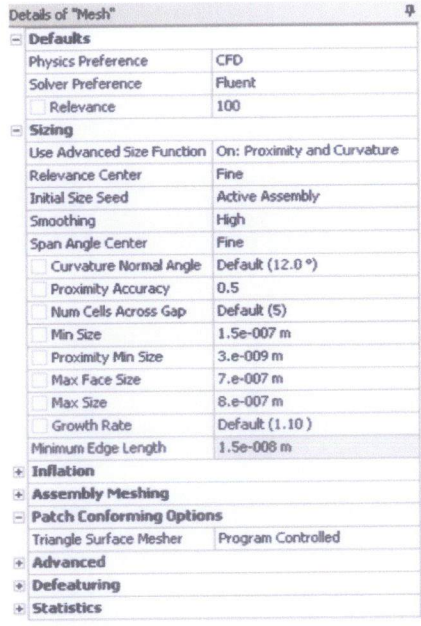


Figure 3-6 Name selection for the model

The details of mesh were established prior to meshing for *Defaults* and *Sizing* setting while the other settings were remain untouched. As for *Physics Preference*, CFD (Computational Fluid Dynamics) was chosen to execute the project goal specification and accordingly Fluent option is selected for *Solver Preference*. *Relevance* setting which the scale range from -100 to 100 was adjusted to 100 for the model. Proximity and Curvature option was selected for *Sizing Function* where proximity was used to specify the number of mesh-element cells to be located in gaps between surfaces in a volume while curvature meant to specify the maximum angle between normals for adjacent mesh elements. The *Relevance Center* functions to adjust mesh uniformity of the model into course, medium or fine where fine is the best option since the output result will be more accurate when the uniformity is high.

Other parameters that have been adjusted are Min Size, Proximity Min Size, Max Face Size and Max Size as in Figure 3-7.



Details of "Mesh"	
Defaults	
Physics Preference	CFD
Solver Preference	Fluent
Relevance	100
Sizing	
Use Advanced Size Function	On: Proximity and Curvature
Relevance Center	Fine
Initial Size Seed	Active Assembly
Smoothing	High
Span Angle Center	Fine
Curvature Normal Angle	Default (12.0 °)
Proximity Accuracy	0.5
Num Cells Across Gap	Default (5)
Min Size	1.5e-007 m
Proximity Min Size	3.e-009 m
Max Face Size	7.e-007 m
Max Size	8.e-007 m
Growth Rate	Default (1.10)
Minimum Edge Length	1.5e-008 m
Inflation	
Assembly Meshing	
Patch Conforming Options	
Triangle Surface Mesher	Program Controlled
Advanced	
Defeaturing	
Statistics	

Figure 3-7 Setting for Details of Mesh

Refinement is a one of the method in ANSYS Fluent to change the accuracy of the solution at a certain region. Performing refinement for the mesh can guarantee the best analysis results for the problem, decreases the need for additional analysis runs, and improves predictive capabilities. Two refinements of meshing scaled at 3 have been done to the model which was at the inlet and nanowire structure excluding its tip of it to notify the solver to calculate the problem more on that specific part.

3.1.2.1 Mesh generated model

The following Figure 3-8 below shows the complete meshing of the model with the refinements for all types of nanowire configuration.

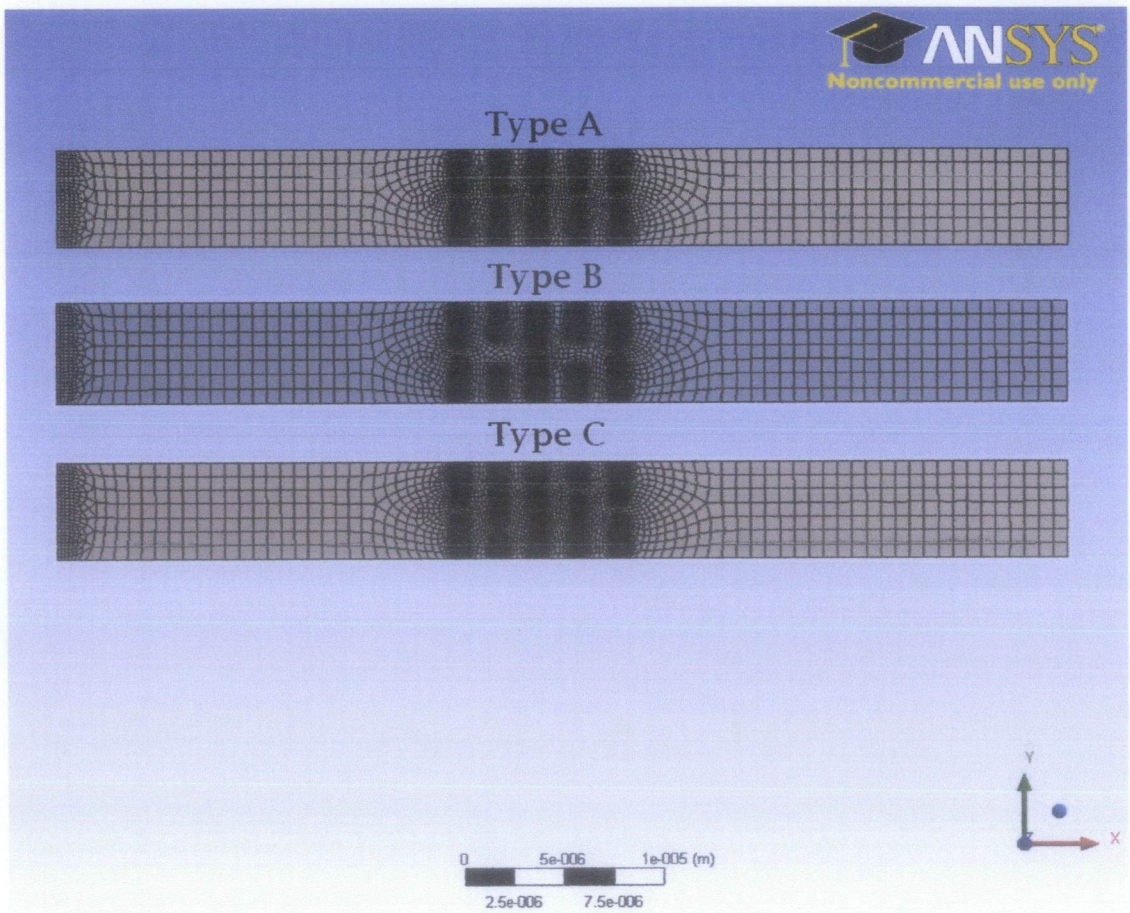


Figure 3-8 Generated mesh configurations of Type A, Type B and Type C

3.1.3 Solver Setup

Solver setup is a procedure to determine the mathematical equations involved along the simulation process. Properties such as type of fluid flow, material to be used, and characteristics of the material flowing in the microchannel as well as selection of model involves in the simulation are important to be defined in order to compute the calculation to obtain the result.

Most of the settings of the problem setup are maintained at the default value. The value of *Gravitational Acceleration* was set at y-axis with $-9.81 ms^{-2}$. In model option, *Energy* setting was set as "on". *Laminar* flow was chosen for viscous model since the Reynolds number calculated from the highest suggested velocity was less than 2300 which is considered as characteristics of laminar flow.

3.1.3.1 Reynolds Number

Instead of using velocity to differentiate between the flow of the gases, Reynolds number was used since the value is able to show the behavior of the fluid inside the microchannel. The materials used in this simulation involve three different types of gases which is hydrogen, nitrogen and carbon dioxide. In determining the Reynolds number of the gas mixture, Re_{mix}, viscosity of mixing gases first need to be computed. Below is the formula used in calculating the Reynolds number for the mixing gases obtained from (Wilke, 1950):

$$\mu_m = \frac{\mu_1}{1+(x_2/x_1)\phi_{12}+(x_3/x_1)\phi_{13}+\ldots} + \frac{\mu_2}{1+(x_1x_2)\phi_{21}+(x_3/x_2)\phi_{23}+\ldots} + \ldots$$

Where ϕ_{ij} is given by the equation:

$$\phi_{ij} = \frac{[1+(\mu_i/\mu_j)^{\frac{1}{2}}(M_j/M_i)^{\frac{1}{4}}]^2}{(4/\sqrt{2})[1+(M_i/M_j)]^{\frac{1}{2}}}$$

where x is mole fraction of a component in the mixture, μ_1 μ_2, refer to pure components at the temperature and pressure of the mixture, μ_m is the viscosity of the mixture, M is the molecular weight of the component and ϕ is dimensionless constant.

The Reynolds number equation of the gas mixture is given by:

$$\mathrm{Re}_{mix} = \frac{\rho_{mix} D v}{\mu_m}$$

where ρ_{mix} is the density of the gases mixture = 0.6345 kg/m^3, D is the diameter of the microchannel = 5 x 10^{-6} m and v is the inlet velocity of the mixture.

Species Transport with *Diffusion Energy Source* and *Full Multicomponent Diffusion* were selected in species model window. Since the project is focusing on urea production, urea-water-air was chosen for *Mixture Properties* where there are nitrogen and carbon dioxide component while hydrogen was added later from *FLUENT Database Materials*. The *Mass Diffusion Coefficient* of the gaseous component was added in the solver by editing the urea-water-air selection as presented in table 3-3 below.

Table 3-3 Mass diffusion coefficient (Perry & Chilton, 1973)

Gas component	**$N_2 - H_2$**	**CO_2 - H_2**	**$CO_2 - N_2$**
Mass diffusion coefficient	0.674e-04	0.646e-04	0.165e-04

In *Discrete Phase* model, the injection of gas is introduced in order for the CDF post to be able to read the particle track of the gases. Injection of hydrogen, nitrogen and corbon dioxide were adjusted at fixed temperature 300 K and a total flow rate of 1 x 10^{-10}, and by changing the variable diameter (diameter molecular of each gas) and velocity magnitude according to inlet velocity. The values of point properties Brownian Motion is selected for physical models because the material involve in the simulation is in gas phase.

Boundary Conditions was the critical component in the solver setup as it is used to specify the flow and thermal variables on the boundaries of the physical model. All the zones were remained as the default except for inlet type which was changed to velocity-inlet. The inlet velocity magnitude for this model was setted at $78ms^{-1}$, $780\ ms^{-1}$ and $7800\ ms^{-1}$ with pressure specified at 0.2 Pa, while in the *Species* setting, the number of mole of both N_2 and CO_2 is 0.2 according to the balance chemical reaction. The same setting was set up for outlet boundary.

In the solution methods, SIMPLE (Semi-Implicit Method for Pressure-Linked Equations) scheme was selected because the fluid was setted at steady state where the velocity of the fluid affects the pressure inside the microchannel. Standard Initialization was chosen as solution initialization according to the simulation setup which is not necessarily to use Hybrid.

After all values of the model was initialized, the calculation was started with 500 iterations to solve the related equations with the specified value to get the result.

3.2 Fluid Flow Rate

Three values of different velocities for the inlet fluid also been taken into consideration aside from proposing different nanowire arrangement in order to measure the mixing efficiency of the gases. Hence, three distinguished sets for N_2, H_2 and CO_2 velocity were planned to be tested in this case study which shown as in Table 3-4 below.

Table 3-4 Inlet flow rate for nitrogen, hydrogen and carbon dioxide

Inlet gas	Inlet velocity 1 (m/s)	Inlet velocity 2 (m/s)	Inlet velocity 3 (m/s)
N_2	6	60	600
H_2	28	280	2800
CO_2	44	440	4400
TOTAL	78	780	7800
Re	20.77	207.70	2077.00

3.3 Gantt Chart

Activities	WEEK																													
	FYP (I) MAY 2013															FYP (II) SEPTEMBER 2013														
	1	2	3	4	5	6	7	8	9	10	11	12	13	14		1	2	3	4	5	6	7	8	9	10	11	12	13	14	15
Confirmation of Project Title	■	■	■	☆																										
Literature Review & Methodology			■	■	■	☆																								
Draft on extended proposal			■	■	■																									
Submission of Extended Proposal Defense						■																								
Proposal Defense								■	■																					
Ansys training and computational setup										■	■	■	■																	
Simulation work – Preliminary research										■	■	■	■																	
Submission of Interim Draft Report													■																	
Submission of Interim Report														☆																
Simulation project continues																■	■	■	■	■	■	■	■	■	■	■	■	■		
Submission of Progress Report																							☆							
Collected data analysis																■	■	■	■	■	■	■	■	■	■	■	■	■		
Pre-SEDEX																									■					
Submission of Draft Report																										■	■			
Submission of Dissertation (Soft Bound)																												■		
Submission of Technical Paper																												■		
Oral Presentation																												■	■	
Submission of Dissertation (Hard Bound)																														■

SEMESTER BREAK

CHAPTER 4

RESULT AND DISCUSSION

4.1 CFD Simulation Results

The fluids used in this simulation were gaseous hydrogen, nitrogen and carbon dioxide. In revision to the conducted simulation, the value for mass fraction result of each gas was not significant as the result from mass fraction contour shows that the distribution of the mass fraction for all gases shows that the gases were equally distributed throughout the microchannel region.

Hence, velocity vector, pressure and Reynolds Number graph were used as the option to illustrate and analyze the results. The values of pressure in the microchannel and Reynolds Number of the gases were taken at five different random points in microchannel as shown as in Figure 4-1.

i. Point 1 – x = 1.0×10^{-5}
ii. Point 2 – x = 1.9×10^{-5}
iii. Point 3 – x = 2.5×10^{-5}
iv. Point 4 – x = 3.1×10^{-5}
v. Point 4 – x = 4.1×10^{-5}

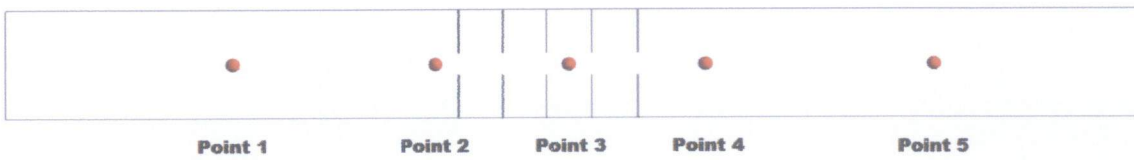


Figure 4-1 Random points for pressure and Reynolds number values

In addition, the results will be discussed in term of Navier Stokes and Euler equations which are used in solving the hydrodynamics problem during the simulation.

4.1.1 Velocity vector results

The result of velocity vector test on different nanowire configurations was observed in order to determine the suitable nanowire arrangement for the specified inlet velocity. By using velocity vector to display the result of the simulation, both the velocity magnitude and the direction or behavior of the gases in study can be clearly observed. The results of velocity vector are categorized and compared according to Reynolds Number of inlet fluid velocity and nanowire configuration. Figure 4-2 (a) is the velocity vector result of hydrogen for Type A, Type B and Type C nanowire arrangement when inlet velocity is introduced at 78 ms^{-1} while figure 4-2 (b) shows the velocity vector of hydrogen for Type C nanowire configuration at different inlet fluid velocity.

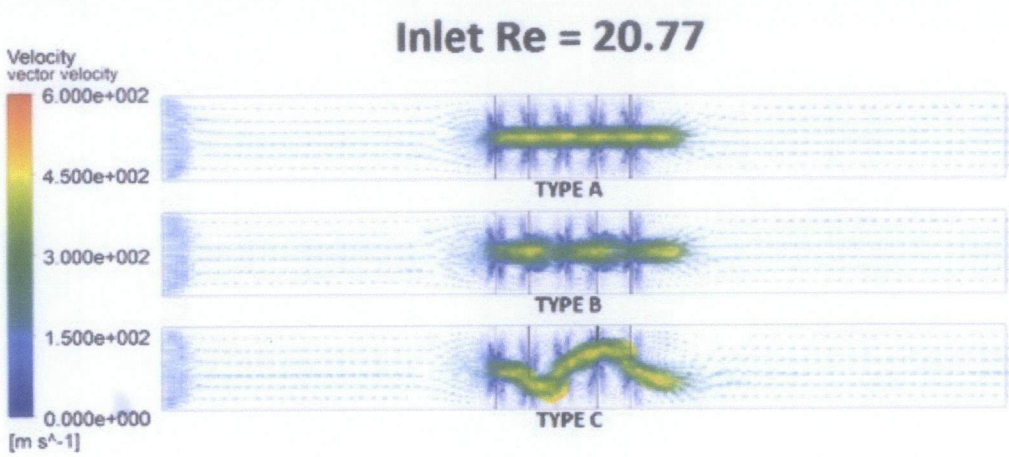


Figure 4-2 (a) Velocity vector of hydrogen at inlet flow Re = 20.77

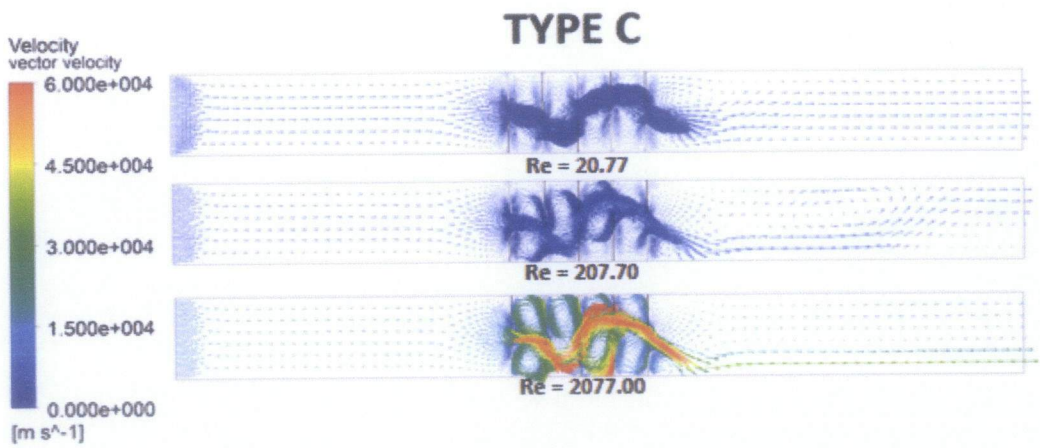


Figure 4-2 (b) Velocity vector of hydrogen for Type C configuration

From Figure 4-2 a), the velocity vector results are arranged in the order of different nanowire configuration to observe the fluid behavior at specified inlet velocity. The red colour indicated high velocity vector with 600.00 ms^{-1} as the highest scale while the blue colour indicated low velocity vector with 0 ms^{-1} as the lowest value. The comparison of simulation results above illustrates that the highest velocity vector recorded is at 552.04 ms^{-1} by Type C arrangement while the lowest reading was 488.75 ms^{-1} for Type B arrangement. As for Figure 4-2 (b) the velocity vector results were arranged in the order to observe fluid behavior based on different inlet fluid velocity. The highest velocity vector was recorded by the fluid with inlet Re of 2077.

At high velocity, the flow of the gases has high probability to create turbulence pattern that will help the fluid to mix more efficiently. Based on the velocity vector in figure 4-1, turbulent flow is probably formed when the fluid inlet velocity is 7800 ms^{-1} for Type C configuration.

4.1.2 Particle track results

Figure 4-3 shows the comparison of particle track between inlet velocity introduced at Re = 20.77 and Re = 207.7. The result demonstrates that the gas particles with inlet Re = 207.7 introduced for Type B configuration shows the tracked particles were untouched by the tip of nanowire with length of 1.5 μm. The result obtained from Re = 2077 also shows the same pattern of particle track as the inlet fluid Re = 207.7 for Type B configuration where the gas particles did

not touch the 1.5μm nanowire. Even though the tracked particles for Type A and Type C configuration were in contact with all the nanowire at inlet Re = 207.7 and Re = 2077, the chance to get into contact with nanocatalyst is lower since the flow become thinner as the velocity is increased. Hence, it can be deduced that higher inlet fluid velocity is unfavorable for the reaction. Thus 78 ms^{-1} or Re = 20.77 was selected as the best inlet velocity.

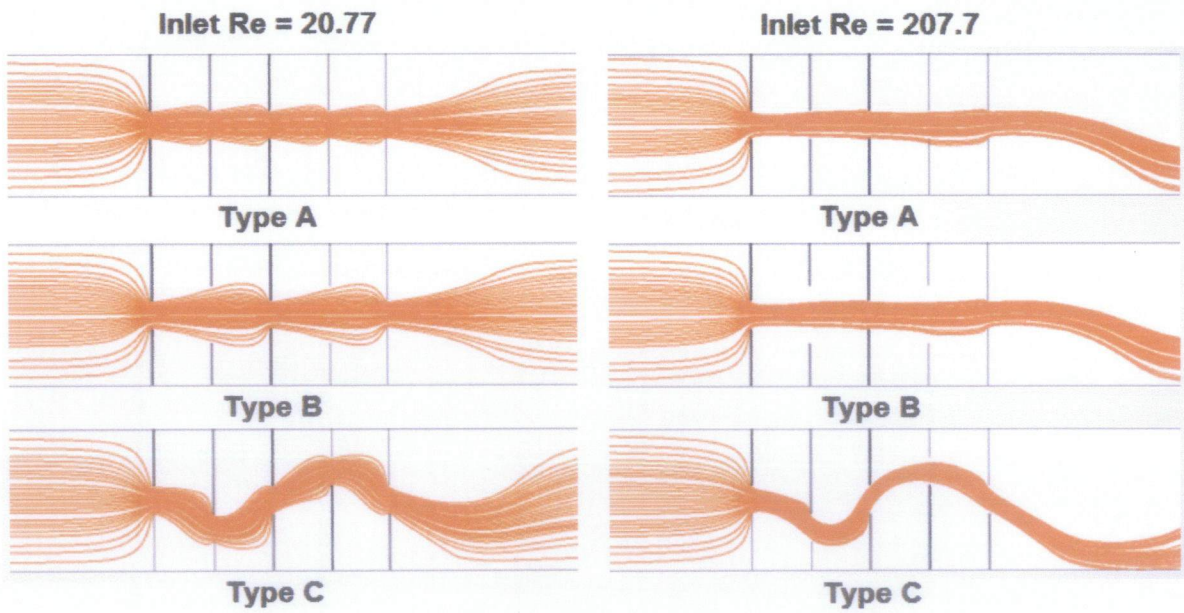


Figure 4-3 Comparison of tracked particle at different inlet velocity

4.1.3 Navier Stokes Equation

There are three main components of Navier Stokes equation to be explained regarding hydrodynamics of fluid. Pertaining to simulation results, only two components will be discussed mainly divergence and particle movement over pressure change.

$$\frac{dv}{dt} = \underbrace{-(v \cdot \nabla) \cdot v}_{\text{Divergence}} \underbrace{- \frac{1}{\rho} \nabla P}_{\text{Particle movement}} + \gamma \nabla^2 v + f$$

4.1.3.1 Divergence component

The divergence component affects the velocity of fluid. As a channel diverge, the fluid will spread out hence decrease the overall flow of the fluid particles and create a pressure drop. Fluid particles spreads out as a channel diverge hence decrease the overall flow of the fluid particles and create a pressure drop. Higher pressure drop within the nanowire structures decrease the volume of gas particle in that region henceforth lead to less gas particle volume fraction for reaction to occur at certain region.

Based on Figure 4-4, 4-5 and 4-6, the results for all inlet velocity and configuration show that the velocity of the gases increases slowly at the beginning. This is caused by the constant microchannel diameter at 5 μm. The fluid velocity increased when approaching the first pair of nanowire structure with the opening gap of 1 μm for all type of configuration. For Type A nanowire, the gap between two vertical nanowires was constant for all the five pairs hence the velocity of the fluid is quite the same throughout the flow. Consequently, referring to Figure 4-4, the Reynolds number of fluid passed through the nanowire keep at almost constant value, yet Type A configuration results in quite significant pressure drop about 370788 Pa. In Figure 4-5, Type B nanowire arrangement decreases the velocity of the gases when passed through 2 μm gap between the nanowire structures. Effect from this arrangement, it results in the lowest pressure drop compared to Type A and Type C which is 276450 Pa. The fluid velocity in Type C nanowire was barely changing except at the last point. However, this configuration creates the highest pressure drop compared to other arrangements with pressure drop 515653 Pa as shown in Figure 4-6.

Therefore, it is most favorable for gas particles to flow within Type B nanowire configuration. Pressure and Reynolds number graph also shows

that velocity inlet of 78ms^{-1} creates the lowest pressure drop compared to other inlet velocity.

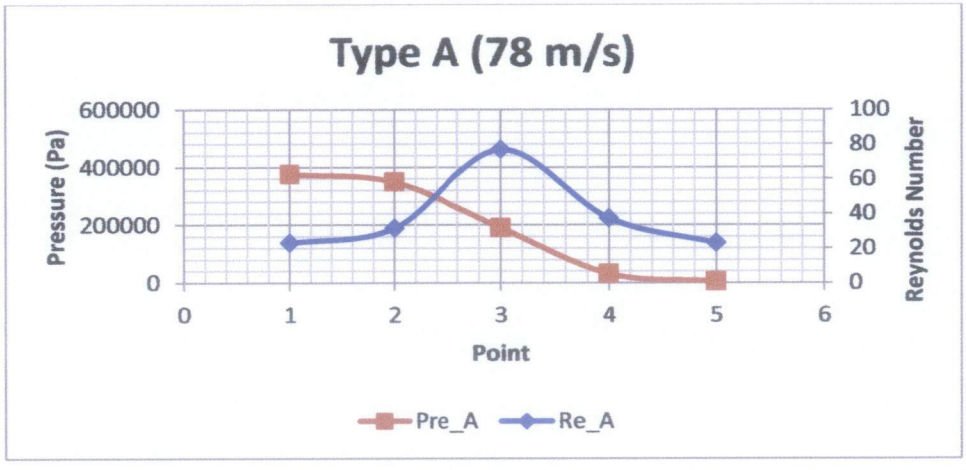


Figure 4-4 Pressure and Reynolds Number for Type A at inlet velocity 78 ms^{-1}

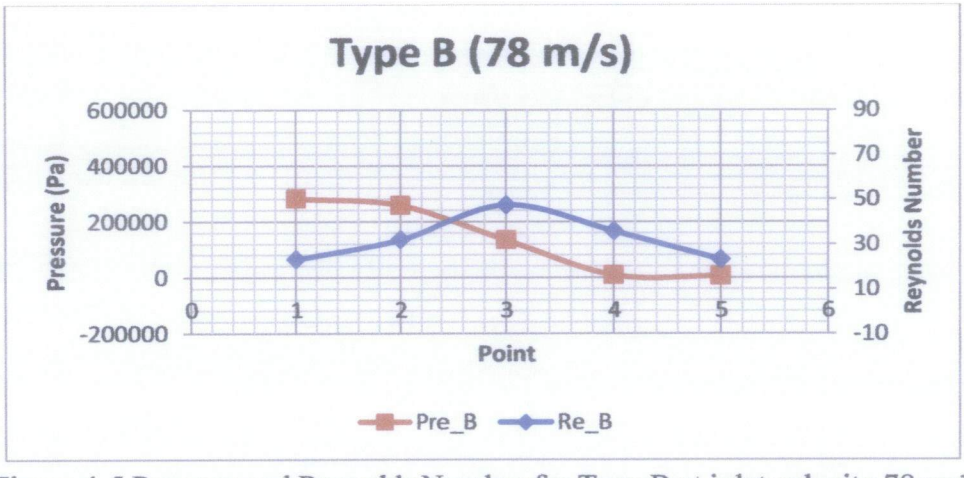


Figure 4-5 Pressure and Reynolds Number for Type B at inlet velocity 78 ms^{-1}

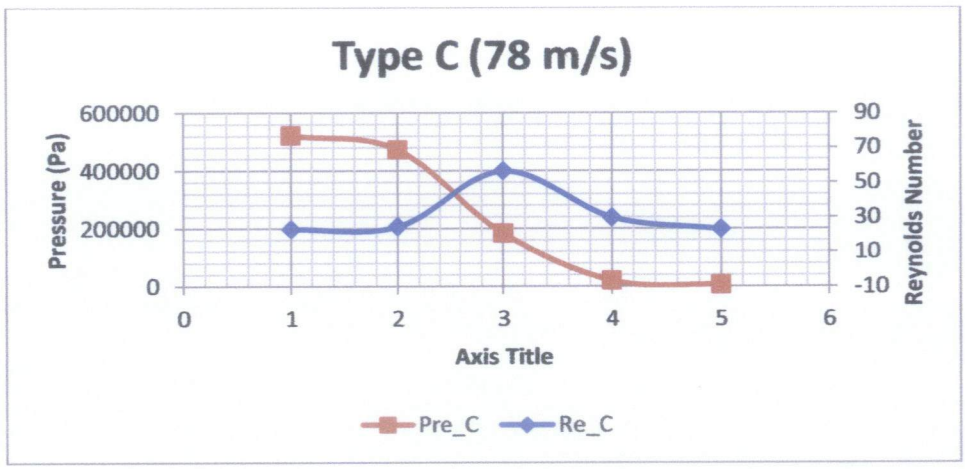


Figure 4-6 Pressure and Reynolds Number for Type C at inlet velocity 78 ms^{-1}

4.1.3.2 Particle movement due to pressure

Navier Stokes equation implies that particle tends to move away from a higher pressure region by travelling faster at high pressure point. Compared to a less dense fluid, it is harder for a denser fluid to move away from a high pressure region because it is restricted to its density that limits the movement of the particle from spreading or diffuse in all direction. The velocity of each gas varies when the particles reach the nanowire structures. However, good mixing is expected to occur when all the gases in the microchannel travel at the same velocity. According to Figure 4-7 and Figure 4-9, hydrogen particles travel faster than nitrogen and carbon dioxide within the nanowire structures. Apparently, hydrogen, nitrogen and carbon dioxide particles travel almost at the same velocity when Type B configuration is used as shown in Figure 4-8. Therefore, good mixing is expected to occur within Type B arrangement since all the three gases travel at the same velocity.

Following figures are the Reynolds Number graph of hydrogen, nitrogen and carbon dioxide at inlet velocity 78 ms^{-1}

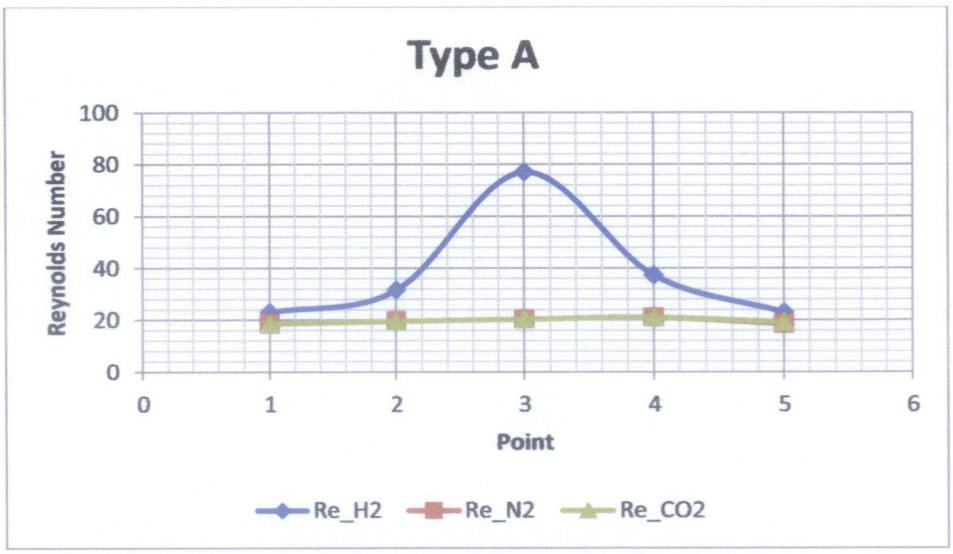


Figure 4-7 Reynolds number hydrogen for Type A

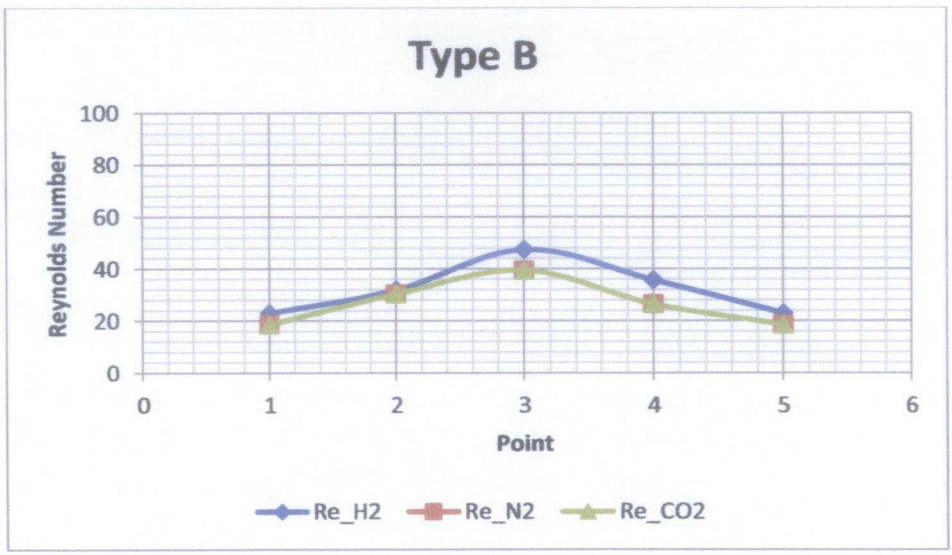


Figure 4-8 Reynolds number hydrogen for Type B

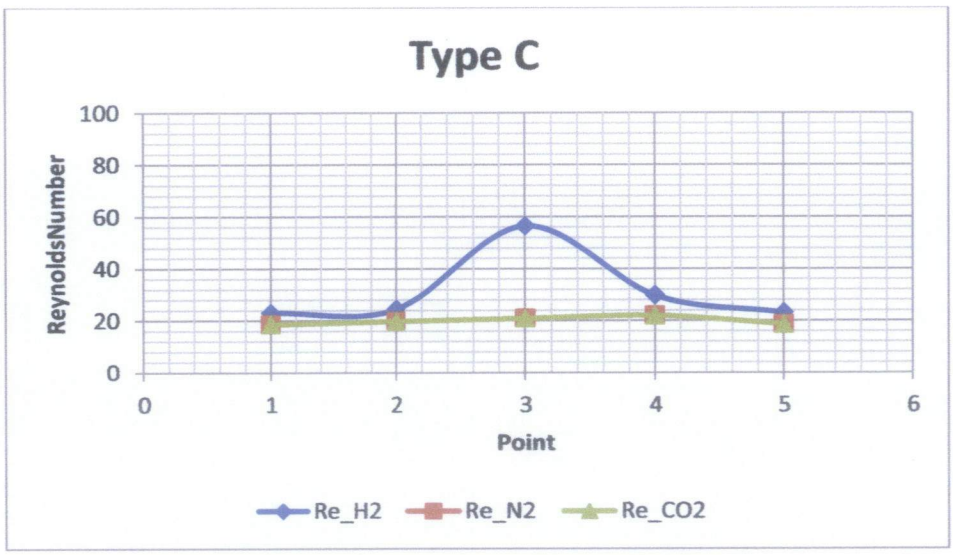


Figure 4-9 Reynolds number hydrogen for Type C

4.1.4 Continuity equation

Euler equation represents three sub equations which are conservation of mass (continuity), momentum and energy. Nonetheless, only continuity equation will be discussed in this project. In continuity equation, the mass rate of outlet particle is expected to be the same as the mass rate of inlet particle which means no particle left in the microchannel.

Illustration in Figure 4-10 shows the number of incomplete tracked hydrogen particle for nanowire configuration type C at inlet fluid velocity of 7800 ms^{-1}. Only 21 particles out of 28 tracked particle of hydrogen escaped from the microchannel. Seven of the tracked particle failed to pass through the nanowire structure. Meanwhile in Figure 4-11, all 28 tracked nitrogen particles were successfully passed through the nanowire structures of the same type and inlet fluid velocity that is type C at 7800 ms^{-1}. This is because, hydrogen particle have a lower density (0.08189 kg/m^3) compared to nitrogen molecule (1.138 kg/m^3), hence results in the hydrogen particle to disperse more in all direction compared to nitrogen molecule and stuck within the microchannel. Hence, it can be

assumed that Type C nanowire configuration at 7800 ms^{-1} is not favorable for hydrogen particles.

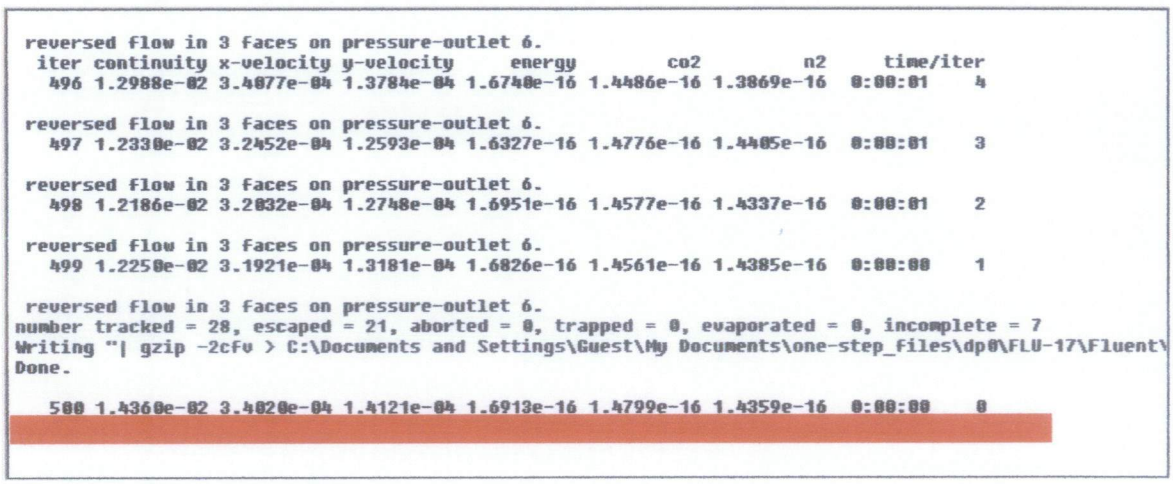


Figure 4-10 Particle track of hydrogen gas for Type C at inlet velocity of 7800 ms^{-1}

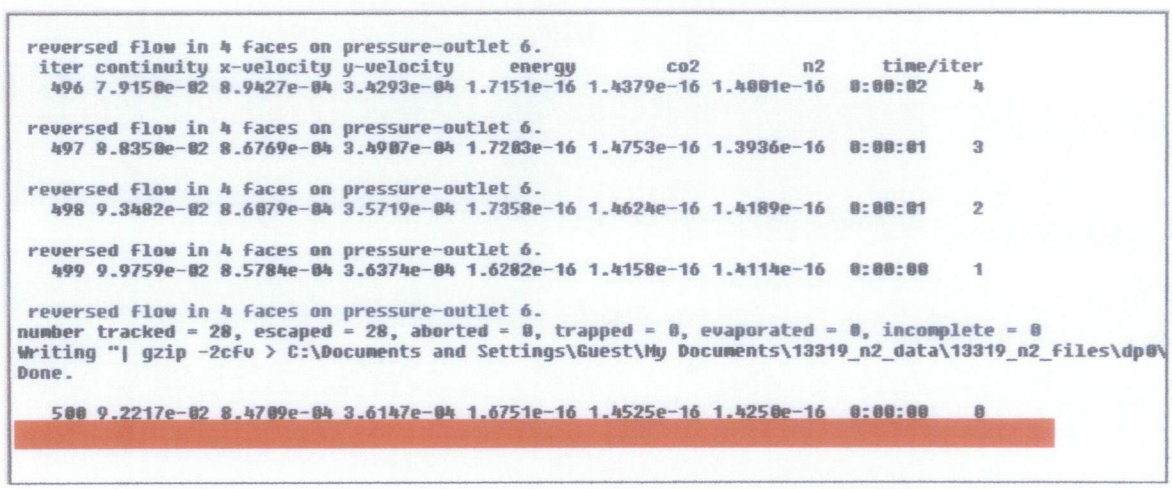


Figure 4-11 Particle track of nitrogen gas for Type C at inlet velocity of 7800 ms^{-1}

CHAPTER 5

CONCLUSIONS

In conclusion, the main objective of this study was achieved which is to develop a numerical simulation of one-step urea synthesis to predict the hydrodynamics interaction between molecular flow with nanocatalyst. Besides, the effect of nanowires configuration and fluid velocity on mixing efficiency also had been accomplished using suggested arrangement and specification.

Result from velocity vector give that Type C configuration is the most favorable design as the arrangement able to form turbulence pattern of the fluid which increase the chance for the gas particle to mix well. Nevertheless, result analyzed based on particle movement due to pressure proved that the highest mixing efficiency can be achieved by using Type B configuration since this arrangement allows hydrogen, nitrogen and carbon dioxide to travel in the microchannel at almost the same velocity. Besides, Type B configuration results in the lowest pressure drop among other suggested configuration. Referring to results from particle track, the gases get into contact with the nanocatalyst at most when the inlet fluid velocity is at 78 ms^{-1}. Based on pressure and Reynolds number graph for overall tested fluid inlet velocity, it come out that 78 ms^{-1} is the best velocity to be introduced into the microchannel because pressure drop is the lowest at this velocity.

Despite the fact that hydrodynamics simulation was successfully been carried out, the geometry model of the microreactor was done in 2 dimensional model. In addition, there was no study of meshing specification being conducted, hence the quality of the

result could be less accurate. It is recommended to construct the geometry and body of the microchannel in 3 dimensional image and further improvement on meshing quality might be required to construct a better simulation and solution. Besides, enhancement on simulation setup during solver phase is necessary in order to observe the most efficient configuration and specification.

REFERENCES

Abd Razak, J., Sufian, S., Zilati K., Yahya ,N., (2011) Synthesis of α-Fe_2O_3 Nanorods / Nanowires through Oxidation-Diffusion Growth Mechanism, One Baja Colloqium

Chen, C., Chang C. C., (2008) A combined active/ passive scheme for enhancing the mixing efficiency of microfluidic devices, Journal of Chemical Engineering Science 63,3081-

Chueh, Y-L., Lai, M-W., Liang, J-Q., Chou, L-J. and Wang, Z.L.: Adv. Func. Mater. 16, 2243-2251 (2006)

Fu, Y.Y., Wang, R.M., Xu, J., Chen, J., Yan, Y., Narlikar, A.V. and Zhang, H. (2003): Chem. Phy.Lett.379, 373-379

H Meessen, J., (2012) Urea, Ullmann's Encyclopedia of Industrial Chemistry

Hsieh,S, Huang,Y(2008) Journal of micromechanical.microengineering 18, 1-11.

J.M. Modak, (2002) Haber Process for Ammonia Synthesis

Lockman, Z., Ismail, S., (2011) Formation of Oxide Nanotubes: A Review, One Baja Colloqium, 21-

Perry, R. & Chilton, C. (1973). *Chemical engineer's handbook.* New York: McGraw-Hill.

PotashCorp. Nitrogen Market - Overview. Retrieved on June 22, 2013 from http://www.potashcorp.com/overview/nutrients/nitrogen/overview/world-uses-and-top-producers

Roberge, D., Ducry, L., Bieler, N., Cretton, P., Zimmermann, B. (2005) Chemical Engineering Technology 28 No. 3

Schlichting H. (1979), Boundary-Layer Theory, 7th Edition, McGraw-Hill.

Watts, P., Wiles, C., (2007) Recent advances in synthetic micro reaction technologyChem. Commun., 443-467

Wilke C.R. (1950). A Viscosity Equations for Gas Mixtures. *The Journal for Chemical Physics*, 18 (4), 517-519.

Yahya, N. (2011). High Ammonia Yield Using Magnetic Induction Method. Retrieved from http://www.allacademic.com/meta/p94581_index.html

Yahya, N., Hussain, T., (2011) Enhance Urea and Ammonia Yield by Using Magnetic Induction Method, One Baja Colloqium, 7-9