Effect of Different Temperature Using Safety Analysis for Power to Methanol Production Plant

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***Abstract*— Global warming has become worst for the past 50 years due to the greenhouse effect. Carbon dioxide is the most important greenhouse gases that contribute to global warming. This emission of the CO_2 need to be reduces in order to preserve the Earth. There are strategies to reduce the emission of CO_2, for examples Carbon Captured and Storage (CCS) and Carbon Captured and Utilization (CCU). The example of CO_2 utilization is as the raw material to produce methanol. This methanol can be produced when CO_2 react with hydrogen where the H_2 can be produce in electrolysis of water. The limitation of this plant is that researchers had done the research on CO_2 captured producing methanol but they only focusing on the conversion and selectivity without consider the risk that might occur. Therefore, in this research project, the objectives are to design and simulate power to methanol production plant using different temperature in the reactor and to analyze the risk on the power to methanol production plant using different temperature in the reactor. The plant is designed using Aspen Hysys and the risk that being analyzed is toxicity, vapor cloud explosion and flash fire using Quantitative Risk Assessment (QRA). Threat zone were generated by ALOHA and being export to the MARPLOT to observe the area affected by the case study. It is found that plant 3 with pressure 442 bar and temperature 210°C has the highest risk and the safest plant is plant 2 with pressure 76 bar and 280°C.**

Keywords*— *Quantitative Risk Assessment, Carbon Captured, Methanol Plant.

I. INTRODUCTION

Global temperature has increase rapidly for the past 50 years [1]. By definition, global warming means rises of Earth average atmospheric temperature makes the changes of the climate due to the greenhouse effect where greenhouse effect means heating phenomenon of the atmospheric that trap heat radiating from earth towards the space. Water vapor, carbon dioxide, methane and nitrogen oxide are the gasses that act as thermal blanket for the Earth absorbing heat and warm the Earth surface [2].The most important component of the greenhouse gases is the carbon dioxide.

In 2015, at the United Nations Climate Change Conference held in Paris, with the aim to reduce the temperature of Earth where the increase should not more than 2°C, 195 countries agreed on a plan to decreased the emissions of CO_2 and other greenhouse gases [3]. As we burn fossil fuels, the concentration of CO_2 is increasing by years which will warm the planet and enhances the natural greenhouse effect [3]. In 2013, 58% of the human source of CO_2 is contributed by the burning of fossil fuels. Not only burn of fossil fuels, there is other source of CO_2 such as cement production and deforestation which comes from human activities. There are also natural sources of CO_2 that are decomposition, ocean release and respiration. Since the Industrial Revolution, the atmospheric concentration of CO_2 has been rose up extensively and reached the dangerous level [4]. Although the human source of CO_2 is much smaller than the natural source, it has troubled the natural balance by adding extra CO_2 to the atmosphere.

Solution for this problem had been found that is energy efficiency renewable energy production and CO_2 capture and storage (CCS). CCS is an effective strategy to reach CO_2 mitigation targets while sustaining the source of energy supply. To make the CCS practicable, economic methods to capture CO_2 from flue gases of power plants and also to store the captured CO_2 is needed [5]. In order to capture the CO_2, there must be methods of doing it. One of the most profound method is chemical absorption because of the availability of the solvent and techniques that had been established [6]. After captured the CO_2, it is then being transport to the suitable site for storage. Some of the possible location to stored CO_2 is deep oceans, depleted oil reservoir and deep saline aquifers.

Other than CCS, there is one more method that is Carbon Captured and Utilization (CCU). In CCU, when the CO_2 has been captured, it needs to be utilized. One of the CO_2 utilization is producing methanol. Methanol is an important chemical in the industry where it can further produce other chemical such as formaldehyde and acetic acid which are used to produce product for instance washer fluid, solvents and subfloors. In this production, methanol is produced by hydrogen which comes from water electrolysis and CO_2 from flue gas which had been captured [7]. The study of methanol plant that used CO_2 captured as the raw material has been conducted but it only focusing on the selectivity and conversion without consider the safety issues. The purpose of this paper is to design and simulate power to methanol production plant using different temperature in the reactor and to analyze the risk on the power to methanol production plant using different temperature in the reactor.

Safety is a very important study in order to build plant. In this research project, safety is evaluate using Quantitative Risk Assessment (QRA). The QRA permits the quantification of the current risks of an installation in order to deliver data for their acceptance. It also helps to contribute decisions and arrangement of choices in order to reduce unacceptable ones. Not only during use, the risk also need to be evaluated during the transport, manipulation and storage of hazardous materials during the manufacture. It shows the risk caused by some activity and gives related evidence about the acceptability of the activity to the competent authorities [8].

Used of CO_2 in the production need a proper safety study since CO_2 can be hazardous where it exhibits a level of toxicity that may lead it to have major accident [9]. To maintain the acceptable level of risk, legislative controls have been built up for those who could be harmed by it. CO_2 is usually considered a threat to life through asphyxiation when it replaces the oxygen in air thus drop the oxygen to dangerously low levels. Dangerous Toxic Load (DTL) has been established by Health and Safety Executive (HSE) to measure the toxicity of substances where it calculates the exposure condition in terms of concentration and duration of exposure. In this appraisal, it describes the specified level of toxicity (SLOT) and the significant likelihood of death (SLOD). SLOT has been defined by HSE where it will cause severe pain to nearly everyone in the area, medical attention was required by the exposed population, continued treatment was required by the people who seriously injured and can cause 1-5% lethality rate in a certain concentration over a particular time from single exposure. For SLOD, HSE has defines it as single exposure over a certain time that will cause 50% lethality rate.

There are many incidents of natural and industrial releases of CO_2 that cause injuries and death due to CO_2 inhalation. For instance, in 2008, Monchengladbach, Germany had release approximately 15 tonnes of CO_2 from a fire extinguishing installation by accident. The released CO_2 was not enclosed by the building due to spontaneous failure of door seals, thus it spread outside where there were very still air conditions. 107 people were woozy and no death occurs [10].

For hydrogen, it is odorless, colorless and tasteless therefore, when it leaks, human sense will not detect it. In order to detect the leak, industry usually will use hydrogen sensor to maintain the safety. Although other natural gas has the same properties that is odorless, colorless and tasteless, industry usually add mercaptan that is sulfur-containing odorant, to make it detectable by people. Researchers still finds the suitable detector for the hydrogen so that it can be trace by human [11].

In order for fire to happen, the presence of ignition source and oxidizer such as oxygen must be present at the same time [11]. Upon leaving the pipeline or escape from leaking joint, ignition will occur when the hydrogen comes into contact with the dust particles. Other than that, fine water droplets also can trigger the ignition. Explosion may occur if the hydrogen cloud were ignites in form of deflagration or detonation [12].

There are accidents that occur due to hydrogen that is Hindenburg disaster occur on May 1937. 200,000 m^3 of hydrogen were release thus ignited in less than a minute. The deaths recorded were 35 out of 97 passengers. The ignition source were not known but the combined combustion occur between hydrogen and the coating of the shell that are butyrate, iron and aluminium oxide [12].

Methanol on the other hand is also a dangerous chemical with significant toxic, flammable and reactive properties that can create harmful effects on human health and the environment when not appropriately controlled. It can easily enter the body through many routes. When it in contact with eye, it can cause burning sensation followed by tearing, redness and swelling. Other than that, symptoms that can be feel when methanol had exposed are headache, dizziness, vomiting, severe abdominal pain, back pain and difficult to breathe. Blindness and death can occur when exposed to high doses of methanol.

When involves in methanol handling, it needs a controlled environment. Failure to control the dangers associated with a little amount of methanol can be a problem and losing great control quantities can lead to disaster. Methanol can easily ignite since it is a flammable liquid and can explode in air. Methanol containers are subjected to boiling liquid expanding thus when heated externally, vapor explosion can occur. It is miscible in water where it can retain its flammability even at dilute solution. A solution can be considered as a flammable liquid when 25% of volumes are methanol while the rest are the water. In additional, methanol can burns with nonluminescent flame where the flame is invisible in bright sunlight. This is a very important issue in the implication of firefighting.

One of the examples of accident occurs due to methanol are in the Southern Energy Co. facility in Shelbyville, on the November 2013, the internal larger vat had overflowed caused the methanol vapors to leak into the air. This occurs when the tanker truck tries to transfer methanol into an external storage tank. The vapor ignited thus cause the initial explosion at the facility and spread underneath of the tanker truck. The tanker truck contained 6,000 gallons methanol thus sparking a secondary explosion. In this accident, a man was burns on more than half of his body [13].

Methanol is a flammable gas which can easily ignited where it can cause fire and also explosion to occur. Therefore, safety management need to monitor the condition of methanol so that no situation can cause methanol to be release. Methanol has lower flammability limit and upper flammability limit of 6% and 36% respectively in air, thus, fire and explosion can be avoided by avoiding those condition. NW Innovation Works had conducted the Quantitative Risk Assessment (QRA) where they conclude that the suitable operating condition and dimension for methanol loading line is 87 psig for pressure with 16 inch pipe diameter and 1000 feet pipe length [14].

II. METHODOLOGY

Three plant were simulated using Aspen Hysys with different condition before entering the reactor. The condition for plant one is 442 bar and 280 ^oC, plant two is 76 bar and 280 ^oC and plant three is 442 bar and 210 ^oC.

A. Process Description

In order to produce methanol in this plant, one step reaction that is hydrogenation of CO_2 is employed where the equation is as in equation below. The raw material that is CO_2 is the CO_2 that had been captured from the flue gas of power plant by post-combustion method while H_2 is from the electrolysis of water where the water molecule is break down into hydrogen and oxygen.

$$CO_2 + 3H_2 \rightarrow CH_3OH + H_2O$$

The catalyst that used in this reaction is $Cu/ZnO/Al_2O_3$. The catalyst will enhance the reaction without any reaction occurs on it. The plant is as in the Figure 1. The feed stream of CO_2 is 2831 kg/hr with pressure at 1 bar and temperature at 25 °C while H_2 fed is 386.1 kg/hr with pressure at 30 bar and temperature is the same as the CO_2 stream. With a series of compressors and intercooling, the CO_2 is compressed to 76 bar while H_2 is compressed in a single stage to 76 bar. The two gas that are CO_2 and H_2 are mixed in mixer 1 (MIX1) and will further mixed with recycle stream in mixer 2 (MIX2). The mixture is then heated in the heat exchanger 4 (HX4) to and further heated in (HX5) to 280 °C and will flow into fixed bed reactor (R1). The reactor is packed with the fixed bed of 1431.6 kg of catalyst. The product leaving the reactor is then divided into two streams in the splitter (DIV1) where 60% of the stream are used to heat the fresh feed in the (HX4) while the other 40% will be heated in (HX7) for it to heat the feed of the distillation column in heat exchanger 6 (HX6) [15].

In the mixer 3 (MIX3), the two streams are re-mixed and cooled to 35 °C by heat exchanger 8 (HX8). The product that is methanol and water are then flow into the knock-out drum (KO1) to be separated from the unreacted reactant. To minimize the accumulation of inerts and by-product in the reaction loop, 1% of the unreacted gases that had been separated will then being purged while the others being recycle into the mixer 2 (MIX2). The liquid stream leaving the KO1 is then being expanded to 1.2 bar through series of valves (VLV1 and VLV2). The flash tank (TFKL1) is used to further remove the remaining gases nearly complete. In heat exchanger 6 (HX6), the liquid stream being heated to a temperature of 80 °C and will then send to distillation column (DT1). The distillation column is used to purify the product that is methanol where it has 57 stages with the feed is fed at stage 44. The reflux ratio is 1.2. The product methanol left the distillation column in gas phase at 64 °C and 1 bar while the bottom product that is water left at 102 °C and 1.1 bar [15].

B. *Properties of Methanol*

Methanol, or can be called methyl alcohol, is made up of one carbon, four alcohols and one oxygen with the formula CH3OH. It is the simplest form of alcohol from a group of organic chemicals. Methanol has the physical structure as liquid that is colorless, volatile, flammable and soluble in water.

The molecular weight of the methanol is 32.04 g/mole and it is high flammability where it can be ignited under almost all ambient temperature conditions. It has the alcoholic smells with melting point of -97.6°C and boiling point of 64.5 °C that is under the boiling point of water. The pH value is 7.2 which makes it slightly alkaline chemical and with density 0.79 g/m3 at 25°C. The autoigniton temperature is 464 °C where it is the lowest temperatue in the normal atmosphere that ignites spontaneously without external source of ignition. The heat of combustion and heat of vaporization at 25°C are 726.1 kJ/mole and 37.34 kJ/mole respectively. Heat of combustion is the energy released in form of heat when the substance undergoes complete combustion with oxygen while heat of vaporization is the measure of heat that need to be absorbed if a certain quantity of liquid is vaporized at a constant temperature. Flammability limit is the concentration where the molecule can cause fire in the presence of ignition source. The lower and upper flammability limit of methanol is 6 volume % and 36 volume % respectively.

Methanol is a very reactive substance. According to Material Safety Data Sheet (MSDS), methanol is one of the toxic substances when exposed at high concentration. Explosion can occur when it mixes with concentrated sulfuric acid and concentrated hydrogen peroxide. When methanol reacts with hypochlorous acid in water solution or in carbon tetrachloride solution it gives methyl hypochlorite, substance that may explode when exposed to sunlight or heat [16]

C. *Propertied of Carbon Dioxide*

Carbon dioxide is the molecule that occurs naturally which consist of a carbon atom and two oxygen atoms with the formula CO_2. CO_2 is a colorless and odorless molecule with molecular weight of 44.01 g/mole. It is a non-flammable molecule where it is stable under atmospheric condition. CO_2 can be used to eradicate the fire where it can take away the oxygen element of the fire triangle. The melting point and boiling point of CO_2 are -56.56 °C and -78.46 °C respectively. The density and vapor pressure of CO_2 at 20 °C are 1.84 g/L and 56.5 atm respectively. CO_2 react vigorously with some substance such as ammonia and amines. Carbonic acid can be produced when CO_2 dissolve in water which can lead to corrosion effect on carbon steel and few non-ferrous metals.

In the gas cylinder, CO_2 is in liquid phase where the pressure in the cylinder is approximately 57 bar at 20 °C. Gaseous CO_2 will be produced when the CO_2 is remove from the cylinder where the outlet pressure is less than 5.2 bar. When it has been withdrawn, 1 kg of liquid CO_2 will expand to about 550 litres of gas at atmospheric pressure. It is considered as a risk to transfer CO_2 from one cylinder to another. Certain requirement needs to be filled by the cylinder so that they can tolerate with the pressure. Only the trained personnel can determine whether the cylinder is appropriate to be used. 0.75 kg of CO_2 per litre of cylinder volume is the maximum comprise in a cylinder. If an overfilled CO_2 cylinder exposed to sunlight, it can burst out.

CO_2 cylinder that usually made up of carbon steel must be protected from water or aqueous fluid such as beer and lemonade. This is because, when the CO_2 react with water, it will produce carbonic acid that can cause corrodes. It is important to checked water presence in the cylinder before filling the CO_2 in it [17].

D. *Properties of Hydrogen*

Hydrogen is the simplest chemical molecule. It consists of two hydrogen atom that bonded together where the formula is H_2. Hydrogen is a colorless and odorless gas that has a molecular weight of 2.02 g/mole. It is highly flammable and has the autoignition temperature of 500 °C. The melting point is -259.2 °C while boiling point is -252.76 °C. The lower flammability limit and upper flammability limit are 4 volume % and 75 volume % respectively.

Since it is highly flammable, hydrogen need to be keep away from any heat, sparks and open flame to ensure that it will not ignites. In order to moves hydrogen cylinders, do not drag or roll the cylinder instead use an appropriate hand truck. Make sure that the hydrogen cylinder has carefully connected with the utilization equipment before open the valve. This is to make sure that the hydrogen gas will not escape to the atmosphere since it is very light molecule that can dispersed easily [18].

E. *Safety Equation*

1) *Toxic Release and Dispersion Model*

To evaluate the concentrations downwind of a release in which the gas is mixed with fresh air to the point that the resulting mixture, neutrally buoyant dispersion models can be used. There are two types of neutrally buoyant vapor cloud dispersion models that are commonly used that are the plume and the puff models. The steady-state concentration of material released from a continuous source is the plume model while puff model defines the temporal concentration of material from a single release of a fixed amount of material [19].

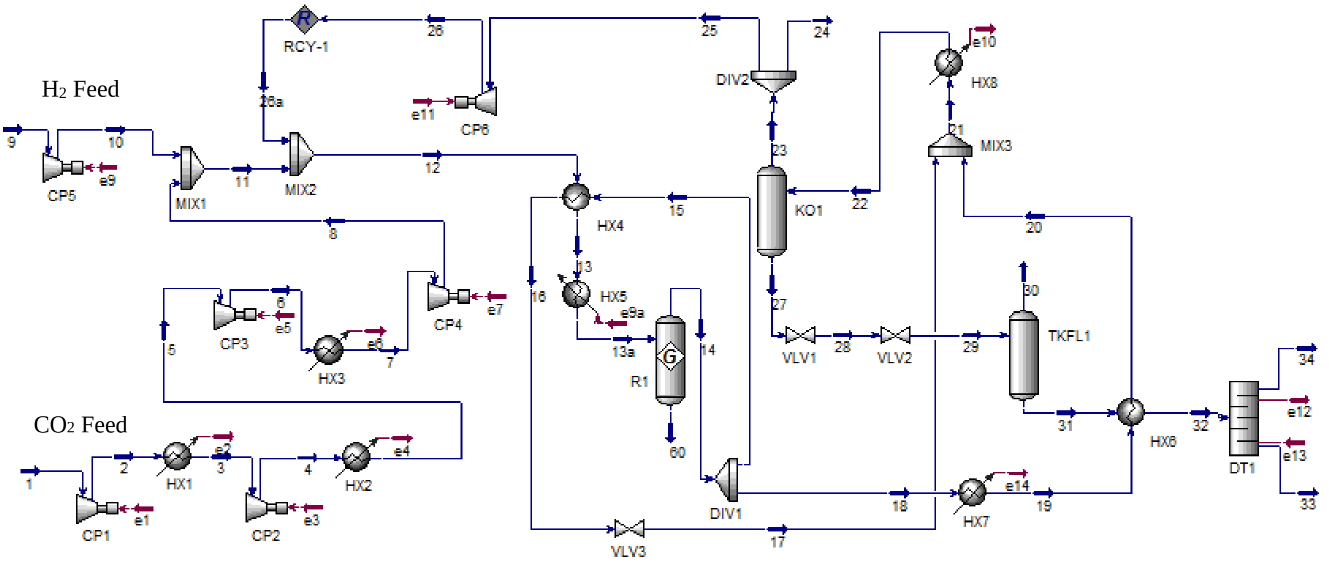

Figure 1. Process Flow Diagram of Methanol Plant

The equation (1) is the basis for the dispersion model where it can solve variety of cases. For this model, the coordinate system was used where x axis is the centerline directly downwind from the release point and is rotated for different wind directions, y axis is the distance off the centerline, and the z axis is the elevation above the release point. [19]. From equation (1), u_j is the velocity of the air where subscript j represents the summation overall coordinate directions x, y, and z and C is the concentration of material resulting from the release.

$$\frac{\delta C}{\delta t} + u_j \frac{\delta C}{\delta x_j} = \frac{\delta}{\delta x_j}\left(K_j \frac{\delta C}{\delta x_j}\right) \tag{1}$$

From the equation (1), it will derive to specific case to be calculated. For this paper, one case of puff and one case of plume will be study. The case of puff studied is puff with instantaneous point source at ground level, coordinates fixed at release point, constant wind only in x direction with constant velocity, u as in equation (2) while plume studied is plume with continuous steady state source at ground level and wind moving in x direction at constant velocity (3).

$$\langle C\rangle(x,y,z) = \frac{Q_m^*}{\sqrt{2}\pi^{3/2}\sigma_x\sigma_y\,\sigma_z} \tag{2}$$

$$C(x,y,z) = \frac{Q_m}{\pi\sigma_y\,\sigma_z u} \tag{3}$$

2) *Vapor Cloud Explosion*

Reaction front that moving outward from the ignition source preceded by a shock wave or pressure front will results in the explosion of a dust or gas. Pressure wave continues its outward movement even when the reaction front terminates, after the combustible material is consumed. A blast wave is composed of the pressure wave and subsequent wind. Most of the damage is caused by the blast wave [19]. The overpressure will cause explosion to occur. The overpressure can be can be predicted using equivalent mass of TNT and the distance from point of explosion, ras in equation (4) thus the overpressure can then be calculated using equation (5).

$$\mathrm{z_e} = \frac{\mathrm{r}}{\mathrm{m_{TNT}}^{\frac{1}{3}}} \tag{4}$$

$$p_s = \frac{p_o}{p_a} = \frac{1616\left[1+\left(\frac{z_e}{4.5}\right)^2\right]}{\sqrt{1+\left(\frac{z_e}{0.048}\right)^2}\sqrt{1+\left(\frac{z_e}{0.32}\right)^2}\sqrt{1+\left(\frac{z_e}{1.35}\right)^2}} \tag{5}$$

3) *Flash Fire*

Fire and explosion are the accidents that commonly occur in the chemical plant where the most common source is organic solvents. In order for fire to occur, three elements need to be exist simultaneously that are fuel, oxidizer and ignition source. From the equation (6) below, I_e is the effective radiation intensity (W/m2), Q_m is the mass release (kg), r is distance from source of fire (m).

$$I_e = \frac{828 \times Q_m^{0.771}}{r^2} \tag{6}$$

4) *Probit Analysis*

Exposure such as exposed to heat, pressure, radiation, impact and sound can be compute using Models for Dose and Response. For a single exposure, probit method can be used. The probit can be seen in the Table 1. Table 2 gives variety of probits equation for variety of cases that probably could occur. This table could be used to compute the probit, thus knowing the percentage from the Table 1. Equation below used to calculate the value of probit (Y) from the exposure as in the Table 2.

$$Y = k_1 + k_2 \ln V \tag{7}$$

Table 1:Transformation from Percentages to Probits.

%	0	1	2	3	4	5	6	7	8	9
0	–	2.67	2.95	3.12	3.25	3.36	3.45	3.52	3.59	3.66
10	3.72	3.77	3.82	3.87	3.92	3.96	4.01	4.05	4.08	4.12
20	4.16	4.19	4.23	4.26	4.29	4.33	4.36	4.39	4.42	4.45
30	4.48	4.50	4.53	4.56	4.59	4.61	4.64	4.67	4.69	4.72
40	4.75	4.77	4.80	4.82	4.85	4.87	4.90	4.92	4.95	4.97
50	5.00	5.03	5.05	5.08	5.10	5.13	5.15	5.18	5.20	5.23
60	5.25	5.28	5.31	5.33	5.36	5.39	5.41	5.44	5.47	5.50
70	5.52	5.55	5.58	5.61	5.64	5.67	5.71	5.74	5.77	5.81
80	5.84	5.88	5.92	5.95	5.99	6.04	6.08	6.13	6.18	6.23
90	6.28	6.34	6.41	6.48	6.55	6.64	6.75	6.88	7.05	7.33
%	0.0	0.1	0.2	0.3	0.4	0.5	0.6	0.7	0.8	0.9
99	7.33	7.37	7.41	7.46	7.51	7.58	7.65	7.75	7.88	8.09

Table 2: Probit Correlations for a Variety of Exposures (The causative variable is representative of the magnitude of the exposure.)

Type of injury or damage	Causative variable	Probit parameters k_1	Probit parameters k_2
Fire[1]			
Burn deaths from flash fire	$t_e I_e^{4/3}/10^4$	−14.9	2.56
Burn deaths from pool burning	$tI^{4/3}/10^4$	−14.9	2.56
Explosion[1]			
Deaths from lung hemorrhage	p^o	−77.1	6.91
Eardrum ruptures	p^o	−15.6	1.93
Deaths from impact	J	−46.1	4.82
Injuries from impact	J	−39.1	4.45
Injuries from flying fragments	J	−27.1	4.26
Structural damage	p^o	−23.8	2.92
Glass breakage	p^o	−18.1	2.79
Toxic release[2]			
Ammonia deaths	$\Sigma C^{2.0}T$	−35.9	1.85
Carbon monoxide deaths	$\Sigma C^{1.0}T$	−37.98	3.7
Chlorine deaths	$\Sigma C^{2.0}T$	−8.29	0.92
Ethylene oxide deaths[3]	$\Sigma C^{1.0}T$	−6.19	1.0
Hydrogen chloride deaths	$\Sigma C^{1.0}T$	−16.85	2.0
Nitrogen dioxide deaths	$\Sigma C^{2.0}T$	−13.79	1.4
Phosgene deaths	$\Sigma C^{1.0}T$	−19.27	3.69
Propylene oxide deaths	$\Sigma C^{2.0}T$	−7.42	0.51
Sulfur dioxide deaths	$\Sigma C^{1.0}T$	−15.67	1.0
Toluene	$\Sigma C^{2.5}T$	−6.79	0.41

t_e = effective time duration (s)
I_e = effective radiation intensity (W/m^2)
t = time duration of pool burning (s)
I = radiation intensity from pool burning (W/m^2)
p^o = peak overpressure (N/m^2)
J = impulse (N s/m^2)
C = concentration (ppm)
T = time interval (min)

5) *Area Affected by Case Study*

ALOHA and MARPLOT software will be used in this study to observe the area that will be affected by the case study. This plant is suggested to be built in Seri Manjong, Perak, near the Sultan Azlan Shah Power Station. The location was chosen because the carbon will be captured from this power plant as the raw material to be used. The location is as in the Figure 2.

Based on the information about the chemical release, the details will enter in the ALOHA and ALOHA will generate the threat zone estimates for various types of risk. The threat zone will then being export to the MARPLOT to observe the affected area.

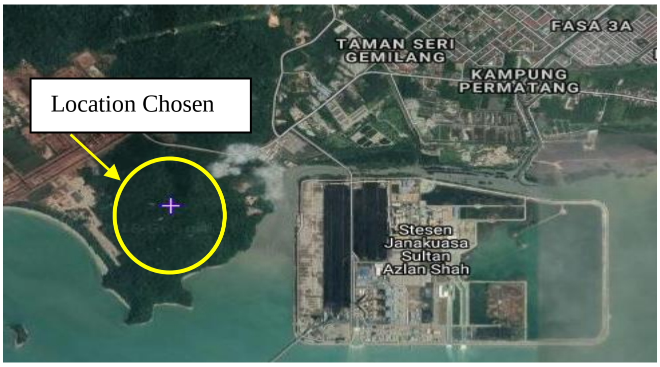

Figure 2. Location Chosen to Built the Plant

III. RESULTS AND DISCUSSION

A. *Simulation of Three Plant with Different Condition*

There are three plants simulated using Aspen Hysys in this studied. The first plant with pressure 442 bar and temperature 280 ^oC, followed by second plant with pressure 76 bar and 280 ^oC and the third plant with pressure and temperature of 442 bar and 210 ^oC respectively. All the condition is specific at inlet of the reactor. Series of compressor and heat exchanger are used to varies the pressure and temperature. The condition of each plant is tabulated in Table 3.

Table 3: Condition of Plant Simulated

	Plant 1	Plant 2	Plant 3
Raw Material (kg/hr)	H_2: 386.1 CO_2: 2831.4	H_2: 386.1 CO_2: 2831.4	H_2: 386.1 CO_2: 2831.4
Temperature Before Reactor (^oC)	280	280	210
Pressure Before Reactor (bar)	442	76	442
Methanol Produced (kg/hr)	1896	1878	1875
Purity of Methanol (%)	99.92	99.4	99.9

B. *Toxicity of Carbon Dioxide*

Equipment could release toxic material and this toxic will spread in the environment dangerously during an accident. In this plant, the toxic material is carbon dioxide. The possible release of carbon dioxide during accident is in the pipeline through the leaking part. To study this, the concentration of carbon dioxide is calculated based on the different diameter of the leaking hole at the pipeline that is 10 mm, 50 mm and full rupture of the pipeline. For the 10 mm and 50 mm leaking, it is assumed to be continuous flow as can be seen in plume model while for the full rupture, the release is instantaneous that can be seen in puff model.

CO_2 is considered as a danger to life through asphyxiation where it can replace oxygen in the air that could drop the oxygen level to the lowest limit. It is typical for the CO_2 to be in blood but at low concentration but at high concentration, it is poisonous to life. The symptoms that human can feel when exposed to CO_2 such as headaches, respiratory and heart rate rises, dizziness and more. When the CO_2 inhaled increase, it will trigger respiratory, cardiovascular and central nervous system in a poor way as the blood become acidic where death can occur.

By assuming the diameter of leaking hole is 10 mm, 50 mm and full rupture of the pipe, the rate of mass release rate can be obtained thus the concentration of CO_2 release can be determine. When the pipe leak, the CO_2 will be dispersed in the environment since it exists in gas phase. In this paper, the area that is studied is at 100 m distance from the source of CO_2.

To calculate the concentration of CO_2 release, the mass release rate for plume model need and mass release for puff model need to be calculated first. The mass release rate is calculated based on the diameter of the leak occur. The result for plume model is in Table 4 for 10 mm leak and Table 5 for 50 mm, the highest mass release rate for 10 mm leak is in plant 3 that is 7680.502 g/s while for 50 mm leak was also in plant 3 that is 192057.993 g/s. To calculate the mass for instantaneous release, the volume and the density in the pipeline are used. For puff model, the highest mass release was also occurred in plant 3 that is 320979.85 g. Table 6 shows the result for puff model.

The concentration can be determined once the mass release rate and mass release are calculated. The highest concentration for 10 mm and 50 mm leak are 6.398 ppm and 159.976 ppm respectively while for full rupture of the pipeline, the highest concentration is 28.420 ppm. From the concentration, the probit can be determined. Probit is used to identify the percentage of fatality that will occurred. For these three plants, all the probit gives negative value which indicate that 0% of fatality occur. This means that no death would occur when the CO_2 pipeline leak. Even though no death occur, human is believed to feel the symptoms of CO_2 release since the concentration of CO_2 at the time is higher than usual. The concentration of CO_2 that will be toxic to human is 60,000 ppm [20] thus, for this study, the concentration of CO_2 will not cause any death to occur.

Table 4: Result for 10 mm diameter rupture of the pipeline

	Q_M (g/s)	Concentration (ppm)	Probit	Fatility (%)
Plant 1	7178.09	5.979	-70.590	0
Plant 2	1247.84	1.039	-84.727	0
Plant 3	7680.50	6.398	-70.043	0

Table 5: Result for 50 mm diameter rupture of the pipeline

	Q_M (g/s)	Concentration (ppm)	Probit	Fatility (%)
Plant 1	179494.8	149.512	-44.580	0
Plant 2	31203.5	25.991	-58.716	0
Plant 3	192057.9	159.976	-44.033	0

Table 6: Result for full rupture of the pipeline

	Concentration (ppm)	Probit	Fatility (%)
Plant 1	24.822	-59.088	0
Plant 2	3.414	-75.117	0
Plant 3	28.420	-57.995	0

For plume dispersion that is 10 mm and 50 mm leak, there is no threat zone generated for all the plants as the effect of near-field patchiness make dispersion prediction less reliable but for puff model that is full rupture of the pipeline, ALOHA has generated the threat zone and the threat zone are exported to the MARPLOT to observe the area affected. From the threat zone, it shows red zone that is immediate dangerous to life or health (IDLH) zone.

Figure 3,4 and 5 shows the area affected by the puff dispersion. From the three figure it can be seen that toxic release from plant 3 will have more affected area followed by plant 1 and plant 2.

Figure 3. Puff Dispersion at Plant 1

Figure 4. Puff Dispersion at Plant 2

Figure 5. Puff Dispersion at Plant 3

C. Vapor Cloud Explosion

Explosion can result from the moving of reaction front outward from the ignition source preceding by a shock wave or pressure front will result in the explosion of dust or gas. The study of explosion in this paper is focusing on the hydrogen pipeline and reactor. Hydrogen is highly flammable and can explode easily. Hydrogen is odorless, colorless and tasteless thus, when it leaks, human sense will not detect it. It has lowest viscosity makes it easy to diffuse the porous walls and easily escape through the smallest gaps.

To study the explosion of the hydrogen pipeline, the pipe is assumed to be full ruptured. To calculate the mass released, the volume of the pipe need to be identified using the length and the diameter of the pipe. The diameter of the pipe is 75 mm [21] while the length is depending on the individual plant. The explosion will be studied is the blast damage resulting from overpressure where the equivalent mass of TNT will be calculated in order to know the peak side-on overpressure. When the mass release known, the equivalent mass of TNT can be then calculated followed by the scaled distance, ze. the peak side-on overpressure can then be calculated. From the peak side-on overpressure, the probit can be calculated. From the Table 7, the probit of the explosion of hydrogen pipeline can be seen. The probit calculated are deaths from lung hemorrhage, eardrum ruptures, structural damage and glass breakage. There is 0% of probability for death from lung hemorrhage, eardrum ruptures, structural damage for all the plant but for glass breakage, plant 1 and plant 3 gives 12% and 14% of probability of the breakage while for plant 2, the probability is 0%. The most risk plant is plant 3 that is with pressure and temperature 442 bar and 210 ^{o}C.

Reactor in this plant is exothermic process where it releases heat. Risk at the reactor is identified such that it leaks and fully rupture of the reactor. It is assumed that only fully rupture of the reactor will cause explosion. The volume of the reactor assumed to be 42 m^3 [22]. The chemical in the reactor that will cause the explosion to occur need to be identified based on the highest mass fraction. Since the properties in the reactor is not available in the Aspen Hysys, it is assumed that the properties in the reactor is the same as the properties at the outlet of the reactor that is stream 14. For all the plant, hydrogen has the highest mass fraction, thus the properties of hydrogen will be used in order to calculate the explosion.

Table 8 shows the result for the explosion that occur on the reactor. It can be seen that there is 0% probability of the death from lung hemorrhage for all the plant. For eardrum ruptures, only plant 3 has 1% of probability compared to the other two plant that has 0% probability. For structural damage, plant 2 has 0% probability while plant 1 and plant 3 has the probability of 6% and 13% respectively. Among all the damages and injuries occur, glass breakage has the highest probability of breakage resulting from the explosion occur. Plant 1, plant 2 and plant 3 gives 99.8%, 93% and 100% probability respectively. From this result, the highest risk will be plant 3 that is 442 bar and 210 ^{o}C while the safest will be plant 2 that is 76 bar and 280 ^{o}C.

Table 7: Explosion in hydrogen pipeline

	Plant 1		Plant 2		Plant 3	
Probit		Fatality (%)		Fatality (%)		Fatality (%)
Death from lung hemorrage	-22.79	0	-27.71	0	-22.48	0
Ear rupture	-0.430	0	-1.80	0	-0.34	0
Structural damage	-0.849	0	-2.93	0	-0.71	0
Glass breakage	3.829	12	1.84	0	3.95	14

Table 8: Explosion in Reactor

	Plant 1		Plant 2		Plant 3	
Probit		Fatality (%)		Fatality (%)		Fatality (%)
Death from lung hemorrage	-12.52	0	-16.22	0	-11.57	0
Ear rupture	2.44	0	1.40	0	2.70	1
Structural damage	3.49	6	1.93	0	3.89	13
Glass breakage	7.98	99.8	6.48	93	8.36	100

For explosion that occur in pipeline, the area affected are as in Figure 6,7 and 8. There are three zone that can be seen that is red zone, orange zone and yellow zone. Red zone is potentially lethal occur, orange zone is second degree of burns and yellow zone is pain that can be felt. From the figure, the threat zone for plant 1 and plant 3 seems to affect the same area but by the reading given by MARPLOT, plant 3 actually cover larger area compared to plant 1.

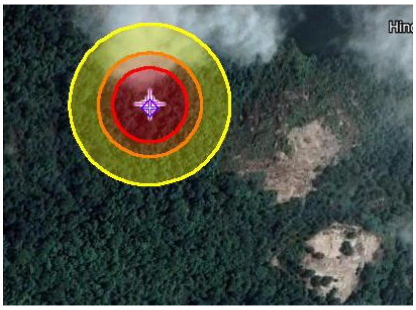

Figure 6. Explosion at Hydrogen Pipeline in Plant 1

Figure 7. Explosion at Hydrogen Pipeline in Plant 2

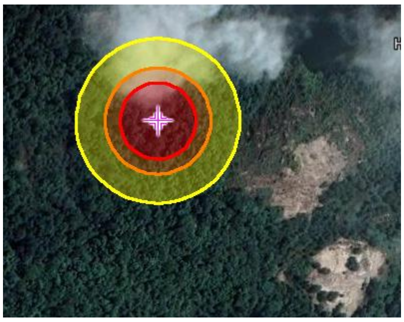

Figure 8. Explosion at Hydrogen Pipeline in Plant 3

Area affected by the explosion of reactor can be seen in the Figure 9,10 and 11 where there is large area will be affected by this case. This case shows larger affected area compared to other case as this case of plant 1 and 3 will affect the Hindu Temple nearby. Plant 3 still shows the higher risk followed by plant 1 and plant 2.

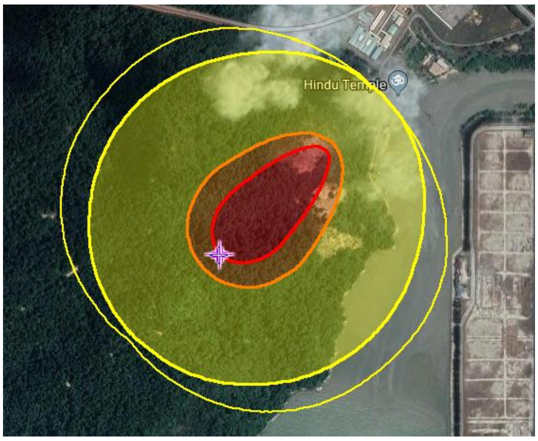

Figure 9. Explosion at Reactor in Plant 1

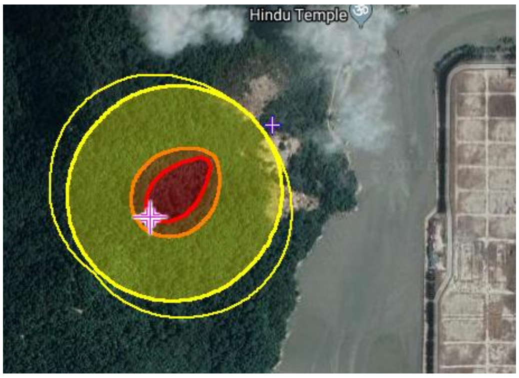

Figure 10. Explosion at Reactor in Plant 2

Figure 11. Explosion at Reactor in Plant 3

D. Flash Fire

Fire can occur in the presence of oxygen, fuel and ignition source. Compared to explosion that release energy rapidly, fire release energy slowly. As the study of explosion, fire study will also focus on the hydrogen pipeline and reactor but for fire, the pipeline and the reactor will be assumed to be leak with 10 mm and 50 mm diameter. For fire, the mass release rate need to be calculated based on the area of the leaking. From the mass release rate, it is assumed that after 5 minutes, fire will ignite thus the mass release can then be determined.

For the 10 mm leak of hydrogen pipeline, no death will occur in all the plant since all the probability gives 0% of probability but for 50 mm leak, only plant 2 give 0% of probability. The other two plant that is plant 1 and plant 3 gives 97% and 98% respectively. This show that plant 2 is the safest plant while plant 3 has the highest risk of fire to occur. The result for leak on the hydrogen pipeline can be seen in the Table 9 and Table 10.

For the reactor, since the properties in the reactor is not available in the Aspen Hysys, it is assumed that the properties in the reactor is the same as the properties at the outlet of the reactor that is stream 14. For all the plant, hydrogen has the highest mass fraction, thus the properties of hydrogen will be used in order to calculate the fire that might be occurred. Same goes to hydrogen pipeline, it is assumed that after 5 minutes, fire will ignite thus the mass release can be determined.

No death will occur if the leak diameter is 10 mm since all the plant gives 0% probability. For 50 mm leak, plant 3 gives highest probability that is 96% followed by plant 1 that is 95% probability of death burn. Plant 2 shows that it is the safest plant since it gives 0% probability of the death burn. The result for reactor leak can be seen in the Table 11 and Table 12.

Table 9: 10 mm Leakage of Hydrogen Pipeline

	M (kg)	Ie (W/m2)	Probit	Fatality (%)
Plant 1	472.29	9546.53	-3.528	0
Plant 2	82.10	2477.43	-9.252	0
Plant 3	505.35	10057.68	-3.306	0

Table 10: 50 mm Leakage of Hydrogen Pipeline

	M (kg)	Ie (W/m2)	Probit	Fatality (%)
Plant 1	11810.05	114218.52	7.004	97
Plant 2	2053.07	29641.02	1.280	0
Plant 3	12636.66	120334.14	7.225	98

Table 11: 10 mm Leakage of Reactor

	M (kg)	Ie (W/m2)	Probit	Fatality (%)
Plant 1	426.64	8826.93	-3.860	0
Plant 2	80.79	2446.80	-9.305	0
Plant 3	436.98	8991.41	-3.782	0

Table 12: 50 mm Leakage of Reactor

	M (kg)	Ie (W/m2)	Probit	Fatality (%)
Plant 1	10668.58	105608.89	6.671	95
Plant 2	2020.20	29274.53	1.227	0
Plant 3	10927.14	107576.88	6.750	96

For fire at 10 mm leak of hydrogen pipeline, no threat zone generated since the zone affected is below 10 m but for fire at 50 mm leak of pipe, the threat zone generated only for plant 1 and 3. Plant 2 has no threat zone generated as the zone affected are also below 10 m. The threat zone for plant 1 and 3 are as in Figure 12 and 13. The threat zone generated only shows the yellow zone since the red and orange zone is below then 10 m.

Figure 12. Fire by 50 mm Leak of Hydrogen Pipeline at Plant 1

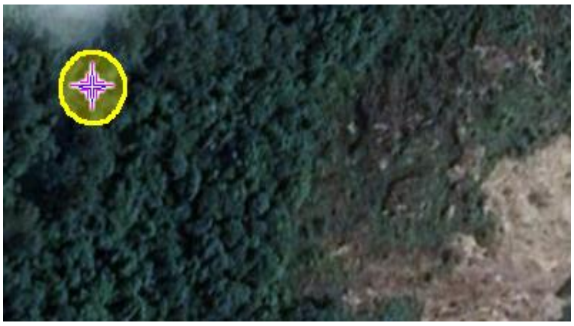

Figure 13. Fire by 50 mm Leak of Hydrogen Pipeline at Plant 3

For fire at 10 mm leak of reactor, no threat zone generated for plant 2 since the zone affected is below 10 m but the threat zone for plant 1 and plant 3 are as in Figure 14 and 15. The threat zone only shows orange and yellow zone as the red zone is below 10 m.

Figure 14. Fire by 10 mm Leak of Reactor at Plant 1

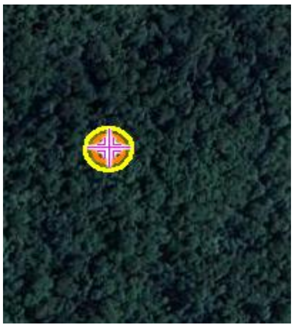

Figure 15. Fire by 10 mm Leak of Reactor at Plant 3

For fire at 50 mm leak of reactor, the threat zone for plant 1,2 and plant 3 are as in Figure 16,17 and 18. From the figure, it can be seen that the least affected area is plant 2 where only small area is affected.

Figure 16. Fire by 50 mm Leak of Reactor at Plant 1

Figure 17. Fire by 50 mm Leak of Reactor at Plant 2

Figure 18. Fire by 50 mm Leak of Reactor at Plant 3

E. Analysis of the result

a) Toxic Release

Toxicity of CO_2 is not that significant since CO_2 exists naturally in environment as living life exhale CO_2 from the body but it is considered as a danger to life through asphyxiation when exist in high concentration where it can replace oxygen in the air that could drop the oxygen level to the lowest limit. It is typical for the CO_2 to be in blood but at low concentration but at high concentration, it is poisonous to life. The symptoms that human can feel when exposed to CO_2 such as headaches, respiratory and heart rate rises, dizziness and more. When the CO_2 inhaled increase, it will trigger respiratory, cardiovascular and central nervous system in a poor way as the blood become acidic where death can occur. In the probit calculation, all the fatality that has been determined is 0%. This is because the mass release concentration is low. When living things fell the symptoms of dizziness or other symptom, they will eventually escape from the area.

There is no threat zone generated for the plume model since the effect of near-field patchiness make the dispersion less reliable for short distance but ALOHA has predicted the IDLH zone that is red zone. IDLH means immediate dangerous to life or health. This is where when living things feel the symptoms, it depends on their response whether to leave the area or not. From the red zone predicted by ALOHA, plant 1 and plant 3 will affect more area than plant 2. Comparing on the condition of each plant, it can be said that pressure gives higher impact to the toxic release as both plant 1 and plant 3 has the same pressure that is 442 bar rather than 76 bar in plant 2. Although the temperature of plant 1 and plant 3 is not the same, they still affect the same area of the red zone.

For puff model, ALOHA has generated the threat zone and being export to the MARPLOT. the highest affected area is by plant 3 followed by plant 1 and plant 2. As said before, pressure gives high impact to the toxic release. The temperature of plant 3 and plant 1 that is 210^{o}C and 280^{o}C respectively. Plant 3 has lower temperature compared to plant 1 but it gives higher affected area than plant 1. This is because, the lower the temperature, the density will be higher thus increase the mass release of the CO_2 which will higher the concentration. In this model, temperature gives significant effect to the area affected.

b) Vapor Cloud Explosion

Gas is released from the reactor and pipeline can cause vapor cloud explosion when ignite in a few seconds. By using TNT Equivalency Model, percentage of fatality when explosion occur can be obtained. From the result obtained by explosion of the hydrogen pipeline, all three plant gives 0% probability of death from lung hemorrhage, ear rupture and structural damage. This is due to the small value of mass that release from the pipeline. For glass breakage, plant 2 still has 0% probability but plant 1 has 12% probability and plant 3 has 14% probability. The threat zone for explosion shows three levels of area affected that is red zone, orange zone and yellow zone. From the threat zone generated, it can be seen that plant 2 has the smallest zone affected. From the value given, it can be seen that plant 3 gives higher value of the affected area.

For reactor, it is assumed that hydrogen will give significant effect to the explosion compared to CO_2, methanol and water. This is because hydrogen is the most abundant in the reactor. Plant 3 still gives the highest probability among the other plant. For ear rupture, plant 3 has 1% probability while other has 0%. It has 13% probability for structural damage and 100% for the glass breakage. The threat zone generated for reactor is much larger from the hydrogen pipeline. This is because the mass release of reactor is more than mass release in hydrogen pipeline. For plant 1 and plant 3 it can be seen that when explosion occur, it could affect the Hindu Temple that is the person at the Hindu Temple can feel the pain as it shows that it will affected by the yellow zone. The affected area of plant 3 could cover up to 667.5 m from the source of explosion compared to plant 1 that is 576 m and plant 2 that is 304.5 m.

As discussed in the toxic release part, pressure will have more significant to the case study as higher the pressure, higher the mass release thus higher the over-pressure. In the case of reactor, it can be seen clearly as the temperature is lower, it will have higher probability of damages. This is because lower temperature will give higher density that release higher mass and higher over-pressure.

c) Flash Fire

Gas is released from the reactor and pipeline can cause flash fire to occur. All the plant gives 0% fatality to the 10 mm leakage of hydrogen pipeline but for 50 mm leakage, only plant 2 gives 0% fatality but plant 1 and plant 3 gives 97% and 98% fatality respectively. There is also no threat zone generated by ALOHA for 10 mm leak of hydrogen pipeline since the zone that affected is below 10 m. for 50 mm leaking, the threat zone has generated but it only shows the yellow zone. This is because, the red and orange zone are below 10 m.

Same as the leak of hydrogen pipeline, the 10 mm leak of reactor gives 0% fatality. This is because the mass release is only a small amount that will not cause death to occur. For 50 mm leak, plant 3 has 96% fatality, followed by plant 1 with 95% fatality. Plant 2 will not cause the death to occur. For the threat zone for 10 mm leaking of reactor, only orange and yellow zone are generated for plant 1 and 3 while no threat zone generated for plant 2. Threat zone had produced for all the plant for 50 mm leaking and all the zone can be seen. The highest area generated is plant 3 followed by plant and plant 3.

Plant 3 still gives the highest probability and affected area for flash fire as in toxic release and vapor cloud explosion. Pressure is significantly affect the risk while temperature only slightly affect the risk.

IV. CONCLUSION

This study has analyzed three different plant that have different condition at the inlet of the reactor. Plant 1 has the condition of 442 bar and 280 ^{o}C, plant 2 is 76 bar and 280 ^{o}C while plant 3 is 442 bar and 210 ^{o}C. The study is focusing on the toxicity that caused by the carbon dioxide at the CO_2 pipeline, flash fire and vapor cloud explosion that caused by the hydrogen at the hydrogen pipeline and reactor. Risk is being analyzed using Quantitative Risk Assessment (QRA). From the studied, it is found that the highest risk can occur on the plant 3 followed by plant 1.

Plant 3 and plant 1 has the same pressure that is 442 bar but at different temperature which plant 1 has higher temperature that is 280^{o}C while plant 3 is 210^{o}C. This shows that the lower the temperature, the higher the mass release, thus higher the risk. This has been shown theoretically too where it can be seen in the equation where lower the temperature will increase the density thus increase the mass release. Pressure on the other hand, gives more significant to the risk calculated. This is shown by plant 2 where it has lower pressure that is 76 bar compared to the other two plant.

The risk generated in plant 2 is much lower compared to plant 1 and plant 3. From this result it can be seen that pressure is more significant in giving the higher risk.

There are two objectives for this study that are to design and simulate power to methanol production plant together different temperature in the reactor and to analyze the risk on the power to methanol production plant using different temperature in the reactor. Both objective has been achieved where three plants had been simulated with different condition, the simulation had been converged and the risk had been studied with different condition. The result of the risk studied has shown that plant 3 has the highest risk while plant 2 is the safest.

In conclusion, it is suggested to build plant 2 rather than plant 1 and 3 since it still gives high production of methanol that is 1878 kg/h and 99.4% purities with lowest risk compared to 1896 kg/h and 99.92% for plant 1 and 1875 kg/h and 99.9% for plant 3 where both these plants give higher risk. For further studies, it is suggested that the risk assessment is studied for the other equipment as well and all the component in the equipment is considered involving in giving the impact of the case study.

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