

Effect of Different Volumetric Flowrates using Safety Analysis for Power to Methanol Production Plant

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Abstract— The increasing atmospheric concentration of carbon dioxide, CO_2 nowadays are very concerning every human being as the concentration of carbon dioxide in the largely produced from the fossil fuel and industrial process, [1][1]. As the CO_2 concentration increase in the air, the temperature of the Earth also increasing and the worsen effect are the Global warming and Climate changes [2]. So, the Power to Methanol, [3] has been introduced, [4] which is by using carbon capture process. The plant is simulated by Aspen Hysis and analyzed the safety analysis by using different flowrates that involved in the process. Then, it is analyze that the as the concentration of CO_2 increasing, the toxicity of the area surrounding also increasing. As the process also involving hydrogen gas, also will attempt to cause fire and explosion. In this article, we will study the safety of the plant in order to establishing absolute safe chemical plant. Based on this research, plant1 states the highest percentage of fatalities when the explosion occur, while for the fire and toxicity, there is no fatalities at all for all the plants that have been simulated. In conclusion, higher flowrates of carbon dioxide and hydrogen has will cause more risk for the methanol production plant.

Keywords—Carbon Capture Process, Climate Change, Global Warming, Power to Methanol.

I. INTRODUCTION

Recently, greenhouse effect has been estimated that if the gas emissions continue at the present rate, then the Earth will have very high temperature and will harm the living things in the world. Thus, this estimation will lead to Global warming. Furthermore, Figure 1 shows the greenhouse emission gas.

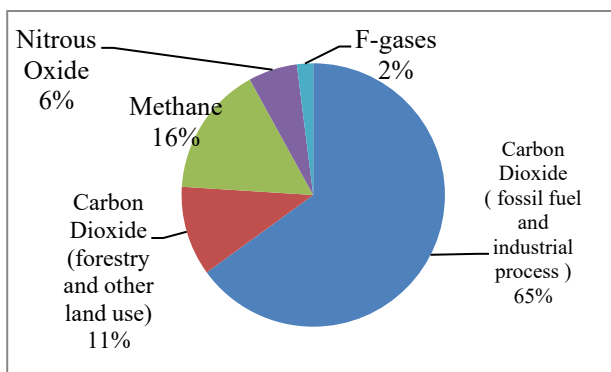


Fig 1: Overview of the greenhouse gasses and sources of emissions. (Sources: Contribution of Working Group III to the Fifth Report of the Intergovernmental Panel on Climate Change)

A. Carbon Capture and Storage

Fortunately, there are many types of ways for utilizing the carbon dioxide such as carbon capture. Usually, this method of carbon dioxide utilization has been used in power plants, oil refineries, iron and steel industry. Generally, there are three types of options during the carbon dioxide capture which are Post conversion capture, Pre-conversion capture and Oxy-fuel combustion. Post conversion capture is an option that also called as post-combustion capture. It consists of e combustion of the carbon sources of carbon dioxide followed by the separation of carbon dioxide from waste gas stream. Pre-conversion capture means that the generated capturing carbon dioxide is an undesired co-product of an intermediate reaction of a conversion process. Absorption process that has been used in this process is using Monoethanolamine, MEA,[5]. Oxy-fuel combustion is an option only can be used when involving combustion. For example power generation in fossil fuelled plants, cement production and the iron and steel industry.

From the three options of carbon dioxide capture, the difference is when the major product such as energy, fertilizer, ammonia and ethylene oxide is produced. However, there are two types of carbon utilization which are Carbon Capture Storage, CCS and Carbon Capture Utilization, CCU [6]. The final destination of the captured carbon dioxide is what differs from CCU and CCS. For the CCS process, the captured carbon dioxide will be placed in a specialized site for a long period of time of storage process. Meanwhile, the CCU process, the captured carbon dioxide will be converted to a commercialize product.

For carbon dioxide storage option, there are many options such as to be stored in the ground, ocean or as a mineral carbonate after the captured carbon dioxide was compressed and shipped. For example, in geological storage, the carbon dioxide needs to be injected into geological formation such as depleted oil and gas reservoir.

B. Safety Related Incident and Hazardous on H_2

Hydrogen has been widely produced as a synthesis gas for use in chemical production or recovered as by-product for use in oil refineries. Considering that safe handling of the hydrogen by workers in industry is well understood so, it would not bring any harmful situation to occur. Yet, the problem is the usage of hydrogen in the public realm. Thus, the need to explain about the inherent safety element, safety management and case study are important to avoid any disaster happen. Inherent safety is techniques that can reduces or eliminate risk without using device and procedural measures,[7].

C. Safety Related Incident and Hazardous on Methanol

There are a lot of incident happen in the plant that caused by the hazardous methanol such as in biodiesel production [8]. Due to high demand, nowadays the production of biodiesel become larger and the amount of handled methanol also increases greatly. Thus, increase the risk at the plant. This is because there are already a lot of case histories in biodiesel power plant. From the case histories, it is analyzed that most of the incident happen during the process take place. Moreover, most of the potential loss of life per year is caused by the leakage of methanol or rupture from the pipelines that trigger the Vapor Cloud Explosion (VCE), [9]

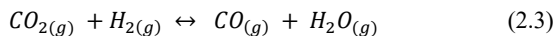
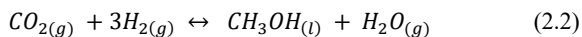
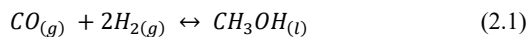
D. Effect of Process Condition in Methanol Production Plant in Term of Safety Risk

Methanol, which is a colorless organic liquid at normal pressure, is a hygroscopic and able to entirely soluble in water. It is also have lower specific gravity compared to water. This makes the methanol is a light fuel and a volatile solvent. The safety management need to always monitor the condition of methanol due to flammability of methanol which are easily ignited that can burn and worsen case, can explode in air.

However, the fire and explosion can be avoided because it will happen in limited conditions such as when concentration of methanol vapor is between 6 % and 36 % in air,[6]. Since the molecular weight of methanol vapor is higher than water, methanol liquid will pool and vapor may migrate near the ground and collect in confined spaces and low lying areas but depends on the condition of the spill or release. Moreover, for a mixture of water and methanol that have volume fraction as 75% / 25%, it is existed as flammable liquid. Thus, for safety management, it is advised to use fire suppression foam stored onsite, as well as fixed foam monitors, for the methanol storage tanks. According to quantitative risk assessment (QRA) conducted by NW Innovation Works, the suitable dimension and operating conditions for methanol loading line are the pipe diameter is 16 inch, pipe length is 1,000 feet and the operating pressure is 87 psig, [10].

E. CO₂ to Methanol

CO₂ can be converted into methanol in 2 steps[6] [11] . The first step is the steps that involve direct hydrogenation of CO₂ to methanol and the second step is firstly, CO₂ converted to CO then, will be hydrogenated to methanol via Reverse Water Gas Shift, RWGS reaction. The chemical equations involved are presented below:



So, the main of this research is to study the effect of the different feed reactor volume using safety analysis for Power to Methanol plant. The method of safety analysis that is used in this research is Quantitative Risk Assessment, QRA. The plant in this research will be designed and simulated by using software Aspen Plus.

II. METHODOLOGY

A. Process Flow Diagram and Process Description

At the beginning, CO₂ and H₂ are fed and compressed in a series of compressors for intercooling process. The initial condition of CO₂ is 1 bar and 25°C while H₂ at 30 bar and 25°C. After the intercooling process, H₂ is compressed to 78 bar in a single stage. Next, in the MIX1, both of the gases are mixed and are remixed in the recycle stream, MIX2. Then, the stream is heated by HX4 to 210°C and then being fed into fixed bed adiabatic reactor. DIV1 divide the outlet gas that leaving the reactor into two streams which are first stream consist of 60% of initial stream while the second stream is used in reboiler and also to heat the feed of the distillation column HX5. In the meanwhile, the first stream is then used in the HX4 to heat the fresh feed. MIX3 mixed the two streams are remixed and cooled to 35°C by water in HX6. Water and methanol that has been condensed from HX6 are separated from the non-reacted gases which is 1% are purged in order to reduce the accumulation of inerts and by-products in the reaction loop.

The crude methanol, which is the liquid stream leaving the knock-out drum, KO1 is consist of methanol and residual dissolved gases. VLV1 and VLV2 are expands the crude methanol to 1.2 bar. Next, in flash tank, TKFL1, the residual gases are almost completely removed. HX5 heats the remaining stream until 80°C and then, the sent to a distillation column, DT1. The water that produced from the bottom of the column is composed of 23 wt-ppb of methanol while the methanol gas that produced on top of column is composed of 69 wt-ppm of water and some non-reacted gases. Then, methanol is compressed in CP7 and cooled in HX8 until 40°C. Non-reacted gases come out of the top of knock-out drum, KO2 and methanol product comes out from the bottom in liquid form [11].

Figure 2 shows the process flow diagram for the process description.

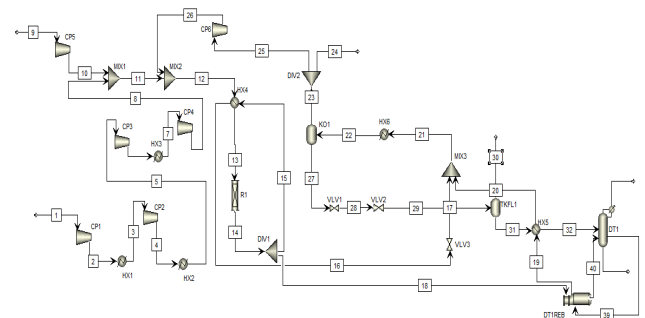


Figure 2 shows the process flow diagram for the process description.

By referring to process flow diagram of the 3 plants, the dominant gas by weightage by volume ratio is hydrogen gas. So, this safety analysis analyzes hydrogen gas that are assumed has been released from the leaking also the full rupture of the reactor. The conditions for reactor in each plant are:

Plant	Pressure, kPa	Temperature, °C
1	7,600	280
2	7,600	210
3	7,600	210

B. Properties of the Elements in the Methanol Plant

1) Properties of Methanol

Methanol is a colorless, flammable, poisonous, mobile, highly polar liquid with slight alcohol odor. Methanol can be dissolved in

water, ether, alcohol, ketones and most other organic solvent. OSHA has restricted the concentration of methanol that can be stored in a particular place for one time. The maximum concentration for methanol is 200 ppm while the remaining composition of water is not established. This is because the exposure of methanol is very hazardous and can bring many consequences such as health effect to the persons that have been infected. First, methanol can absorb through skin, eye contact, inhalation or ingestion. The primary vapor exposer and skin contacts are from industrial exposures. The initial sign that the person has been poisoned is inhalation will be mild intoxicant. However, it might be severe after 12-18 hours [12] [11].

2) Properties of Hydrogen

At room temperature, hydrogen also colorless, odorless gas and is the lightest gas due to being quarter as dense as air. Hydrogen can react with oxygen easily which will cause burns and form water. This property made the fact that of hydrogen is possible to be used as energy medium. However, safety precautions are necessary because of mixture of hydrogen and air can be ignited even at very low energy spark [13].

3) Properties of Carbon Dioxide

Carbon dioxide is a nonflammable, colorless, and odorless in gas and liquid phase. Even though carbon dioxide is a minor composition in the earth, however it becomes an important constituent of the atmosphere. This is because the average carbon dioxide in the atmosphere is 0.036% or 360 ppm by volume. Besides, it also is the end-product of human and animal metabolism.

Carbon dioxide gas is 1.5 times denser than air thus, it is found in greater concentrations at low levels. So, in order to exhaust from the lowest levels and allow make-up air to enter at higher levels, ventilation systems should be designed. For the exposure to carbon dioxide, the effects get worse when the concentration of infection is increasing, may cause unconsciousness and convulsions in less than 30 seconds. OSHA regulates that employee exposure to carbon dioxide in any 8- hour shift of a 40-hour work week shall not exceed that 8-hour time-weighted average of 5,000ppm or (0.5%;9,000mg/m³) [14].

C. Toxic Release and Dispersion Models

Toxic release and dispersion models are the model to study and analyze the risk assessment [11] For this research, the carbon dioxide gas can be considered toxic where it can caused immediate danger to the human health but only in certain concentration, [15]. This is because in the higher concentration of carbon dioxide which is more than 50,000 ppm at the atmosphere, it will harm and cause fatalities to the living things surrounding.

1) Neutrally Buoyant Dispersion Models

- a) Case 11: Puff with Instantaneous Point Source at Ground Level, Coordinates Fixed at Release Point, Constant Wind Only in x Direction with Constant Velocity u

$$y = \sigma_y \sqrt{2 \ln \frac{C(x, 0, 0, t)}{C(x, y, 0, t)}} \quad (3.1)$$

- b) Case 12: Plume with Continuous Steady State Source at Ground Level and Wind Moving in x Direction at Constant Velocity, u

$$C(x, y, z) = \frac{Q_m}{\pi \sigma_y \sigma_z u} \exp \left[-\frac{1}{2} \left(\frac{y^2}{\sigma_y^2} + \frac{z^2}{\sigma_z^2} \right) \right] \quad (3.2)$$

Where Q_m is constant mass release rate and K is constant eddy diffusivity.

D. Fires and Explosion

1) Blast Damage Resulting from Overpressure

Where r is distance from the ground-zero point of the explosion and m_{TNT} is equivalent mass of TNT.

$$z_e = \frac{r}{m_{TNT}^{1/3}} \quad (3.3)$$

2) TNT Equivalency

$$m_{TNT} = \frac{\eta m \Delta H_C}{E_{TNT}} \quad (3.4)$$

Where m_{TNT} is equivalent mass of TNT, η is empirical explosion efficiency which is unitless, m is mass of hydrocarbon, ΔH_C is energy of explosion and flammable gas, E_{TNT} is energy of explosion of TNT.

III. RESULTS AND DISCUSSION

A. Gas Release from Stream 8 and 10

From the plant that has been simulated by Aspen Hysis, although there are three total of plant that have different reactor volume, but the similarities from the simulated methanol plants are the composition of gases contain in the stream 8 and 10. There are pure of hydrogen gas that passes through the stream 10 as the stream supply the hydrogen feed. Next, pure carbon dioxide gas passes through stream 8. Then condition of hydrogen gas in the stream 10 is at 7600 kPa and the temperature varied for 210°C and 280°C for plant 2, 3 and 1 respectively.

B. Gas Release from Reactor, R1

By referring to process flow diagram of the 3 plants, the dominant gas by weightage by volume ratio is hydrogen gas. So, this safety analysis analyzes hydrogen gas that are assumed has been released from the leaking also the full rupture of the reactor. The conditions for each plant are:

C. Results and Discussion of the Fatalities

1) Explosion

Based on the result obtained in the Table 4.1, it shows that the fatalities only occur for the types of glass breakage, as the percentage of the fatalities are 72%, 7% and 7% for Plant 1, Plant 2 and Plant 3 respectively. Thus, the Plant 1 states the highest percentage of incident glass breakage for the case assumed is full rupture of the hydrogen pipeline. From the result that shows no percentage fatality for death from lung hemorrhage, eardrum rupture and structural damage can be happen because the high

requirement of the overpressure peak. So, only glass breakage injury that require lowest overpressure peak and the overpressure peak of the Plant 1 have achieve the required overpressure of the glass breakage injury , thus, cause its percentage fatalities is the highest. When comparing the value of the percentage of glass breakage among the plants that has been simulated, it can be seen that Plant 1 have the highest percentage of fatalities which is 72%, which means that Plant 1 have the highest risk that might be occur during the operation. However, the conclusion only based on the explosion's types of injury, so next are the analyzing from the fire and toxicity of the carbon dioxide released.

From Figure 4.2 and 4.2, it shows that the red zone that have 313 yards with the overpressure greater than 8.0 psi will cause the destruction of buildings while the orange zone, which is consist of 352 yard, the surrounding living things such as human and animals will serious injury likely because of the overpressure greater than 3.5 psi. Lastly is the yellow zone, where it consist of 572 yards will face overpressure sa much as 1.0 psi, will cause shatters glass happen. The Figure 4.2 and 4.3 shows the effect from the plant 1 and actually the effect for plant 2 and plant 3 is approximately the same.



Figure 4.1: Result from the Effect of the Hydrogen Pipeline Explosion that simulated by using software MARPLOT

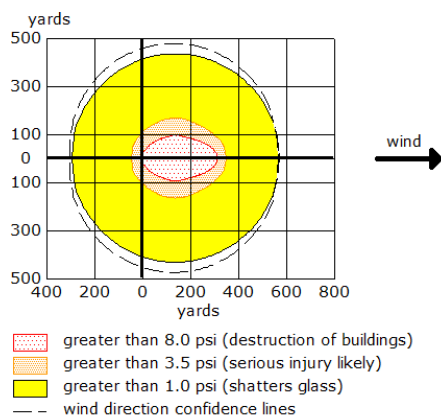


Figure 4.2: Result from the Effect of the Hydrogen Pipeline Explosion that simulated by using software ALOHA

Result for Hydrogen Pipeline

Types Of Injury	Plant 1			Plant 2			Plant 3		
	P ₀ , kPa	Probit, Y	Fatalities, %	P ₀ , kPa	Probit, Y	Fatalities, %	P ₀ , kPa	Probit, Y	Fatalities, %
Death from lung hemorrhage $Y = -77.1 + 6.91 \ln(P_0)$	4884.7	-18.40	0	2346.0	-23.475	0	2346.016392	-23.475	0
Eardrum rupture $Y = -15.6 + 1.93 \ln(P_0)$	4884.7	0.7931	0	2346.0	-0.622	0	2346.0	-0.622	0
Structural damage $Y = -23.8 + 2.92 \ln(P_0)$	4884.7	1.0020	0	2346.0	-1.139	0	2346.0	-1.139	0
Glass breakage $Y = -18.1 + 2.79 \ln(P_0)$	4884.7	5.5978	72	2346.0	3.551	7	2346.0	3.551	7

Table 4.2:

Result for Hydrogen Reactor

Types Of Injury	Plant 1			Plant 2			Plant 3		
	P ₀ , kPa	Probit, Y	Fatalities, %	P ₀ , kPa	Probit, Y	Fatalities, %	P ₀ , kPa	Probit, Y	Fatalities, %
Death from lung hemorrhage $Y = -77.1 + 6.91 \ln(P_0)$	685,992	15.76	100	52,568	-1.99	0	2346.016392	15.019	100
Eardrum rupture $Y = -15.6 + 1.93 \ln(P_0)$	685,992	10.34	100	52,568	5.378	64	616,238	10.129	100
Structural damage $Y = -23.8 + 2.92 \ln(P_0)$	685,992	15.44	100	52,568	7.940	99.8	616,238	15.127	100
Glass breakage $Y = -18.1 + 2.79 \ln(P_0)$	685,992	19.394	100	52,568	12.227	100	616,238	19.094	100

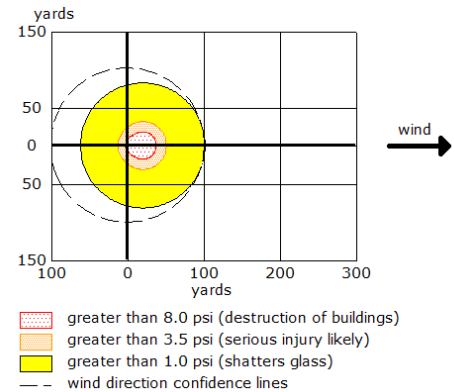


Figure 4.3: Result from the Effect of the Hydrogen Reactor Explosion that simulated by using software ALOHA

2) Fire

For fire, the only type of injury that has been investigated is the burn death from pool burning. Pool burning which is the simplest form of combustion, also always applied to a large series of industrial fire defense concern, [16]. Based on the Table 4.2, the irradiation of intensity of pool burning can be said to be factor to the probit value. This is because, the higher the irradiation of intensity of pool burning, the higher the probit thus higher percentage fatalities. According to result in Table 4.2, it can be stated that there is no percentage of fatalities at all for the three simulation plants either for the hydrogen released from the pipeline or the hydrogen released from the reactor and no matter what it's leaking. Even the highest of intensity of irradiation of pool burning in Plant 2 and 3 when the leakage is 50mm, 79.020 W/m², still does not show any sign of possible fatalities.

This is because the molecules of hydrogen very small compared to all the other gases. So, it can diffuse through a lot of airtight or impermeable to other gases material. Furthermore, the behavior causes the hydrogen is more difficult to be composed of compared to other gases. Because of the extremely low boiling point of hydrogen, the leaks of liquid hydrogen will be evaporating rapidly. However, for small hydrogen leaks, the presence of air currents from a slight ambient wind will dominate the buoyancy and diffusion effects in the air, [17]. This statement strengthen the reason why there is no fatalities occur when the fire occur among all the three simulated plants.

Table 4.3:

Result for Hydrogen Pipeline

Plant	Plant 1				Plant 2				Plant 3			
Leaking, mm	Po, kPa	I, W/m ²	Y	Fatalities, %	Po, kPa	I, W/m ²	Y	Fatalities, %	Po, kPa	I, W/m ²	Y	Fatalities, %
10	113.2	6.27	-29	0	70.119	21.28	-24	0	70.119	21.281	-24	0
50	1298	75.00	-18	0	751.47	254.5	-13	0	751.47	254.57	-13	0
Full Rupture	4.884	0.032	-51	0	2.346	0.035	-50	0	2.346	0.0358	-50	0

Table 4.4:

Result for Hydrogen Reactor

Plant	Plant 1				Plant 2				Plant 3			
Leaking, mm	Po, kPa	I, W/m ²	Y	Fatalities, %	Po, kPa	I, W/m ²	Y	Fatalities, %	Po, kPa	I, W/m ²	Y	Fatalities, %
10	28.78	6.270	-29	0	29.763	6.6058	-29	0	29.763	6.6058	-29	0
50	220.9	75.00	-18	0	232.50	79.020	-18	0	232.50	79.020	-18	0
Full Rupture	686	232.4	-13	0	52.567	14.813	-25	0	616.23	208.91	-14	0

3) Toxicity

For the toxicity of the carbon dioxide, there are two types of possible case that will happens which are plume when the leaking as much as 10 mm and 50 mm and puff when full rupture occurs. Same as the fire's percentage of fatalities, there is no percentage of fatalities for the toxicity either. The non-fatalities can be reasoned because according to [18], the carbon dioxide gas can only considered to be dangerous to living things when its concentration is more than 5% which is 50,000 ppm. Even, when the carbon dioxide's concentration is 0.5% which is 5,000 ppm, it is considered as toxic enough to harm the health of human and animal. The concentration of carbon dioxide involved in the process under the 60 minutes as the assumption of the time of gas exposure, the highest value only 50.655ppm which is in Plant 2 and Plant 3 that have leaking as much as 50 mm at the carbon dioxide pipeline. So, even though that is the highest carbon dioxide concentration released, but it still much lower than 5,000 ppm. That is one of the reason why there is no fatalities that might be occur to the three simulated plant. This result will conclude that all the plant is safe from the toxicity from the carbon dioxide gas because of low mass and concentration released of the gas.

Table 4.5

Plume Result for Carbon Dioxide Pipeline

Plant	Plant 1				Plant 2				Plant 3			
Leaking, mm	Concentration, ppm	Y	Fatalities, %		Concentration, ppm	Y	Fatalities, %		Concentration, ppm	Y	Fatalities, %	
10	1.8937	-81.50	0		2.0262	-80.96	0		2.0262	-80.96	0	
50	47.3430	-55.49	0		50.655	-54.95	0		50.655	-54.95	0	

Table 4.6

Puff Result for Carbon Dioxide Pipeline

Plant	Plant 1				Plant 2				Plant 3			
Leaking, mm	Concentration, ppm	Y	Fatalities, %		Concentration, ppm	Y	Fatalities, %		Concentration, ppm	Y	Fatalities, %	
Full rupture	0.0101	-123.8	0		0.0119	-122.4	0		0.0119	-122.4	0	

According to Table 4.2, it shows that the percentage of fatalities of explosion from the reactor happens at Plant1 and Plant 3 has 100% value for all types of injury. That is means that the Plant 1 and 3 has highest risk that can harm human and animal or living things. However, for plant 2, the percentage of fatalities is quite high but nit as much as Plant 1 and Plant 3. This is because the percentage of fatalities of death from lung hemorrhage is 0% but, the for eardrum rupture, structural damage and glass breakage are 64%, 99.8% and 100% respectively. Therefore, Plant 2 also can be considered as risky simulated plant based on the explosion case.

However, when comparing from all the risk aspect of the plants, it shows that Plant 1 is the highest because the plant have the highest total percentage of fatalities which are 472%, followed by Plant 3 that have 407% of fatalities and lastly Plant 2 that have 263.8% of fatalities.

IV. CONCLUSION

Plant 1 had been proven as the methanol production plant with the most risk because of its process condition involve as the collected percentage of fatalities for 6 types of injury after 3 incident happen which are fire, explosion and toxicity. However, the toxicity's and the fire's types of injury and fatalities does not affect any human being and animals. This is because the low range

of mass released of hydrogen and carbon dioxide gas, which are 0.2942 to 6,845 g/s for hydrogen, [17] and 1.894 to 47.343 ppm, [18]. Same as the other plants only is affected by explosion, not by toxicity and fire because of low mass released of hydrogen and carbon dioxide gas.

So, it can be concluded that the volumetric feed does affect the safety analysis for Power to Methanol production plant.. The higher the volumetric feed of the production plant, the higher the total risk that has to be faced by the workers in the production plant and surrounding as Plant 1 have higher volumetric feed of carbon dioxide and hydrogen gas. From the results that obtained after the safety aspect of the plants has been analyzed, it would be suggested that this power to methanol is established in the larger scale but the storage of the hydrogen need to be in not extreme condition after produced by alkaline electrolysis, acid proton exchange membrane electrolysis and electrolysis of steam within a solid oxide electrolysis cell, [3]

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