

Fatality assessment for high pressure reactor of methanol production plants from CO₂ hydrogenation

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Abstract

New technology emerges for carbon dioxide hydrogenation where captured carbon dioxide reacts with hydrogen for methanol production using high pressure condition up to 442 bar. The research on high pressure process focus on how much percentage of carbon dioxide and hydrogen converted, accompanied with how much percentage of methanol selectivity. There is no comprehensive study on safety, especially in term of consequences to human fatalities if incident occurred at this high-pressure plant. Therefore, the purpose of this paper is to assess percentage of fatalities occur for reactor methanol (MeOH) plant operates at high pressure of 442 bar. It studies the possibility on (i) various events occurred in term of toxicity, thermal radiation, and overpressure; and (ii) estimation of percentage of fatalities when all that events occurred in comparison with reference plant operating at reactor pressure of 76 bar. Process plant is simulated using HYSYS and the obtained mass density of mixture, mass fraction, and volume fraction of chemical are used to calculate amount of toxicity (ppm), thermal radiation (kW/m²), and overpressure (psi) using consequence model simulated in ALOHA software. Threat zones generated by ALOHA software are then exported to the MARPLOT software to observe the area affected by the case study. The studied methanol reactor releases chemical mixture consists of hydrogen, carbon dioxide, MeOH, carbon monoxide (CO), and water, which only water is not considered as hazardous material. The release of chemical mixture observed for 10 mm, 25 mm, and 160 mm leakage, simulated at day and night conditions. The result for plant that operates at pressure of 442 bar has the highest severity of 44% fatality, which comes from the event of flammable methanol jet fire at daytime, leakage of 160 mm hole size. Meanwhile, for plant operating at 76 bar, the highest fatality is 27%, occurred from toxicity release of carbon dioxide at nighttime, leakage of 160 mm hole size.

Article Info

Article history:

Received date: 24 March 2019

Accepted date: 03 May 2019

Keywords:

Fatality assessment
High pressure methanol
production plant
Incidents
Area affected
Percentage fatalities

1.0 Introduction

Global temperature has increased rapidly for the past 50 years (MacMillan, 2016). By definition, global warming means the rise of Earth's average atmospheric temperature that makes changes in the climate temperature due to the greenhouse effect, where greenhouse effect refers to the heating phenomenon of the atmosphere that traps heat radiating from earth towards the space. Water vapour, carbon dioxide, methane, and nitrogen oxide are the gasses that act as thermal blanket for the Earth to absorb heat and warm the Earth's surface (Lallanila, 2016). The most important component of the greenhouse gases is carbon dioxide.

In 2015, 195 countries have agreed on a plan to reduce the emissions of CO₂ and other greenhouse gases at the United Nations Climate Change Conference held in Paris, with the aim to reduce the temperature of Earth where the increase should not be more than 2 °C (Anderson et al., 2016). As fossil fuels are burnt, the

concentration of CO₂ also increases by the year, which result in the warming of the planet and increases the natural greenhouse effects (Anderson et al., 2016). In 2013, 58% of the CO₂ from human source is contributed by the burning of fossil fuels, cement production and deforestation, as a result of human activities. There are also natural sources of CO₂, which are decomposition, ocean release, and respiration. Since the Industrial Revolution, the concentration of CO₂ of the atmosphere has risen extensively and reached a dangerous level (Levin, 2013).

Solutions for this problem have been found including energy efficient renewable energy production and CO₂ capture and storage (CCS). CCS is an effective strategy to reach CO₂ mitigation target while sustaining the source of energy supply. To make the CCS practicable, economical methods to capture CO₂ from flue gases of power plants and to store the captured CO₂ are needed (Liu et al, 2012). One of the most profound, practical methods for CO₂ capture is chemical absorption due to

the availability of the solvent and established techniques (Ikmal et al., 2016). After capturing the CO₂, it is then transported to suitable sites for storage such as deep oceans, depleted oil reservoir, and deep saline aquifers.

Other than CCS, there is another method for carbon capture called carbon captured and utilisation (CCU). In CCU, when the CO₂ has been captured, it needs to be utilised. One of the CO₂ utilisations is to produce methanol (MeOH). MeOH is an important chemical in the chemical industry, where it can further produce other chemicals such as formaldehyde and acetic acid that are used to produce various products, for instance, washer fluid, solvents, and subfloors. In this production, methanol is produced by reacting hydrogen (H₂), that comes from water electrolysis with CO₂ from the flue gas that had been captured (Bellotti et al., 2017). The production of methanol involved reaction between CO₂ and H₂ as raw material with catalyst of Cu/ZnO/Al₂O₃. This reaction is called as CO₂ hydrogenation, where the products of this reaction are methanol and water, with carbon monoxide (CO) as the by-product.

Safety is a very important study in plant construction. A quantitative safety study is conducted using fatality assessment (FA). The FA permits the quantification of the severity of an installation in order to deliver data for their acceptance. It also helps in making decisions and arrangement of choices so as to reduce unacceptable ones. It shows the risk caused by some activities and gives related evidence about the acceptability of the activity to the competent authorities (Di Domenico et al., 2014). Therefore, the use of CO₂ as raw material needs a thorough safety study since CO₂ can be hazardous because it exhibits a level of toxicity that may lead to the occurrence of major accidents (Wilday et al., 2009).

The study of methanol production at high pressure condition up to 442 bar from CO₂ hydrogenation has been conducted for lab scale experiments (Gaikwad et al., 2016) but they only analysed on the methanol selectivity, conversion of CO₂ and H₂ without considering the safety assessment. Another assessment, at production scale methanol plant has been proposed by Van-Dal and Bouallou (2013) with another effort by Pérez-Fortes et al. (2016), however, their research limited to the economic and energy assessment, at 76 bar pressure condition with no safety related assessment at higher pressure (pressure more than 76 bar). Therefore, the purpose of this paper is to simulate high pressure methanol production plant using 76 bar and 442 bar in the reactor, and to assess the fatalities of the methanol production plant.

2.0 Methodology

Two plants producing methanol from CO₂ hydrogenation in Seri Manjung, Perak were simulated using simulator software (Aspen HYSYS) with different conditions before entering the reactor. The conditions for Plant 1 are 76 bar with outlet temperature of 288 °C and Plant 2 at 442 bar with outlet temperature of 288 °C.

2.1 Plant location

This plant is suggested to be built in Seri Manjung, 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 Fig. 1.

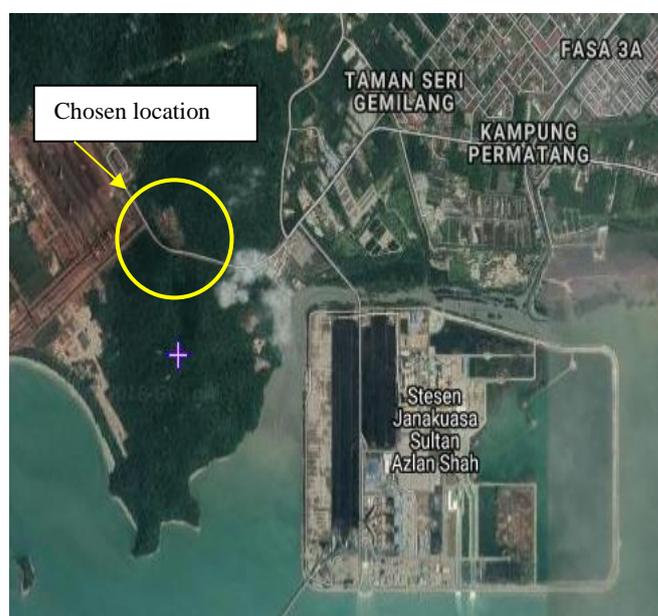
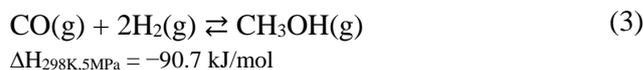
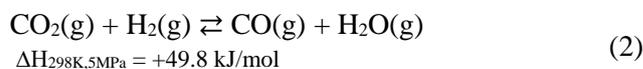
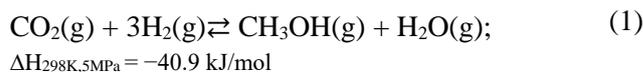


Fig. 1: Location chosen to build the plant in Manjung, Perak.

2.2 Process plant description

To produce methanol in this plant, a one-step reaction, that is the hydrogenation of CO₂, is employed; the equation is as in the Eq. (1), (2), and (3). The raw material is the CO₂ that had been captured from the flue gas of power plant by post-combustion method, while H₂ is from the electrolysis of water, where the water molecule is broken down into hydrogen and oxygen. The catalysts used in this reaction were Cu/ZnO/Al₂O₃.



2.3 Meteorological data of selected location

The meteorological data for Manjung was assessed using weather station at Sitiawan, a small district in Manjung. Table 1 shows the meteorological data used to simulate events occurred for all case studies. Wind direction of W means that the wind coming from West direction to East direction, SSW (south-southwest) direction to NNE (north northeast) and WNW (west-northwest) to ESE (east-southeast).

Table 1: Meteorological data of Manjung, Perak.

Period	Air Temp. (°C)	Humidity (%)	Wind velocity (m/s)	Stability class	Wind direction
Day	29	84	2.23	B	W, SSW, WNW
Night	29	84	1.03	F	W, SSW, WNW

2.4 Properties of carbon dioxide

Carbon dioxide is the molecule that occurs naturally, which consists of one carbon atom and two oxygen atoms with the formula of CO₂. CO₂ is a colourless and odourless molecule with a molecular weight of 44.01 g/mole. It is a non-flammable molecule and is stable under atmospheric condition. CO₂ 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 CO₂ are −56.56 °C and −78.46 °C, respectively. The density and vapour pressure of CO₂ at 20 °C are 1.84 g/L and 56.5 atm, respectively. It reacts vigorously with substance such as ammonia and amines. Carbonic acid can be produced when CO₂ dissolves in water, which can lead to corrosion effect on carbon steel and a few non-ferrous metals (Linde AG, 2001).

2.5 Properties of hydrogen

Hydrogen is the simplest chemical molecule. It consists of two hydrogen atoms that bonded together and has the formula of H₂. Hydrogen is a colourless and odourless gas that has a molecular weight of 2.02 g/mole. It is highly flammable and has the auto ignition temperature of 500 °C. The melting and boiling point is −259.20 °C and −252.76 °C, respectively. The lower flammability limit and upper flammability limit are 4 and 75 vol.%, respectively.

Since it is highly flammable, hydrogen needs to be kept away from any heat, sparks, and open flame to avoid ignition. In order to move the hydrogen cylinders, the cylinder must not be dragged or rolled over; instead, an appropriate hand truck is to be used. The hydrogen

cylinder has to be carefully connected with the utilisation equipment prior to opening the valve. This is to ensure that the hydrogen gas will not escape to the atmosphere since it has very light molecules that can disperse easily (Overview, 2003).

2.6 Properties of methanol

Methanol or methyl alcohol has a chemical formula of CH₃OH. It is the simplest form of alcohol from a group of organic chemicals. Methanol has the physical structure as liquid that is colourless, volatile, flammable and soluble in water.

The molecular weight of the methanol is 32.04 g/mol 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 while the boiling point is 64.5 °C that is below the boiling point of water. The pH value is 7.2, which makes it a slightly alkaline chemical with a density of 0.79 g/m³ at 25 °C. The auto-ignition temperature is 464 °C, where it is the lowest temperature in the normal atmosphere that ignites spontaneously without external source of ignition. The heat of combustion and heat of vaporisation at 25 °C are 726.1 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 vaporisation is the measure of heat that needs to be absorbed if a certain quantity of liquid is vaporised 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 vol.% and 36 vol.%, respectively.

Methanol is a very reactive substance and according to the material safety data sheet (MSDS), methanol is a toxic substance when exposed at high concentrations. 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 out methyl hypochlorite, a substance that may explode when exposed to sunlight or heat (Components and Limits, 2001).

2.7 Properties of carbon monoxide

Carbon monoxide is a colourless, odourless gas. Prolonged exposure to carbon monoxide rich atmospheres may be fatal. It is easily ignited. It is just lighter than air and a flame can flash back to the source of leak very easily. Under prolonged exposure to fire or

intense heat the containers may violently rupture and rocket.

Inhalation causes headache, dizziness, and weakness of limbs, confusion, nausea, unconsciousness, and finally death. Inhalation of 0.04% concentration of CO for 2–3 hours or 0.06% concentration in one hour can cause headache and discomfort. Meanwhile, 0.1–0.2% will produce throbbing in the head in about half an hour, a tendency to stagger in about one and half hour, and confusion, headache, and nausea in about two hours. A 0.20–25% CO concentration usually produces unconsciousness in about half an hour. Inhalation of a 0.4 % concentration can prove fatal in less than one hour while inhalation of higher concentrations can cause sudden, unexpected collapse. Contact of liquid with skin will cause frostbite. (USCG, 1999).

2.8 Consequence model equation

In order to assess fatalities, the consequences incidents predicted from the leakage of reactor vessel must be identified. The consequences incidents of gas mixture (CO₂-H₂-MeOH-CO-H₂O) release to the atmosphere that could occur are toxic dispersion, vapour cloud explosion, and fire.

2.8.1 Toxic release dispersion

Toxic release dispersion related to the concentrations of a downwind release in which the gas is mixed with fresh air to the point that the resulting mixture can be evaluated using neutrally buoyant dispersion models. There are two common types of neutrally buoyant vapour cloud dispersion models, namely the plume model and the puff model. 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 (Daniel and Crowl, 2013).

Eq. (4) is the basis for the dispersion model, where it can solve variety of cases. For this model, the coordinate system was used, where the x-axis is the centreline directly downwind from the release point and is rotated for different wind directions, while the y-axis is the distance off the centreline, and the z-axis is the elevation above the release point (Daniel and Crowl, 2013).

$$\frac{\delta C}{\delta t} + u_j \frac{\delta C}{\delta x_j} = \frac{\delta}{\delta x_j} \left(K_j \frac{\delta C}{\delta x_j} \right) \quad (4)$$

From Eq. (4), 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. This form a specific case for it to be calculated. One case of puff and one case of plume will be studied. The case of puff studied is puff with instantaneous point source at ground level with its coordinates fixed at release point, constant wind only in x-direction with constant velocity, u as in Eq. (5), while plume studied is plume with continuous steady state source at ground level and wind moving in x-direction at constant velocity Eq. (6).

$$\langle C \rangle(x, y, z) = \frac{Q_m}{\sqrt{2\pi^{3/2}} \sigma_x \sigma_y \sigma_z} \quad (5)$$

$$\langle C \rangle(x, y, z) = \frac{Q_m}{\pi \sigma_y \sigma_z u} \quad (6)$$

2.8.2 Vapour cloud explosion

Vapour cloud explosion (VCE) is a phenomena which a reaction front moving outward from the ignition source preceded by a shock wave or pressure front that will result 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 (Daniel and Crowl, 2013). The overpressure will cause the explosion to occur and can be predicted using the equivalent mass of TNT and the distance from point of explosion, r, as in Eq. (7). Thus, the overpressure can then be calculated using Eq. (8).

$$z_e = \frac{r}{m_{TNT}^{1/3}} \quad (7)$$

$$p_s = \frac{p_o}{p_a} = \frac{1616 \left[1 + \left(\frac{z_e}{4.5} \right)^2 \right]}{\sqrt{1 + \left(\frac{z_e}{0.048} \right)^2} \sqrt{1 + \left(\frac{z_e}{0.32} \right)^2} \sqrt{1 + \left(\frac{z_e}{1.35} \right)^2}} \quad (8)$$

2.8.3 Flash fire

Fire and explosion are accidents that commonly occur in the chemical plants, where the most common source is the organic solvents. Fire occur when fuel, oxidiser and ignition source exist simultaneously. From Eq. (9), I_e is the effective radiation intensity (W/m²), Q_m is the mass release (kg), and r, is the distance from source of fire (m).

$$\langle C \rangle(x, y, z) = \frac{Q_m}{\pi \sigma_y \sigma_z u} \quad (9)$$

2.8.4 Jet fire

A jet fire, also referred to as a flame jet, occurs when a flammable chemical is rapidly released from an opening in a container and immediately catches on fire—much like the flame from a blowtorch. Thermal radiation is the primary hazard associated with a jet fire. Other potential jet fire hazards include smoke, toxic by-products from the fire, and secondary fires and explosions in the surrounding area. For the modelling approaches presented in this paper, it is assumed that the release hole can be approximated as a nozzle. The assumption of a vertical flame will provide a conservative result, since the vertical flame will provide the largest radiant heat flux at any receptor point. Mudan and Croce (1988) provide review of jet flame modelling, begins with the calculation of the height of the flame. The flame height is given for turbulent gas jets burning in still air by Eq. (10);

$$\frac{L}{d_j} = \frac{5.3}{C_T} \sqrt{\frac{T_f}{T_j} \left[C_T + (1 - C_T) \frac{M_a}{M_f} \right]} \quad (10)$$

where;

- L = length of the visible turbulent flame measured from the break point (m)
- d_j = diameter of the jet, that is the physical diameter of the nozzle (m)
- C_T = fuel mole fraction concentration in a stoichiometric fuel-air mixture (unitless)
- T_p, T_j = adiabatic flame temperature and jet fluid temperature, respectively (K)
- α_T = moles of reactant per mole of product for a stoichiometric fuel-air mixture (unitless)
- M_a = molecular weight of the air (mass/mole)
- M_f = molecular weight of the fuel (mass/mole).

The radiative flux at the receiver is determined from Eq. (11);

$$E_r = \tau_a Q_r F_p = \tau_a \eta \dot{m} \Delta H_c F_p \quad (11)$$

where;

- E_r = radiant flux at the receiver (energy/area-time)
- τ_a = atmospheric transmissivity (unitless)
- Q_r = total energy radiated by the source (energy/time)
- F_p = point source view factor, (length²)
- η = fraction of total energy converted to radiation
- \dot{m} = mass flow rate of the fuel (mass/time)
- ΔH_c = energy of combustion of the fuel (energy/mass).

The view factor is given by Eq. (12);

$$F_p = \frac{1}{4\pi x^2} \quad (12)$$

where x is the distance from the point source to the target (length).

2.8.5 Level of concern for every incident

Level of concern (LOC) for every incident outcome must be determined for every chemical release involved. It is to categorise the incident into fatal or non-fatal. For methanol toxicity, the LOC is determined by Acute Exposure Guideline Level (AEGL) where there are categories namely AEGL-3, AEGL-2 and AEGL-1. AEGL-3 is the airborne concentration which can cause death within 60 minutes of exposure, while AEGL-2 is the airborne concentration which can cause serious health problem. AEGL-1 categorise for the concentration that can cause minor health problem. The concentration for methanol for AEGL-3, AEGL-2, and AEGL-1 is 7200 ppm, 2100 ppm, and 530 ppm, respectively.

Meanwhile, for CO toxicity, the LOC measurement also refer to AEGL to determine category of severity. The concentration for CO for AEGL-3 and AEGL-2 is 330 ppm and 83 ppm, respectively, while no AEGL-1 value is recommended.

For value of toxicity of CO₂, the only LOC is immediately dangerous to life or health (IDLH), which only has one category, causing death to the people. A chemical's IDLH is an estimate of the maximum concentration in the air to which a healthy worker could be exposed without suffering permanent or escape-impairing health effects. The concentration of CO₂ that can cause fatality or death is 40,000 ppm.

The LOC used for VCE incident is determined by the level of overpressure received by receptor at certain location. The LOC for overpressure is categorised into red, orange, and yellow threat zone. The red threat zone is for the overpressure value of 8 psi and above, which can cause destruction of building. The orange threat zone, refers to a condition that can cause serious injury, with overpressure values between 3.5 and 8 psi. For the overpressure value between 1 and 3.5 psi, it is categorised into the yellow threat zone, which causes shatter of glass. Lastly, for determination of incident involving jet fire, fireball, pool fire and BLEVE, the LOC is determined by level of thermal radiation received by receptor at certain location. The LOC for thermal radiation is categorised into red, orange and yellow threat zone. The red threat zone is the value radiation of 10k W/m² and above, which can cause death to people within 60 seconds. The orange threat zone, which can

cause second degree burn, has range between 3.5 to 10 kW/m². The yellow threat zone, which value is from 2 to 3.5 kW/m², can cause pain within 60 seconds of exposure.

2.8.6 Fatality assessment

Exposure such as toxicity, thermal radiation, and overpressure can be computed from area footprint in the simulation using ALOHA software. Area affected from the footprint will be the basis to calculate percentage fatality. Results from ALOHA will be exported to MARPLOT software to calculate the area affected zone by case studies. The events are considered fatal when the area affected is on the red zone threat. The ALOHA and MARPLOT software would demonstrate and computed red, orange and yellow threat zone for these events which the red threat zone is considered fatal and other threat are considered non-fatal.

Fig. 2 provides detail of methanol production plant layout which has process area, workshop, administration, control room, tankage, utilities and flare. The areas affected in the footprint, which is calculated using MARPLOT, are then divided by total area of specific location to get the amount of percentage fatality. For example, the area affected footprint is located at process area zone which covered 12,000 ft². The total area for process area zone is 120,000 ft². Therefore, the percentage fatality calculated is 12,000 ft²/120,000 ft², which is 10%.

3.0 Results and discussion

3.1 Conditions for plant of 76 bar and 442 bar

Fatality assessments to these plants are based on mass density, volume fraction, and mass fraction of individual chemical in the mixture of CO₂-H₂-MeOH-CO- H₂O. The first plant has a pressure of 76 bar and temperature of 288 °C, and the second plant operated at a pressure and temperature of 442 bar and 288 °C, respectively. The feed stream of CO₂ is 80,500 kg/hr with a pressure of 1 bar and temperature at 25°C, while H₂ feed is 11,000 kg/hr with a pressure of 30 bar and temperature is the same as the CO₂ stream. With a series of compressors and intercooling, the CO₂ is compressed to 76 bar, while H₂ is compressed in a single stage to 76 bar.

The reactor is packed with a fixed bed of 44,500 kg of catalyst. The product leaving the reactor is then further transferred into separator and distillation column. Plant 1 process condition is referred to simulation work by Perez Fortes et al. (2016) and Van dal & Bouallou

(2013). The condition of each plant is tabulated in Table 2. Figure 3a and 3b provides process flow diagram of Plant 1 and 2. Meanwhile, Table A1 and A2 in Appendix A shows the process condition of Plant 1 and 2 which has mass flowrate, temperature, pressure, vapor fraction, and weight fraction for every stream. Plant 2 has been modified with added coolers and compressors to accommodate pressure condition to reactor of 442 bar.

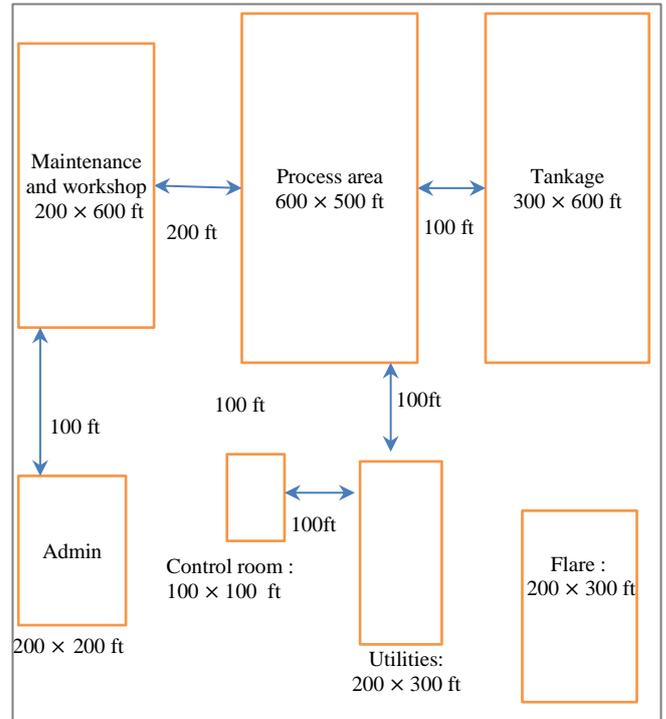


Fig. 2: Plant layout of methanol plant.

Table 2: Process conditions of Plant 1 and 2.

Parameters	Plant 1	Plant 2
Raw material (kg/h)	H ₂ : 11,000	H ₂ : 11,000
	CO ₂ : 80,500	CO ₂ : 80,500
Temperature inlet of reactor (°C)	210	210
Temperature outlet of reactor (°C)	288	288
Pressure reactor (bar)	76	442
Volume of reactor (m ³)	42	42
Density of mixture (kg/m ³)	20.9	346
Volume of each component (m ³)	CO: 2.1	CO: 0.04
	CO ₂ : 11.4	CO ₂ : 1
	H ₂ O: 1.2	H ₂ O: 9.1
	H ₂ : 24.4	H ₂ : 6.4
	MeOH: 3	MeOH: 25.5
	CO: 88.4	CO: 14.4
Mass of each component (kg)	CO ₂ : 505.3	CO ₂ : 401.2
	H ₂ O: 62.1	H ₂ O: 4295.2
	H ₂ : 91.5	H ₂ : 212.7
	MeOH: 129.5	MeOH: 9,616

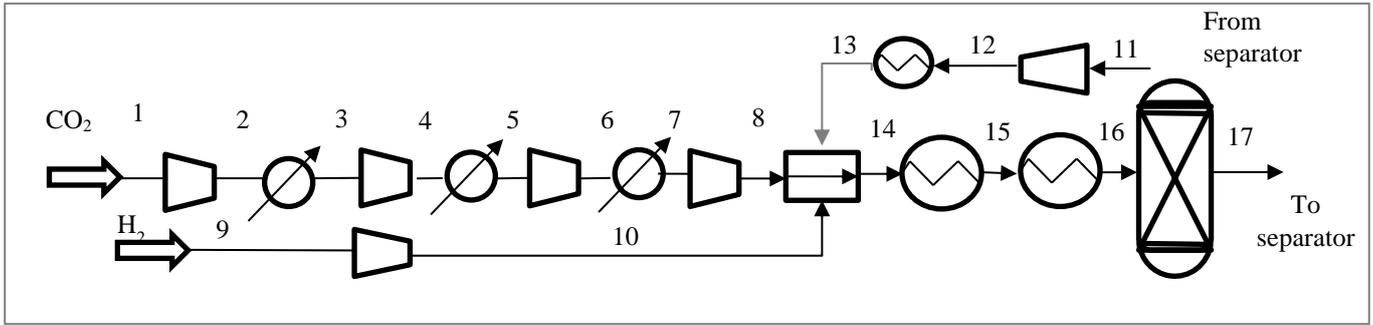


Fig. 3a: Process flow diagram of Plant 1.

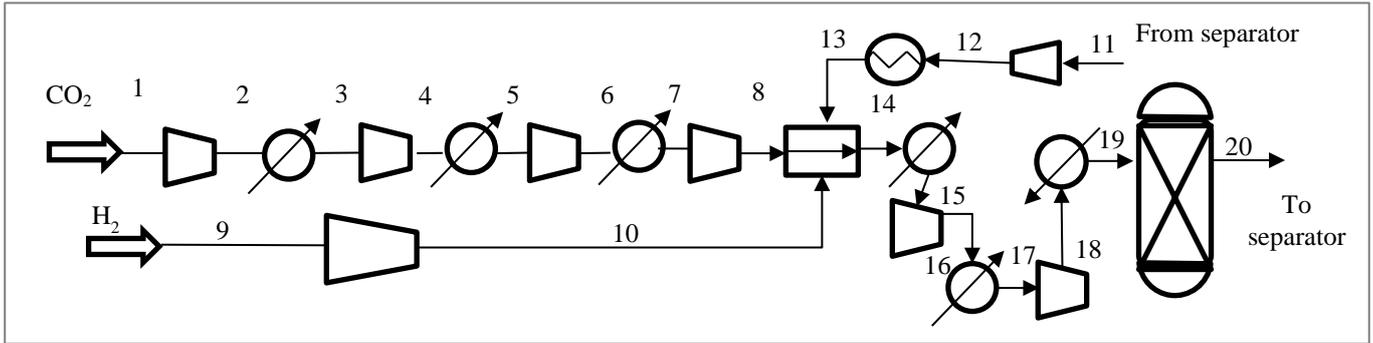


Fig. 3b: Process flow diagram of Plant 2.

3.2 Percentage fatalities of plant 76 bar

There are 54 initiating events occurred at Plant 1 which has minimum 1% fatality. Table 3 presents the list of initiating events occurred and their subjected fatalities. The incident involved all chemicals in the mixture CO₂-H₂-MeOH-CO-water minus water. The most severe event involved release of CO₂ toxic at W and WNW direction, which has 27% fatalities, followed by CO₂ release from SSW, contributed 26% fatalities. All these events occurred at night with leakage is catastrophic failure of vessel, 160 mm.

Another scenario involved CO₂, which was leakage of 25 mm at night, contributes among higher fatalities which are 13%. Second chemical with serious cause for higher fatalities is scenario involved CO, which has 9, 10, 12, and 13% fatalities. This scenario occurred at wind direction W, WNW and SSW, with leakage of 25 mm and 160 mm – day and night conditions.

Hydrogen contributes to two incident outcome cases that cause fatalities, which are vapour cloud explosion (VCE) and jet fire. 9% fatalities caused by VCE of H₂ at instantaneous release from 160 mm leakage at day period while 8% fatalities occurred at night.

Another incident of H₂'s VCE from continuous release at 25 mm leakage causes 6% fatality for day and night. All of the events involved methanol only caused for 1% fatalities involving jet fire and toxicity. The toxicity incident for methanol which could cause 1% fatality occurred at night involved instantaneous release of 160 mm leakage.

Fig. 4 shows the area affected footprint from WNW wind direction, for the instantaneous release of CO₂, at night. The footprint was affected about 27 % of processing plant area, which is bounded by the red line rectangle zone. The diamond symbol is the point where the leakage of the vessel located. The longest red threat zone located at 66 meter from point source to the east south-east (ESE). The area affected calculated within process area boundary is 80,912 ft².

Fig. 5 shows the puff footprint from the instantaneous release of CO, at day, in SSW direction. It was affected about 8% of processing plant area, and 5% of workshop area, totalling fatalities of 13% for this event. The area affected calculated is 23,589 ft² at the processing area while 6,244 ft² at workshop area.

Fig. 6 shows the area affected footprint from W wind direction, for the instantaneous release of H₂, at daytime. The footprint was affected about 8% of processing area, which is bounded by the red line rectangle zone. The longest red threat zone is located at 35 meter from point source to the east. The area affected calculated within process area zone boundary is 26,615 ft².

Fig. 7 shows the area affected footprint, for the instantaneous release of MeOH, at day. The footprint was affected about 1 % of processing plant area, which is bounded by the red line rectangle zone. The longest red threat zone located at 10 meter from point source at all wind direction. The area affected calculated within processing area boundary is 3,445 ft².

Table 3: Initiating events percentage fatalities at plant of 76 bar.

	Chemical	Event	Wind direction	Leakage (mm)	Period	Fatality (%)
1	CO ₂	Toxic	W	160	night	27
2	CO ₂	Toxic	WNW	160	night	27
3	CO ₂	Toxic	SSW	160	night	26
4	CO ₂	Toxic	SSW	25	night	13
5	CO ₂	Toxic	WNW	25	night	13
6	CO ₂	Toxic	W	25	night	13
7	CO	Toxic	SSW	160	day	13
8	CO	Toxic	SSW	25	day	12
9	CO	Toxic	WNW	25	night	10
10	CO	Toxic	WNW	160	day	9
11	CO	Toxic	W	25	night	9
12	CO	Toxic	WNW	25	day	9
13	H ₂	VCE	WNW	160	day	9
14	H ₂	VCE	SSW	160	day	9
15	H ₂	VCE	W	160	day	9
16	CO	Toxic	SSW	25	night	9
17	H ₂	VCE	W	160	night	8
18	H ₂	VCE	SSW	160	night	8
19	H ₂	VCE	WNW	160	night	8
20	CO	Toxic	W	160	day	8
21	CO	Toxic	W	25	day	8
22	CO	Toxic	WNW	10	day	7
23	CO	Toxic	W	10	day	7
24	CO	Toxic	WNW	10	night	6
25	CO	Toxic	SSW	10	day	6
26	H ₂	VCE	SSW	25	night	6
27	H ₂	VCE	W	25	night	6
28	H ₂	VCE	WNW	25	night	6
29	H ₂	VCE	SSW	25	day	6
30	H ₂	VCE	W	25	day	6
31	H ₂	VCE	WNW	25	day	6
32	CO	Toxic	W	10	night	6
33	CO	Toxic	SSW	10	night	5
34	H ₂	Jet fire		160	night	4
35	H ₂	Jet fire		160	day	4
36	H ₂	VCE	W	10	night	4
37	H ₂	VCE	WNW	10	night	4
38	H ₂	VCE	SSW	10	night	4
39	H ₂	VCE	W	10	day	3
40	H ₂	VCE	SSW	10	day	3
41	H ₂	VCE	WNW	10	day	3
42	CO	Toxic	WNW	160	night	3
43	CO	Toxic	W	160	night	3
44	CO	Toxic	SSW	160	night	2
45	MeOH	Jet fire		160	day	1
46	MeOH	Jet fire		160	night	1
47	MeOH	Jet fire		25	night	1
48	MeOH	Jet fire		25	day	1
49	MeOH	Toxic	SSW	160	night	1
50	MeOH	Toxic	W	160	night	1
51	MeOH	Toxic	WNW	160	night	1
52	MeOH	Toxic	SSW	25	night	1
53	MeOH	Toxic	WNW	25	night	1
54	MeOH	Toxic	W	25	night	1



Fig. 4: Puff dispersion at Plant 1–release of CO₂ at night, 160 mm leakage, 27% fatalities (from WNW wind direction).



Fig. 5: Puff dispersion at Plant 1 –release of CO at day, 160 mm leakage, 13% fatalities (from SSW wind direction).

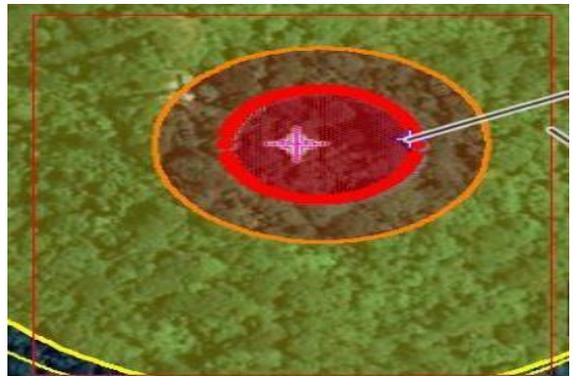


Fig. 6: Footprint of VCE from H₂, Plant 1–day, 160 mm leakage, 9% fatalities (from W wind direction)



Fig. 7: Footprint of jet fire from MeOH, Plant 1–day, 160 mm leakage, 1% fatality

3.3 Percentage fatalities of plant 442 bar

There are 57 initiating events occurred at Plant 2 which has minimum 1% fatality. The incident involved all chemicals in the mixture CO₂-H₂-MeOH-CO-H₂O minus water. Table 4 presents the list of initiating events occurred and their subjected fatalities. The most severe event involved release of MeOH jet fire event at day, which has 44% fatalities, followed by the same event at night, contributed 42% fatalities. These two events occurred with leakage are catastrophic failures of vessel, 160 mm.

Toxic event for MeOH also caused fatalities which are 4% at day and 2% at night, leakage from continuous release of 25mm hole size diameter. Second chemical with serious cause for higher fatalities is scenario involved CO₂, which caused 23 to 25% fatalities. This scenario occurred at wind direction W, WNW and SSW, with leakage of 25 and 160 mm at night condition.

Hydrogen contributes to two incident outcome cases that cause fatalities, which are vapour cloud explosion (VCE) and jet fire. 15% fatalities caused by VCE of H₂ at continuous release from 25 mm leakage at day period while 14% fatalities occurred at night. Another incident of jet fire for day and night involved 10 % fatalities. All of events involved CO caused severity; the highest amounted to 7% fatalities at day from WNW wind direction decreased significantly compared to release events at Plant 1. Meanwhile, this severity reduced greatly at night accounted to 2%, as the footprint of puff release became thinner and further away from the source of released.

Fig. 8 shows the area affected footprint, for the instantaneous release of MeOH, at day. The footprint was affected about 44% of processing area, which is bounded by the red line rectangle zone. The longest red threat zone is located at 65 meter from point source at all wind direction. The area affected calculated within processing area boundary is 132,088 ft².

Fig. 9 shows the area affected footprint, for the continuous release of MeOH, 25 mm leakage, at day. The footprint was affected about 4 % of processing area, which is bounded by the red line rectangle zone. The longest red threat zone is located at 78 meter from point source to the north north-east wind location. The area affected calculated within processing area boundary is 11,142 ft².

Fig. 10 depicted the area affected footprint, for the continuous release of MeOH, 25 mm leakage, at night. The footprint was affected about 2% of fatalities, which is bounded by the red line rectangle zone.

Table 4: Initiating events percentage fatalities at plant of 442 bar.

	Chemical	Event	Wind direction	Leakage (mm)	Period	Fatality (%)
1	MeOH	Jet fire		160	day	44
2	MeOH	Jet fire		160	night	42
3	CO ₂	Toxic	W	160	night	25
4	CO ₂	Toxic	WNW	160	night	24
5	CO ₂	Toxic	SSW	160	night	24
6	CO ₂	Toxic	W	25	night	23
7	CO ₂	Toxic	WNW	25	night	23
8	CO ₂	Toxic	SSW	25	night	23
9	H ₂	VCE	W	25	day	15
10	H ₂	VCE	WNW	25	day	15
11	H ₂	VCE	SSW	25	day	15
12	H ₂	VCE	SSW	25	night	14
13	H ₂	VCE	WNW	25	night	14
14	H ₂	VCE	W	25	night	14
15	H ₂	Jet fire		160	day	10
16	H ₂	Jet fire		160	night	10
17	H ₂	VCE	SSW	10	day	8
18	H ₂	VCE	W	10	day	8
19	H ₂	VCE	WNW	10	day	8
20	H ₂	VCE	WNW	10	night	7
21	H ₂	VCE	SSW	10	night	7
22	H ₂	VCE	W	10	night	7
23	CO	Toxic	WNW	10	day	7
24	CO	Toxic	WNW	25	day	7
25	CO	Toxic	WNW	160	day	7
26	H ₂	Jet fire		25	night	6
27	CO	Toxic	W	10	day	6
28	CO	Toxic	W	25	day	6
29	CO	Toxic	W	160	day	6
30	H ₂	Jet fire		25	day	6
31	CO	Toxic	SSW	10	day	6
32	CO	Toxic	SSW	25	day	6
33	CO	Toxic	SSW	160	day	6
34	MeOH	Toxic	WNW	25	day	4
35	MeOH	Toxic	W	25	day	4
36	MeOH	Toxic	SSW	25	day	4
37	MeOH	Jet fire		25	day	3
38	MeOH	Jet fire		25	night	3
39	MeOH	Toxic	WNW	25	night	2
40	CO	Toxic	WNW	10	night	2
41	CO	Toxic	WNW	25	night	2
42	CO	Toxic	WNW	160	night	2
43	CO	Toxic	W	10	night	2
44	CO	Toxic	W	25	night	2
45	CO	Toxic	W	160	night	2
46	MeOH	Toxic	W	25	night	2
47	MeOH	Toxic	SSW	25	night	2
48	CO	Toxic	SSW	10	night	2
49	CO	Toxic	SSW	25	night	2
50	CO	Toxic	SSW	160	night	2
51	H ₂	Jet fire		10	night	2
52	H ₂	Jet fire		10	day	2
53	MeOH	Jet fire		10	day	1
54	MeOH	Jet fire		10	night	1
55	MeOH	Toxic	SSW	10	night	1
56	MeOH	Toxic	WNW	10	night	1
57	MeOH	Toxic	W	10	night	1

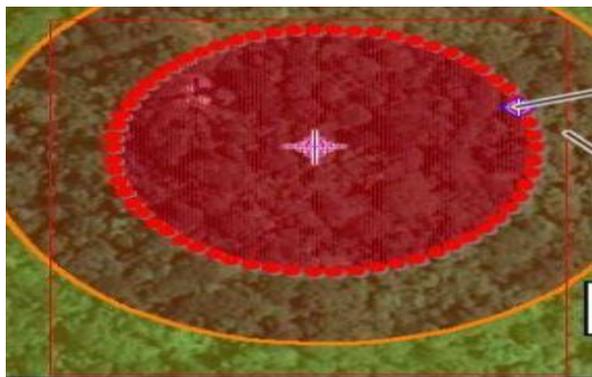


Fig. 8: Footprint of jet fire from MeOH, Plant 2–day, 160 mm leakage, 44 % fatality.

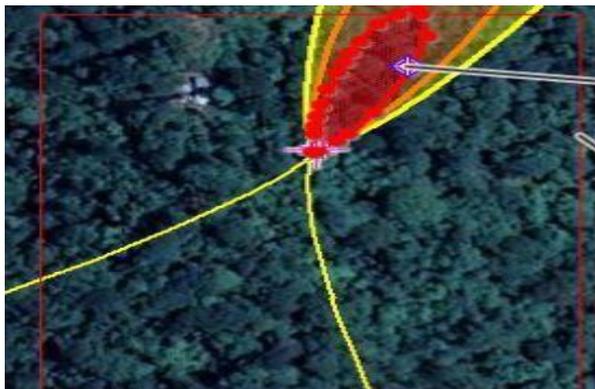


Fig. 9: Footprint of toxicity of MeOH, Plant 2–day, 25 mm leakage, 4% fatality (from SSW wind direction).

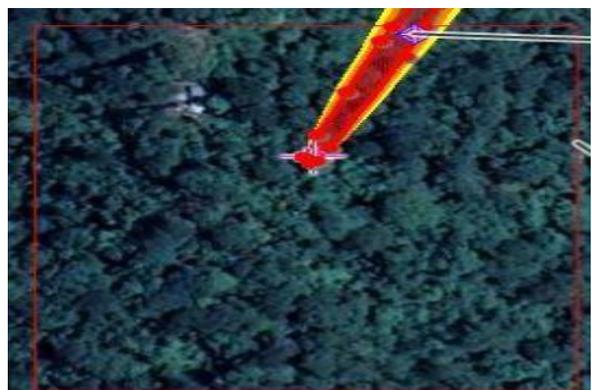


Fig. 10: Footprint of toxicity of MeOH, Plant 2– night, 25 mm leakage, 2% fatality (from SSW wind direction).

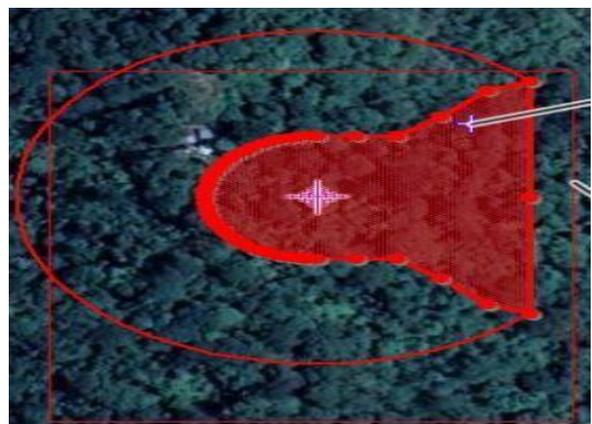


Fig. 11: Puff dispersion at Plant 2–release of CO₂ at night, 160 mm leakage, 25% fatalities (from W wind direction).

The longest red threat zone is located at 124 m from point source to the north-north-east wind location. The area affected calculated within processing area boundary is 6,508 ft².

Fig. 11 projected the area affected footprint from W wind direction, for the instantaneous release of CO₂, at night. The footprint was affected about 25% of processing area operators, which is bounded by the red line rectangle zone. The longest red threat zone located is at 62 m from point source to the east location. The area affected calculated within process area boundary is 74,021 ft².

Fig. 12 indicates the area affected footprint from WNW wind direction, for the continuous release, 25 mm leakage of H₂, at day. The footprint was affected 15 % fatalities, as the area covered for 15 % of processing area. The longest red threat zone located is at 45 meter from point source to the ESE location. The area affected calculated within process area zone boundary is 44,400 ft².

Fig. 13 shows the area affected footprint, for the instantaneous release, 160 mm leakage of H₂, at day. The footprint was affected 10 % fatalities, as the area covered for 10 % of processing area. The longest red threat zone located is at 30 m from point source to all wind direction location. The area affected calculated within process area zone boundary is 29,963 ft².

Fig. 14 and 15 shows the puff footprint from the instantaneous release of CO, at day, from SSW and WNW wind direction. The footprint of Fig. 14 was affected about 6% of processing plant area, but none of workshop area was affected, difference results from Plant 1. Meanwhile, Figure 15 has 7% fatalities from WNW direction, as the footprint affected the area located at ESE. The area affected calculated is 17,261 ft² and 20,008 ft² within processing area boundary for both CO events from SSW and WNW wind direction respectively.

3.4 Analysis of result

3.4.1 Toxic release

Toxic release involved CO₂, CO, and MeOH for both plants with 76 bar and 442 bar. The mass content of CO₂ is 505 kg and 401 kg with corresponding volume of 11.4 m³ and 1 m³ for both Plant 1 and Plant 2, respectively. Although the volume is greatly reduced with increasing pressure condition, the density of the mixture is 16.5 times higher for 442 bar, causing the mass of CO₂ almost unaltered. Therefore, the percentage fatalities for both plants are not much different, only about 2–4%.



Fig. 12: Footprint of VCE from H₂, Plant 2–day, 25 mm leakage, 15% fatalities (from WNW wind direction).

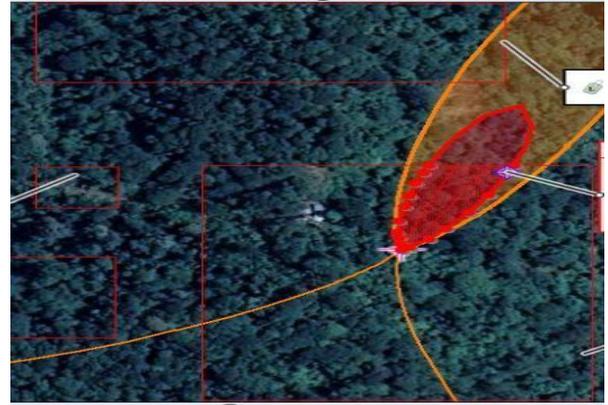


Fig. 14: Puff dispersion at Plant 2–release of CO at day, 160 mm leakage, 6% fatalities (from SSW wind direction).

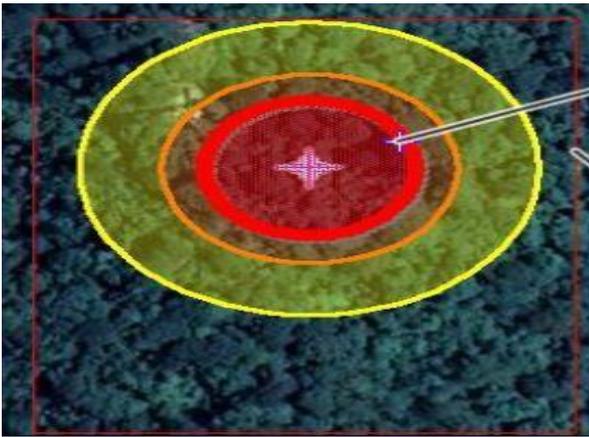


Fig. 13: Footprint jet fire of from H₂, Plant 2–day, 160 mm leakage, 10 % fatalities.

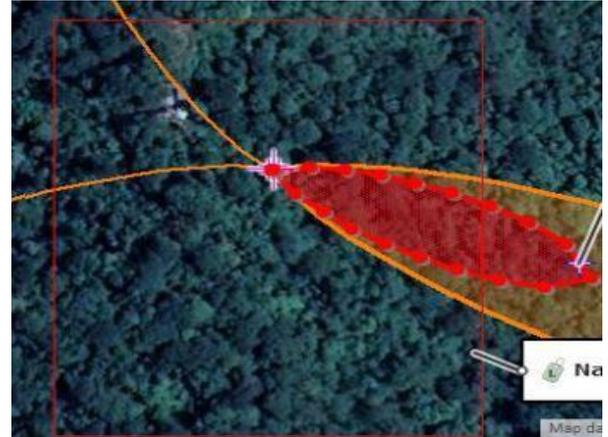


Fig. 15: Puff dispersion at Plant 2–release of CO at day, 160 mm leakage, 7% fatalities (from WNW wind direction).

In contrast, for CO, the effect of toxicity is greater for plant 76 bar because the mass of CO in vessel is 88.4 kg as compared to only 14.4 kg for plant operating at 442 bar. As a result, the amount released to atmosphere is greatly reduced, causing fatalities reduction almost two times for plant operating at 442 bar. It can be observed, for the release from SSW wind direction, where the footprint did not reach the workshop area for Plant 2, in comparison to Plant 1, 5% more fatalities at this workshop, as the footprint is longer and wider.

For MeOH, the amount of mass and volume contained in the vessel is multiplied 74 and 8.5 times, comparing 76 bar condition to 442 bar condition. This condition has substantial effect to the amount of percentage fatalities for both plants in term of toxicity effect. Plant 1 observed only 1%, while 4% fatalities occurred for Plant 2. The fatality caused from toxicity effect during daytime condition for Plant 2 is higher as compared to night condition because of the footprint has higher coverage area, although shorter footprint's length is observed. The night condition has the most stability wind (Class F) which wind speed is 1.03 m/s as

compared to daytime, which is 2.23 m/s. At night, wind with F stability tends to reach longer distance, while having reduced its concentration to left and right-side of the direction.

3.4.2 Vapour cloud explosion (VCE)

VCE incident only happens to the chemical hydrogen, as another flammable chemical, which is methanol; do not have enough concentration to produce area of fatality. The amount of mass increases, comparing between Plant 1 and 2, which are 92 kg and 213 kg, respectively, whereas the volume reduces from 24.4 to 6.4 m³. The mass is increased due to the density of mixture 20.9 m³ which rocketed up to 346 m³, causing mass of hydrogen increases more than double. The volume is decreased as more hydrogen is consumed to produce methanol, decreasing the amount of mole and affecting the volume of hydrogen itself in the mixture.

As a result of increasing mass containing hydrogen in the vessel, the amount of release to the atmosphere is also higher, causing more fatalities for Plant 2 as compared to Plant 1. Plant operating at pressure of 442

bar has 15% fatalities; almost double fatalities observed with plant of 76 bar, involving 9% fatalities. There are differences in 1% fatalities for day and night condition, as the VCE of hydrogen tends to cover wider area at daytime, while smaller area is at night. It is because the explosion characteristic is limiting as the wind is more stable at night, compared to slightly unstable wind at day.

3.4.3 Jet fire

Gas released from the vessel has the probability of causing jet fire after immediate ignition. Highly flammable chemical category such as hydrogen and methanol are subjected to jet fire events when continuous and instantaneous release occurred. CO is also considered as flammable but only as low flammable chemical, with probability of causing jet fire only 0.02. Therefore, in this case study, CO is not considered as having effect of jet fire in release scenario.

The quantity of chemical release for jet fire scenario would greatly affect the amount of area covered by footprint for each leakage size. The larger size of leakage, the greater percentage of fatalities. It can be observed by event when leakage of methanol from instantaneous release occurred. The percentage of fatalities observed is 44% in plant operating at 442 bar but reduced greatly to 1% for plant of 76 bar. The quantity of methanol is 9616 kg in the vessel of 442 bar pressure condition, compared to only 130 kg in vessel of 76 bar condition.

The same result of fatalities is observed to jet fire event involving hydrogen. The percentage fatality is 4% for 76 bar plant but increases to 10% for 442 bar plant. It is because the mass of hydrogen in the vessel increases due to higher density of mixture at high pressure.

4.0 Conclusions

The assessment in this work considers a potential of MeOH production using high pressure condition of 76 bar and 442 bar. Its process flow design, at a production scale, has been simulated in HYSYS, to extract the density, mass fraction, and volume fraction of chemical mixture in the reactor vessel in order to assess release characteristic of the chemicals. The amount of release is then evaluated using ALOHA in term of toxicity, thermal radiation and overpressure severity, transferring the footprint area affected into MARPLOT and calculated percentage fatality based on

area footprint.

Plant 1 with pressure condition of 76 bar has density mixture of 20.9 kg/m³ while Plant 2 with pressure condition of 442 bar has density mixture of 346 kg/m³. The mass and volume of chemical in the mixture in the reactor vessel are different for both plants. The volume of CO₂ decreases drastically from 11.4 m³ to 1 m³ as pressure changes from 76 bar to 442 bar but its mass is not much different, albeit reduces slightly from 505.3 to 401.2 kg. In contrast, the volume and mass of methanol in the mixture increase drastically 8.5 times and 74 times, respectively, from 76 bar to 442 bar. The mass of H₂ increases almost 3 times although its volume decreases almost 6 times from 76 to 442 bar. The amount of CO reduced in term of volume is more than 52 times and mass is more than 6 times as the pressure condition changes from 76 to 442 bar.

The highest percentage fatalities comparing both plants is the event of jet fire release at day time, from methanol leakage of 160 mm hole size diameter, resulting in 44% fatalities. The plant with pressure condition of 76 bar observed highest fatalities of 27%, which the instantaneous release of CO₂ toxicity at night is from leakage of 160 mm hole size diameter.

The change of pressure condition for the production of methanol plant from 76 to 442 bar caused more fatalities at 442 bar. It can be concluded that, for current condition, plant with 76 bar is safer compared to plant with 442 bar.

As future work, the same assessment will be applied to risk reduction measure applied to both plants, which is to reduce the volume of reactor and excluding recycle stream for both pressure conditions. The boundaries of the study will be expanded, to include more pressure condition above 76 bar and adding risk assessment by combining likelihood/frequency analysis.

Acknowledgement

The authors would like to acknowledge the Faculty of Chemical Engineering, Universiti Teknologi MARA (UiTM) and the Ministry of Education (MOE) for the 600-RMI/FRGS/5/3 (0094/2016) grant, for all the funding and support given in establishing this project.

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APPENDIX A

Table A1: Process conditions for Plant 1.

Stream number	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17
Plant 1																	
Mass flowrate (kg/h)	80,500	80,500	80,500	80,500	80,500	80,500	80,500	80,500	11,000	11,000	376,200	376,200	376,200	467,600	467,600	467,600	467,600
Pressure (bar)	1.01	3.44	3.25	9.94	9.78	23.31	23.15	76.6	30	76.6	74.3	78.5	78.3	78	77.22	76	75.5
Temperature (°C)	25	140.8	30	136.6	29	111.1	28	146.3	25	149.8	35	41	62	79	98	210	288
Vapor fraction	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1
Weight fraction																	
CO	0	0	0	0	0	0	0	0	0	0	0.14	0.14	0.14	0.12	0.12	0.12	0.1
CO ₂	1	1	1	1	1	1	1	1	0	0	0.71	0.71	0.71	0.75	0.75	0.75	0.58
H ₂ O	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0.1
H ₂	0	0	0	0	0	0	0	0	1	1	0.14	0.14	0.14	0.13	0.13	0.13	0.07
MeOH	0	0	0	0	0	0	0	0	0	0	0.01	0.01	0.01	0	0	0	0.15

Table A2: Process conditions for Plant 2.

Stream number	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18	19	20
Plant 2																				
Mass flowrate (kg/h)	80,500	80,500	80,500	80,500	80,500	80,500	80,500	80,500	11,000	11,000	376,200	376,200	376,200	467,600	467,600	467,600	467,600	467,600	467,600	467,600
Pressure (bar)	1.01	3.44	3.25	9.94	9.78	23.31	23.15	76.6	30	76.6	74.3	78.5	78.3	78	77.2	200	199.8	442.2	442	441.5
Temperature (°C)	25	140.8	30	136.6	29	111.1	28	146.3	25	149.8	35	41	62	79	38	163.6	38	138.2	210	288
Vapor fraction	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1
Weight fraction																				
CO	0	0	0	0	0	0	0	0	0	0	0.14	0.14	0.14	0.12	0.12	0.12	0.12	0.12	0.12	0.001
CO ₂	1	1	1	1	1	1	1	1	0	0	0.71	0.71	0.71	0.75	0.75	0.75	0.75	0.75	0.75	0.03
H ₂ O	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0.3
H ₂	0	0	0	0	0	0	0	0	1	1	0.14	0.14	0.14	0.13	0.13	0.13	0.13	0.13	0.13	0.01
MeOH	0	0	0	0	0	0	0	0	0	0	0.01	0.01	0.01	0	0	0	0	0	0	0.66