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Quantitative safety assessment for reactor size variation on high pressure methanol production

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Abstract

This work studied carbon capture utilization (CCU) to methanol synthesis, which analyses reactor size's impact on high-pressure methanol production. As high pressure poses a high probability of process vessel leakage, assessment on its potential hazardous chemical impact such as toxicity, fire, and explosion must be conducted. This study examines how reactor size affects high-pressure methanol plant accident scenarios due to different leakage sizes of reactors and at various day and night conditions. HYSYS was used in this investigation to identify significant chemical components at high pressures. The analysis only limited to four hazardous chemical components namely methanol, carbon dioxide, carbon monoxide, and hydrogen. Then, ALOHA specifies the principal chemical component for the worst-case accident scenario. MARPLOT was used to quantify the methanol plant's safety by utilising distance and area plot threat analysis for reactor size variation. The volume of the reactor used is 42, 20, and 5 m^3, with pressure conditions of 76, 184, and 331 bar, as the 10 mm, 75 mm, and 160 mm leakage size of the reactor has been simulated. The simulation in ALOHA was done by considering day and night conditions with one dominant wind direction according to the plant's location. The results show that the highest people affected incident was due to the toxic release of methanol from a 160 mm leak size during the night in Modified Plant 2. This scenario resulted in a percentage people affected for night conditions of 56.53%. This study is useful to predict worst-case people affected with variation for reactor size on high-pressure conditions.

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1.0 Introduction

Carbon capture utilisation (CCU) is the technique of capturing and recycling carbon dioxide (CO_2) (Cuéllar-Franca & Azapagic, 2015). The goal of carbon capture and utilisation (CCU) is not only to reduce the amount of pollution going into the air but also to get benefits from utilisation of CO_2 in different types of industrial processes to replace traditional raw materials (Baena-Moreno et al., 2019). CCU has been widely explored as a model for industrial transformation toward sustainability, particularly among European policy makers. Carbon dioxide captured can be transformed into various products, one of which is hydrocarbons, such as methanol, for use as biofuels and other alternative and renewable energy sources (Pérez-Fortes et al., 2016).

Currently, there is only one commercial Methanol (MeOH)−CCU plant in operation located in Iceland, where fossil-free electricity is cheaply available (Nyári et al., 2020). According to (Nyári, 2018), a MeOH plant simulation model using CO_2 and H_2 as feedstock was developed using Aspen Plus™. This is the first industrial-scale plant that has been studied in comparison to fossil MeOH plant units. Every day, the facility produces 5 kilotonne of chemical-grade MeOH, which can be utilised as a raw material in the chemical industry or as a fuel. Using both CO and CO_2 as carbon sources, the kinetic model achieved a high overall CO_2 conversion rate and near-stoichiometric raw material use. Even at this scale, the MeOH factory is not practicable under present market conditions. The high cost of hydrogen (H_2) produced by water electrolysis is the most critical cost characteristic that renders the plant unviable (Nyári, 2018).

The syngas generation side of the operation emits the majority of CO_2. The CO_2 captured will then be utilised in the production of methanol. CO and CO_2 are combined with H_2 to make methanol. Traditionally, this has been generated in a two-step process that includes the generation of syngas and methanol synthesis. Direct hydrogenation of CO_2 with H_2 or CO_2 conversion into CO and additional hydrogenation of CO are the two catalytic methods to synthesise methanol from CO_2 (Collodi et al., 2017). CO_2 is a generally inert and thermodynamically stable molecule. Its activation often necessitates the utilisation of energy inputs, such as elevated pressure and temperature, as well as practical tactics such as new catalytic processes. According to Le Châtelier's principle, high-pressure and low-temperature reaction conditions are ideal for achieving high CO_2 conversion and methanol selectivity. The methanol synthesis and Reverse Water Gas Shift (RWGS) kinetic model for both stages are based on the experimental works performed by Vanden Bussche and Froment (Khojasteh-Salkuyeh et al., 2021). The reactions that involve in methanol synthesis are:

$$CO_2 + 2H_2 \rightarrow CH_3OH \quad (1)$$

$$CO_2 + 3H_2 \rightarrow CH_3OH + H_2O \quad (2)$$

$$CO_2 + H_2 \rightarrow CO + H_2O \quad \text{(RWGS)} \quad (3)$$

The recent studies are about methanol production which uses high pressure with different gas hourly space velocity (GHSV) and molar ratios (Bansode & Urakawa, 2014; Gaikwad et al., 2016) achieve high conversion of carbon monoxide and hydrogen to methanol. One of the studies have been conducted on the relationship between high pressure and the chemical quantity of products. The maximum tested pressure of 442 bar, CO_2 can potentially be successfully produced to methanol (98.7% at 220 °C and 86.1% at 300 °C) including extremely high selectivity for the temperature range (> 99.9 percent at 220 °C and 99.0% at 300 °C) (Gaikwad et al., 2016).

The flammability of methanol and hydrogen, among some of the outputs to be consumed in the plant, should indeed be addressed (National Center for Biotechnology Information,2023a; National Center for Biotechnology Information, 2023b). At standard temperature and pressure, methanol and hydrogen gas are extremely flammable substances. As it generates a pale blue flame, hydrogen is almost undetectable (National Center for Biotechnology Information, 2023b). The exposure of carbon monoxide to the environment for a long term is surely very deadly (Hanley & Patel, 2023) while carbon dioxide is an asphyxiant gas when working in enclosed areas and poses a serious threat (National Center for Biotechnology Information, 2023c). It effectively eliminates so much oxygen from the external environment that haemoglobin in the blood is unable to gather adequate oxygen from the lungs to thoroughly oxygenate the tissues. Therefore, a detailed assessment must be done at an earlier stage to determine the level of plant safety through quantitative safety assessment.

Whenever safety is also to be integrated with the process designing phase, a study of the process's inherent safety qualities might offer a decent framework for such inclusion (Gupta & Edwards, 2002). According to Kletz (Mansfield et al., 1996) , the primary goal of inherent safety is to eliminate or minimise risks in a processing facility, thus reflecting considerably fewer levels and protective attachments such as substitution, moderation, and simplicity. Temperature and pressure have since been constructed by both to indicate inherent safety. This would be attributed to the reason that temperature is a direct measure of the heat energy present at the time of emission. Pressure is a measure of both the available energy for discharge and the energy required to trig-ger a rupture. The probable reactiveness is measured by chemical interaction in conjunction with the heat of the side reaction. The generation of flammable or toxic gas is an undesired side effect (Heikkilä, 1999).

Quantitative risk assessment (QRA) is a systemised risk evaluation technique for assessing the threats associated with an engineering process's operation. This helps enhance the outcome by identifying the accident events that have the greatest im-pact on total risk. This is designed to show that the suitability criteria were satisfied and that the residual hazards are as low as practically possible (Leonzio et al., 2020). The QRA goal is to verify engagement to safety guidelines as numerical probabilistic criteria, often known as an acceptable risk.

Safety of methanol plant can be categorised according toxic and flammability characteristic. Raw material such as carbon dioxide and carbon monoxide have only toxicity effect. Unreacted raw material such as hydrogen and product, which is methanol has toxic and flammability characteristic, thus resulting toxicity, flash fire, vapor cloud explosion and jet fire scenario. Toxic parameter for methanol has minimum range of 530 ppm, for people to become minor affected at Acute Exposure Guideline Level–1 (AEGL–1). For minimum thermal radiation, which is pain within 60 seconds, the level is 2 kW/m^2, while for overpressure, minimum level is shattered glass of one psi, consider yellow threat zone and can affect people.

Previous researchers (Ahmad et al., 2021a) proposes the expected number of fatalities due to a methanol reactor event at a newly planned facility in Perak, Malaysia. This research examines the impact of carbon dioxide-hydrogen-methanol-carbon monoxide-water mixture discharged from a methanol reactor in respect of expected fatality percentage, considering several events with varying reactor pressure settings. The leakage sizes range from low to high are 10, 25, and 160 mm. As per this analysis, CO_2 and CO contribute to one incidence, H_2 four occurrences, and MeOH release ten scenes. Furthermore, the biggest percentage of deaths is due to CO_2 from 160 mm leaking size, which is 15.7% during the night.

Moreover, for molar ratio variation, hydrogen gas may be the dominant component compared to others. Hence, when high pressure is applied to this reactor in addition to an increase in molar ratio, it is likely to contribute to harm to our plant such as toxic, flammable, and explosion. Enhancing the weight fraction results in a rise in methanol mass in the reactor. As a result, an increment in methanol mass leads to a rise in massive release when subjected to leakage that might also contribute to an increased discharge rate (Ahmad et al., 2021a).

Recent application on Quantitative Safety Assessment (QSA) was simulated using threat zone analysis, which highlighted worst toxicity scenario of red zone threat more than 10 km from absorber leaks containing sulphuric acid (Ahmad et al., 2021b). Fatality assessment of methanol production from the high-pressure reactor also conducted in recent study as plant operated at 442 and 76 bar was compared. The chemical component in methanol production is CO_2, H_2, CO, methanol, and water. Resulting fatalities estimated was 44% and 27% for both plants, respectively (Ahmad & Abdul Rashid, 2019). There is a gap between the study made based on the methanol synthesis since there are not many studies that focus on risk assessment on the methanol synthesis by using the CCU method. The other study was more about economic and environmental assessment (Pérez-Fortes et al., 2016), methanol production capacity and CO_2 conversion based on different pressure condition and GHSV (Gaikwad et al., 2016), and methanol production capacity and CO_2 conversion based on different molar ratio (Bansode & Urakawa, 2014).

The main purpose of this research is to identify the chemical component's mass fraction in the mixture for reactor size variation in methanol production and chemical potential hazard scenarios. Next, to quantify the safety of methanol plants using area plot threat analysis as reactor size and pressure are varied. The significance of this study is possible worst-case scenario from toxicity, thermal radiation and overpressure for methanol plant can be predicted using percentage people affected, thus preventive and mitigative measurement can be prioritised according to the highest into the lowest percentage.

2.0 Methodology

2.1 Plant for case studies

The plant used as reference for this study is a simulation plant in France, as conducted by Mar-Peres Fortez et al. (Pérez-Fortes et al., 2016). The reference plant reactor pressure is 76 bar, the temperature is 288 °C while total mass flowrate into reactor is about 420,000 kg/hr. Fig. 1 shows the reactor that was used for the simulation for the reference plant. This study used Pérez-Fortes et al. (2016) simulation as their research focuses on CCU to methanol plant and have complete data in term of mass flowrate, pressure, and temperature condition for every stream.

2.1.1 Reactor size variation

The reactor size variation used in this simulation is 42, 20, and 5 m^3, based on GHSV study from Gaikwad et. al. (2016), which used GHSV from 2,000 to 100,000 h^{-1} , while molar ratio is 1:3 for all reactor size. GHSV value was calculated from total mass flowrate into reactor divided by reactor size. Therefore, as total mass flowrate into reactor in this study is 20,000 kg/hr based on reference plant

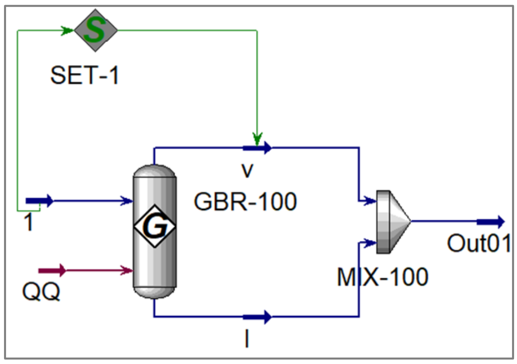

Fig. 1: Reactor process of methanol for reference plant

simulated by Pérez-Fortes et al. (2016), the reactor size 42, 20, and 5 m^3 mimic GHSV of 10,000, 20,000, and 84,000 h^{-1}, which is within experiment range by Gaikwad. Meanwhile, pressure used 76 bar is based on Marz-Perez Fortez et. al. (2016) simulation study while pressure 184 bar and 331 bar are the pressure used by Gaikwad et.al. (2016) in their experiment to synthesise methanol. Table 1 shows the reactor size and operating pressure variation for Reference Plant and Modified Plants. Modified Plant 1 and 2 has pressure condition of 184 bar and 331 bar, using same reactor volume of 42 m^3, as reference plant. Meanwhile, Modified Plant 3, 4, and 5 using volume reactor size of 20 m^3, but varies pressure condition, which are 76, 184, and 331 bar, respectively. Modified Plant 6, 7, and 8 has reactor volume size 5 m^3, however each plant pressure condition is 76, 184, and 331 bar, respectively.

2.1.2 *Process plant location and weather condition*

The plant location is in Pengerang Integrated Petroleum Complex (PIPC), Pengerang, Johor. The plant coordinate is 121.7717° N, 104.3546° E. Since there is no weather station nearby the plant, the weather condition used is based on Singapore Changi Airport taken from WINDFINDER. Based on the weather condition, the dominant wind direction identified is East Southeast (ESE)

2.1.3 *Plant layout facilities*

The Pengerang Integrated Petroleum Complex (PIPC) represents a significant step in Johor's downstream oil and gas value chain. It consists of oil refineries, naphtha crackers, petrochemical plants as well as liquefied natural gas (LNG) import terminals, and a regasification plant (JPDC, 2023). The plant is in the industrial zone and far from the residential and commercial areas, as depicted in Fig. 2.

2.1.4 *Number of people in the plant and surrounding*

There are several residential areas surrounding the plant. The plant is also located near the sea. There are an estimated 4,000 workers and contractors at the site, plus more than 2,000 personnel at the PIPC site(JPDC, 2023).

2.2 *Determination of consequence scenario and percentage people affected*

The software used for this study is HYSYS, ALOHA, and MARPLOT software. HYSYS is required to do the simulation for methanol synthesis for pressure variation. While ALOHA and MARPLOT are

Table 1: Reactor size variation

Plant	Pressure (Bar)	Volume (m^3)
Reference plant	76	42
Modified plant 1	184	42
Modified plant 2	331	42
Modified plant 3	76	20
Modified plant 4	184	20
Modified plant 5	331	20
Modified plant 6	76	5
Modified plant 7	184	5
Modified plant 8	331	5

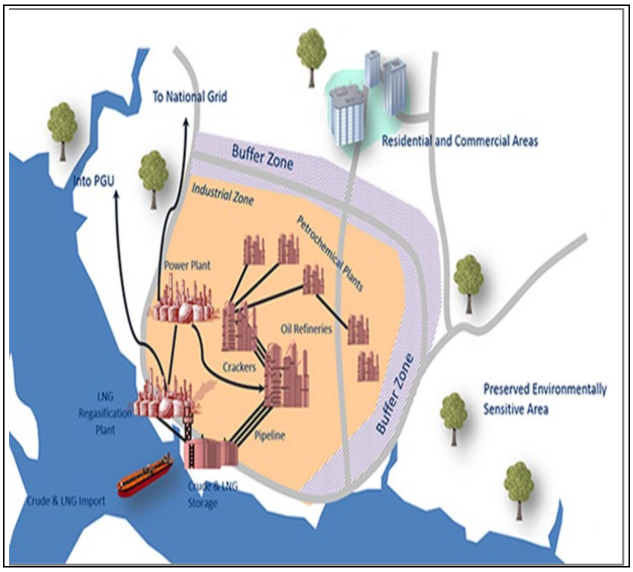

Fig. 2: Pengerang Integrated Complex layout (Pengerang Integrated Petroleum Complex (PIPC) (JPDC, 2023)

needed to do consequence analysis on the reactor. WINDFINDER apps are needed to see the weather condition and lastly google earth is used to locate the plant location.

(a) HYSYS

Pressure variation that is 76, 184, and 331 bar is used for the reactor simulation. First, the reference plant used for this case study is 76 bars at 288 °C. The HYSYS simulation was run at the reference pressure and temperature. The fluid package used The Peng-Robinson equation of state (PRSV). The molar ratio used is the same for all the simulations which is 1:3. The total inlet flowrate used is 467600 kg/hr. Then, the case study was done by using different pressure in the HYSYS simulation which is 184 bar and continued with 331 bar. For every pressure change, the major chemical component is recorded to be used for consequence analysis in ALOHA.

(b) ALOHA

In ALOHA, the chemical component used for the simulation is specified, including the location of the methanol plant. The location of the methanol plant is in Pengerang, Johor. The plant coordinate is 121.7717° N, 104.3546 ° E. After that, the weather condition was specified by using WINDFINDER application (Apps). In this simulation, the volume of the reactor will be varied which is 42, 20, and 5 m^3. The leak size used in this study is 10, 75, and 160 mm. The simulation in ALOHA was done by considering day and night conditions with one dominant wind direction according to the location of the plant. This is to see the effect of reactor size on the threat area and distance.

(c) MARPLOT

The result from ALOHA was used in MARPLOT to plot the area that involved if the consequence such as toxic release, thermal radiation, and overpressure occurs. Finally, the result for the percentage area affected or percentage people affected is calculated by using Eq. (1):

$$\frac{\text{Area affected based on the threat zone}(m^2)}{\text{Total of methanol area }(m^2)} \times 100 \qquad (1)$$

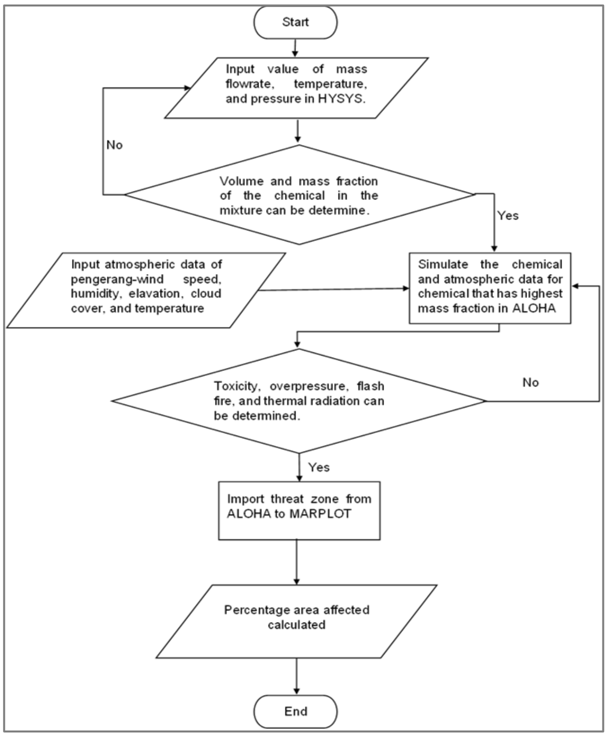

Fig. 3: Summary of methodology flowchart

Fig. 3 shows the summary of the methodology flowchart. The methodology starts with the HYSYS simulation followed by ALOHA and finally the threat zone from ALOHA was plotted inside MARPLOT. Based on the threat zone the percentage area affected or people affected was calculated.

2.3 Theory of consequence scenario

2.3.1 Toxicity

Toxicity is the degree to which a chemical substance or a specific chemical mixture can harm an organism. The term "release" refers to the various ways in which toxic chemicals from industrial facilities enter the air, water, and land. Spilling, leaking, pumping, pouring, emitting, emptying, discharging, injecting, escaping, leaching, dumping, or disposing into the environment are all examples of releases (“Toxics Release Inventory (TRI) Program,” 2022).

2.3.2 Thermal radiation

Thermal radiation is the process when energy is emitted from a heated surface in all directions and reaches the absorption point at the speed of light. It does not require an intermediate medium to transport it. Thermal radiation is dangerous because it has enough heating effect to burn the skin and ignite flammable substances such as clothing (Encyclopaedia of Britannica, 2023).

2.3.3 Overpressure

Overpressure (or explosion overpressure) is the pressure caused by a shock wave above normal atmospheric pressure. Shock waves can be caused by a sonic boom or by an explosion, and the resulting overpressure is a special consideration when measuring the effects of nuclear weapons or thermobaric bombs (Elsayed & Gorbunov, 2007).

3.0 Results and discussion

3.1 Condition for the nine plants

For the simulation, there are 9 plants that are being used. There is one reference plant and eight modified plants. The chemical component involved to calculate the percentage people affected based on the volume fraction, and the mass fraction is carbon dioxide, methanol, hydrogen, and carbon monoxide. All nine plant has the same temperature used for the reactor which is 288 °C. For all the plants, the highest total amount released for the major chemical is when the leak size is 75 mm. Even if the leak size was changed to 160 mm the total amount release of the major chemical is still the same. In the Reference Plant, the highest total amount release of carbon dioxide is 952 kg. Then, in Modified Plant 1 the highest total amount release of carbon dioxide is 2136 kg. For Modified Plant 2, the major chemical component is methanol, and the highest total release rate is 5757 kg. Hence, it can be said that for 42 m^3 reactor size. Modified Plant 2 has the highest total amount release of the major chemical compound.

For the 20 m^3 reactor size, the total amount of carbon dioxide released when the leak size of the reactor is 10 mm for Modified Plant 3 and Modified Plant 4 is 448 kg and 1017 kg, respectively. This result does not change even when the leak size of the reactor is 75 mm and 160 mm. However, in Modified Plant 5, when the reactor leak size is 10 mm, the total amount release of methanol is 2705 kg. Meanwhile, the total amount released for the leak size of 75 and 160 mm is 2741 kg. Therefore, for a reactor size of 20 m^3, Modified Plant 5 has the highest total amount release of the major chemical compound found in the reactor.

For 5 m^3 reactor, the highest total amount release for the major chemical is when the leak size is 10 mm. Even if the leak size was changed to 75 mm and 160 mm the total amount release of the major chemical is still the same. For Modified Plants 6 and 7, the major chemical component is carbon dioxide, and the highest total release rate is 112 kg and 254 kg, respectively. However, in Modified Plant 8, the total amount of release of methanol is 685 kg. Hence, it can be said that for 5 m^3 reactor size Modified Plant 8 has the highest total amount release of the major chemical compound. Results of volume and mass fraction are tabulated in Supplementary Material (SM1), whereas the result of total amount release for every plant is presented in SM2.

3.2 Percentage people affected

There are four major accident scenarios involved that is toxic release, flammable area of the vapor cloud, blast area of the vapor cloud, and thermal radiation from the jet fire. For a plant that has carbon dioxide as the major chemical component inside the reactor, the accident scenario that was involved is only a toxic release. Meanwhile, for a plant that has methanol as the major chemical component inside the reactor, all four major incidents were involved. This simulation of the accident scenario was done by using ALOHA by manipulating the leak size of the reactor which is 10, 75, and 160 mm. The dominant wind direction used for all the simulations is ESE for day and night conditions while the air temperature is 26 °C for day and 27 °C for the night. The relative humidity is set at 80%. This simulation was done at 2:00 p.m. for the day 11:00 p.m. for night conditions

Table 2: Worst percentage people affected (%) for 42 m^3 reactor in all scenarios (Yellow zone area)

Pressure	**Chemical**	**Major Accident Scenario**	**Leak size (mm)**	**Area affected**		**Percentage People Affected (%)**	
				Day	Night	Day	Night
76 (Reference plant)	Carbon Dioxide	Toxic release (Toxic level > 40000 ppm)	160	Onsite	Onsite	0	0.92
184 (Modified Plant 1)	Carbon Dioxide	Toxic release (Toxic level > 40000 ppm)	160	Onsite	Onsite	1.54	2.55
331 (Modified Plant 2)	Methanol	Toxic release (Toxic level > 530ppm)	160	-Onsite -Jalan Petchem N/1 -Living Quarters -Jalan PIC S -Jalan PIC T	-Onsite -Jalan Petchem N/1 -Jalan Petchem U/3 -Living Quarters -Jalan PIC T -Jalan PIC S	36.61	56.53
		Flammable area of vapour cloud Exposure to thermal radiation > 7180 ppm	160	-Onsite -Jalan Petchem N/1	-Onsite -Jalan Petchem N/1 -Jalan Petchem U/3 -Jalan PIC T -Jalan PIC S	5.06	7.53
		Blast area of vapor cloud Overpressure (Blast force) > 1.0 psi	160	-Onsite	-Onsite -Jalan Petchem N/1 -Living Quarters	10.68	21.99
		Thermal radiation from jet fire Exposure to thermal radiation > 2.0 kW/m^2	160	-Onsite -Jalan PIC V	-Onsite -Jalan PIC V	23.36	23.24

3.3 Reactor size of 42 m^3

Table 2 shows the summary for the worst percentage people affected for 42 m^3 reactor in all scenarios for the yellow zone area. Based for reference plant, the toxic release is the major accident scenario happened, which is greater than 40,000 ppm. At this toxic level, exposure to carbon dioxide gas is immediately dangerous to life. The percentage of people affected is at the highest when the leak size of the reactor is 160 mm. Percentage people affected for day condition cannot be detected in the Reference Plant since the damage for the toxic release is lower, therefore, the threat zone cannot be drawn. Meanwhile, for the night condition, the percentage people affected by the toxic release is 0.92%. Only a small number of people in the onsite area will be involved in this accident. Besides, for Modified Plant 1, the major accident scenario is the toxic release of carbon dioxide.

This toxic release also has the same toxicity level as the reference plant. The percentage of people affected of this plant is also at the highest when the leak size is 160 mm. For both day and night conditions, the percentage people affected is 1.54% and 2.55%, respectively, and only affected the onsite area.

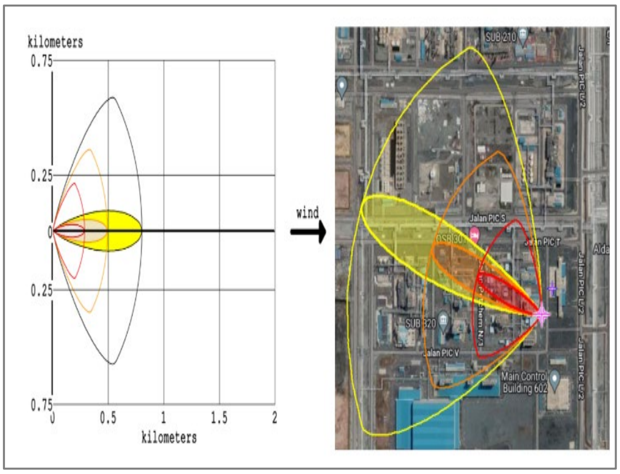

Fig. 4: ALOHA and MARPLOT worst threat zone for plant 2 toxic release of methanol for day

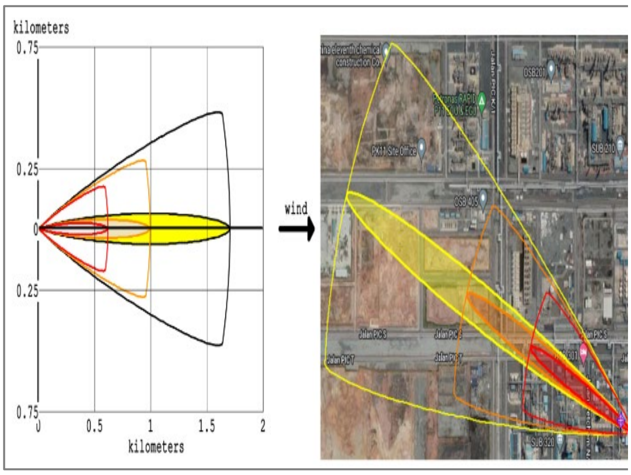

Fig. 5: ALOHA and MARPLOT worst threat zone for plant 2 toxic release of methanol for night

Modified Plant 2 shows that four major accident scenarios can happen. The highest percentage of people affected for all the scenarios is when the reactor leak size was 160 mm. The major chemical component of this plant is methanol. For toxic release, the toxic level can be greater than 530 ppm.

The percentage of people affected for day and night conditions was 36.61% and 56.53% respectively. Fig. 4 and Fig. 5 show the MARPLOT and ALOHA threat zone for the worst people affected percentage of reactor size 42 m^3. The areas affected by toxic release are onsite, Jalan Petchem N/1, Jalan Petchem U/3, living quarters, Jalan PIC T, Jalan PIC S for the night and for the day only onsite, Jalan Petchem N/1. For the flammable area of the vapor cloud, the percentage people affected is 5.06% and 7.53% for day and night, respectively. Besides, blast area of vapor cloud percentage people affected is 10.98% for the day and 21.99% for nights. Thermal radiation of jet fire percentage people affected is 23.36% and 23.24% for day and night conditions, respectively.

3.4 Reactor size of 20 m^3

For Modified Plant 3 and Modified Plant 4, the percentage of people affected only can be calculated on night conditions for Modified Plant 4. The major scenario that could occur in this plant is the toxic release of carbon dioxide under a toxicity level greater than 40,000 ppm. The percentage of people affected for plant 4 on a night condition basis is 1.02%. However, for Modified Plant 5, methanol is the major chemical that is being released. The percentage of people affected is at the highest for the case scenario of toxic release which is 22.33% and 31.92% for day and night respectively. For the flammable area of the vapor cloud, the percentage of people affected is 2.49% and 4.29% for day and night respectively. Besides, the blast area of vapor cloud percentage people affected is 5.14% for the day and 12.10% for nights. Thermal radiation of jet fire percentage people affected is 12.60% and 12.53% respectively for day and night conditions. Table 3 shows the summary for the worst percentage people affected by the 20 m^3 reactor in all scenarios for the yellow zone area. Fig. 6 and Fig. 7 show the MARPLOT and ALOHA threat zone for the worst people affected percentage for reactor size of 20 m^3.

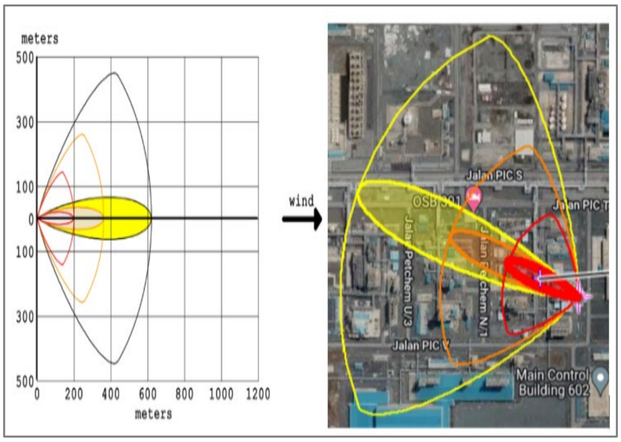

Fig. 6: ALOHA and MARPLOT worst threat zone for Plant 5 toxic release of methanol for day

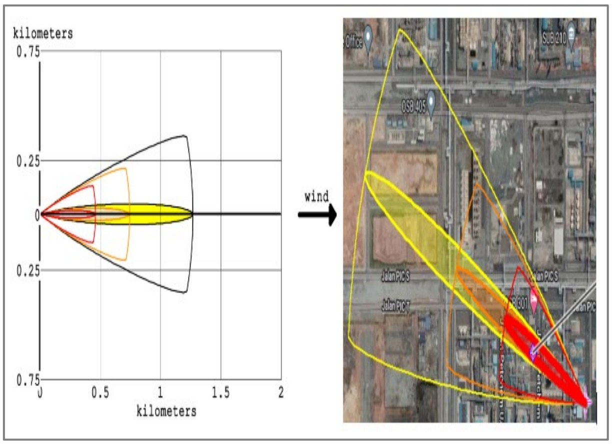

Fig. 7: ALOHA and MARPLOT worst threat zone for Plant 5 toxic release of methanol for night

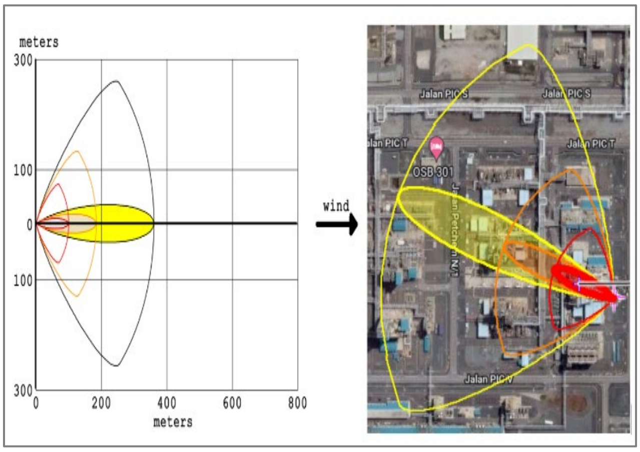

Fig. 8: ALOHA and MARPLOT worst threat zone for Plant 8 toxic release of methanol for day

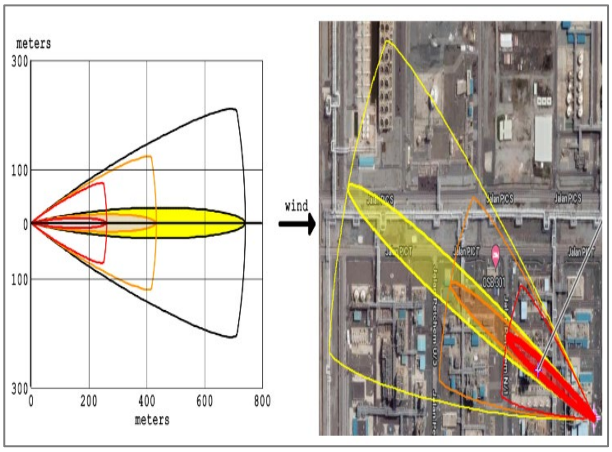

Fig. 9: ALOHA and MARPLOT worst threat zone for Plant 8 toxic release of methanol for night

3.5 Reactor size of 5 m^3

For Modified Plants 6 and 7, it is not possible to determine the percentage of people affected caused by major accident scenario, as the dispersion of the toxic release is too small, which makes it impossible to draw the threat zone. As a result, the affected area for either the day or the night conditions are zero. On the other hand, the pressure inside the reactor at Modified Plant 8 is 331 bars, which means that methanol is the most abundant chemical component inside the reactor. The result for this plant is shown in Table 4. The case scenario of toxic leakage has the largest percentage of people affected for Modified Plant 8, which is 8.15 % during the day and 11.16 % during the night, respectively. This is the scenario with the highest people affected rate. During the day, the percentage of people affected by flammable areas of vapor clouds is 0.62 %, but during the night, that number rises to 1.45 %. In addition, the percentage of people affected by blast areas of vapor clouds is 1.28 % during the day and 3.33 % during the night. In daytime conditions, the percentage of people affected by thermal radiation from jet fire is 3.56 %, and in night-time conditions, it is 3.54 %. Fig. 8. and Fig. 9 shows the MARPLOT and ALOHA threat zone for the worst people affected percentage for reactor size of 5 m^3.

3.6 Analysis of the result

3.6.1 Comparison due to reactor pressure

There are three different pressures used for this study that is 76 bar, 184, bar, and 331 bar. The percentage people affected is calculated from the yellow area threat zone obtained from ALOHA and MARPLOT. Table 5 shows the tabulated result for the people affected percentage for each plant at different pressure. When using pressure 331 bar, the percentage people affected is much higher than when using pressure 76 bar and 184 bar. For the reference plant, the pressure used is 76 bar and the people affected percentage for this plant is 0.92%. For Modified Plant 2, the pressure used is 184 bar and the percentage people affected are 2.55%.

For this reference plant and plant one, the toxic gas that was released is carbon dioxide.

Table 3: Worst Percentage People Affected (%) for 20 m^3 reactor in All Scenario (Yellow zone area)

Pressure	**Chemical**	**Major Accident Scenario**	**Leak size (mm)**	**Area affected**		**Percentage People Affected (%)**	
				Day	Night	Day	Night
76 (Modified Plant 3)	Carbon Dioxide	Exposure to toxic level > 40000 ppm	160	Onsite	Onsite	0	0
184 (Modified Plant 4)	Carbon Dioxide	Exposure to toxic level > 40000 ppm	160	Onsite	Onsite	0	1.02
331 (Modified Plant 5)	Methanol	Exposure to toxic level > 530 ppm	160	-Onsite -Jalan Petchem N/1 -Jalan Petchem U/3 -Living Quarters -Jalan PIC T -Jalan PIC S	-Onsite -Jalan Petchem N/1 -Jalan Petchem U/3 -Living Quarters -Jalan PIC T -Jalan PIC S	22.33	31.92
		Flammable area of vapour cloud Exposure to thermal radiation > 7180 ppm	160	-Onsite -Jalan Petchem N/1	-Onsite -Jalan Petchem N/1 -Jalan Petchem U/3 -Jalan PIC T -Jalan PIC S	2.49	4.29
		Blast area of vapor cloud Overpressure (Blast force) > 1.0 psi	160	-Onsite	-Onsite -Jalan Petchem N/1 -Living Quarters	5.14	12.1
		Thermal radiation from jet					

Table 4: Worst Percentage People Affected (%) for 5 m^3 reactor in all Scenario (Yellow zone area)

Pressure	**Chemical**	**Major Accident Scenario**	**Leak size (mm)**	**Area affected**	**Percentage People Affected (%)**	**Press ure**	**Chemical**
				Day	Night	Day	Night
76 (Modified Plant 6)	Carbon Dioxide	Toxic release (Toxic level > 40000 ppm)	160	Onsite	Onsite	0	0
184 (Modified Plant 7)	Carbon Dioxide	Toxic release (Toxic level > 40000 ppm)	160	Onsite	Onsite	0	0
331 (Modified Plant 8)	Methanol	Toxic release (Toxic level > 530 ppm)	160	-Onsite -Jalan Petchem N/1	-Onsite -Jalan Petchem N/1 -Jalan Petchem U/3 -Living Quarters -Jalan PIC T -Jalan PIC S	8.15	11.16
		Flammable area of vapour cloud Exposure to thermal radiation > 7180 ppm	160	-Onsite -Jalan Petchem N/1	-Onsite -Jalan Petchem N/1	0.62	1.45
		Blast area of vapor cloud Overpressure (Blast force) > 1.0 psi	160	-Onsite	-Onsite	1.28	3.33
		Thermal radiation from jet fire Exposure to thermal radiation > 2.0 kW/ m^2	160	-Onsite -Jalan PIC V	-Onsite -Jalan PIC V	3.56	3.54

Modified Plant 2 has the highest value for percentage people affected which is 11.49%. This occurs under toxic release accidents. Methanol has the highest volume and mass fraction inside the reactor thus since the AEGL-3 for CO_2 (IDLH is 40,000 ppm) is higher than methanol (IDLH is 7200 ppm), this shows that the toxic release of methanol is much more dangerous than carbon dioxide. The area affected by the yellow threat zone are onsite, Jalan Petchem N/1, Jalan Petchem U/3, and Jalan PIC T. The area affected for Plant 2 is much bigger than Plant 1 and Reference 1. Thus, there will be more people affected by Plant 2.

Modified Plant 2 has the highest value for percentage people affected which is 11.49%. This occurs under toxic release accidents. Methanol has the highest volume and mass fraction inside the reactor thus since the AEGL-3 for CO_2 (IDLH is 40,000 ppm) is higher than methanol (IDLH is 7200 ppm), this shows that the toxic release of methanol is much more dangerous than carbon dioxide. The area affected by the yellow threat zone are onsite, Jalan Petchem N/1, Jalan Petchem U/3, and Jalan PIC T. The area affected for Plant 2 is much bigger than Plant 1 and reference 1. Thus, there will be more people that are affected by Plant 2. For Reference Plant, at 76 bar the highest total chemical release is at 160 mm reactor leak size that is 952 kg and for Modified Plant 1 at 184 bar, 160 mm leak size is 2136 kg. For Plant 2, at pressure 331 bar the amount of toxic release is higher which is 5757 kg (Appendix 2) at a leakage size of 160 mm. Hence, this leads to an increase in percentage people affected. For the leakage size of 10 mm and 75 mm, the total release of the chemical is 4648 kg and 5757 kg. Since 75 mm and 160 mm both have the same total amount of chemical release it can be said that inside the reactor there is 5757 kg of methanol. Thus, when the pressure is increased, the total chemical release from the leaking reactor will also increase and this also depends on the time taken for the release of the chemical. Leakage size of 75 mm and 160 mm have same amount of release, compare to 10 mm as the simulation software predicted amount of release within 30 minutes time. Both leakage 75 mm and 160 mm completely release chemical from reactor, while 10 mm leakage only release a part of chemical.

A scenario such as flash fire, blast area of the vapor cloud, and thermal radiation only occurs when there is methanol release since methanol is a flammable gas. Mass fraction and volume fraction of methanol are at the highest when the pressure is 331 bar. Therefore, these three scenarios will only occur in Plants 2, 4, and 8. For vapor cloud explosion there is no yellow threat zone area as the blast force is less than 1.0 psi and the percentage people affected at a pressure of 331. Flash fire and thermal radiation for the yellow threat zone area both have percentage people affected of 2.38% and 5.30% respectively. This percentage people affected is taken at night condition for 42 m^3 volume of the reactor. Hence, this study shows, that an increase in pressure has less effect on methanol release incidents

Table 5: Worst people affected percentages comparison between operating pressure condition for all plant (160 mm leak, during night condition, ESE wind direction, 42 m^2 reactor volume, yellow area threat zone)

Plant	Pressure (Bar)	Percentage people affected (%)
Reference plant	76	0.92
Modified plant 1	184	2.55
Modified plant 2	331	11.49

Table 6: Worst people affected percentages comparison between reactor volume for all plant (160 mm leak, during night condition, ESE wind direction, yellow area threat zone)

Plant	Volume (m^3)	Percentage people affected (%)
Modified plant 2	42	11.49
Modified plant 5	20	6.34
Modified plant 8	5	1.92

involving flash fire, thermal radiation, and VCE. Meanwhile, for the toxic release of methanol, increasing pressure in the reactor has more effect on the percentage people affected than the toxic release of carbon dioxide.

3.6.2 Comparison on different reactor volume

For this study, three different volume was used, that is 42 m^3, 20 m^3, and 5 m^3. Based on the total amount released (Appendix 2), as the volume of the reactor increase, the mass of the chemical component inside the reactor increase, thus the total release of the chemical component also increases. Modified Plant 2 has the highest mass of methanol which is 5757 kg while Plant 5 and Plant 8 have 2741 kg and 685 kg respectively. Table 6 shows the worst people affected percentages comparison between reactor volume for all plants based on the yellow threat zone area.

By comparing Modified Plants 2, 5 and 8, there is a significant change in the percentage people affected as the percentage people affected increase when the volume of the reactor increase. This is because the amount of dominant chemical component inside the reactor volume of 42 m^3 is higher than 20 m^3, and 5 m^3. The percentage people affected of Plant 2 is 11.49% by using night conditions, 160 mm leak, and ESE wind direction. For Plant 5, the percentage people affected is 6.34% and for Plant 8 is 1.92% by using the same condition as Plant 2. The dominant chemical release for this plant is methanol and the pressure is at 331 bar. In plant 2, the amount of methanol release is 5757 kg, this amount of methanol release led to a higher percentage of people affected. In Plant 5, the amount of methanol release is 2741 kg with a people affected rate of 6.34% and for Plant 8 amount of release is 685 kg leading to a people affected rate of 1.92%. Hence it can be noted that 4 times bigger reactor size contribute to 3.3 time higher of people affected while reactor size of 8 times bigger results 6-time higher of people affected. Thus, these results can be used to estimate percentage people affected when using bigger or smaller reactor size.

3.7 Overall analysis

The major chemical component for the reactor is different depending on the pressure of the reactor. For the pressure of 76 and 184 bar, the major chemical component is carbon dioxide while for 331 bar the major chemical component is methanol. Based on the result from HYSYS, the volume fraction of the major chemical component is used to determine the volume of the major chemical component inside the reactor. By using ALOHA simulation, the total amount released of the major chemical composition was determined. From all the simulations, it can be concluded that the worst accident scenario that can have a high people affected percentage is by toxic release. Although the other incident scenario such as flash fire, VCE, and thermal radiation also can occur when involving chemical components such as methanol, the severity is not high compared to toxic release.

Based on the result it can be said that at 42 m^3 reactor size, the total amount of chemical release is much higher than 20 m^3 and 5 m^3. Based on the pressure used, 331 bar has a higher people affected percentage compared to 76 bar and 184 bar. This result also depends on the size of the leak hole as the bigger the leak hole size, will increase the total amount released of the chemical component. The wind speed of the plant location will also result in a long distance from the threat zone. The result from the simulation is the same as the result by Ahmad et al. (2021a). From this study, it can be said that when increasing the pressure and the volume of the reactor, the plant risk will also increase, this will indicate that the increase in pressure and volume will decrease the inherent safety concept inside the plant. The study done by (Ahmad et al., 2021b) also get the same result, the study stated that increasing pressure will increase the societal risk of the plant, indicating that inherent safety decreases as operating pressure increases.

4.0 Conclusion

In conclusion, the major chemical component in the reactor for the pressure of 76 bar, 184 bar, and 331 bar has been determined. To get this result, HYSYS simulation was done to get the mass fraction and volume fraction for all the chemical components that are hydrogen, carbon dioxide, carbon monoxide, and methanol. The major chemical component was decided based on the chemical that has the highest mass fraction in the reactor. The amount of release was determined by using ALOHA simulation in terms of toxic release, flammable area of the vapor cloud, blast area of the vapor cloud, and thermal radiation from the jet fire. The threat zone plot in ALOHA was transferred into MARPLOT to see the total area that was affected. The highest people affected incident based on the yellow threat zone was due to the toxic release of methanol from 160 mm leak size at night condition in Modified Plant 2. This scenario result in a percentage of people affected for night conditions was 56.53%. Based on this study, it can be said that using 5 m^3 of reactor volume is much safer for producing methanol using high pressure of 331 bar, as the percentage of people affected is much lower that using a reactor of 42 m^3. Further study on safety assessment for methanol production plant recommended using small reactor size of 5 m^3 with higher pressure than 331 bar, for example 350 to 1000 bar.

Contribution statement

Mohd Aizad Ahmad: Conceptualisation, experimental design, methodology, investigation, contributed reagents and materials, data analysis and interpretation, and writing/review-original draft; **Anis Adila Rozman**: Conceptualisation, experimental design, methodology, investigation, contributed reagents and materials, data analysis, and writing-original draft; **Zulkifli Abdul Rashid**: Data analysis and interpretation, contributed reagents and materials, data analysis, and writing/review-original draft;.

Conflict of Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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Supplementary Material

Table SM 1: Weight and volume fraction

Composition	Pressure (Bar)		
	76	184	331
Master Comp Mass Frac (Carbon Dioxide)	0.6306	0.4699	0.2261
Master Comp Mass Frac (Hydrogen)	0.0969	0.0686	0.0320
Master Comp Mass Frac (Methanol)	0.0994	0.2658	0.4678
Master Comp Mass Frac (Water)	0.1017	0.1675	0.2673
Master Comp Mass Frac (Carbon Monoxide)	0.0713	0.0281	0.0067
Master Comp Volume Frac (Carbon Monoxide)	0.0361	0.0168	0.0052
Master Comp Volume Frac (Carbon Dioxide)	0.3097	0.2726	0.1716
Master Comp Volume Frac (Water)	0.0413	0.0804	0.1678
Master Comp Volume Frac (Hydrogen)	0.5623	0.4703	0.2872
Master Comp Volume Frac (Methanol)	0.0506	0.1599	0.3682

Table SM 2: Total amount release

A. Day & night, 42 m^3

Pressure	Chemical	Leak size (mm)	Total amount release (kg)	Release rate
Toxic area of vapor cloud				
76 (Reference plant)	Carbon Dioxide	10	894	40.2 kg/min
		75	952	882 kg/min
		160	952	15.9 kg/sec
184 (Modified Plant 1)	Carbon Dioxide	10	2021	98.7 kg/min
		75	2136	2000 kg/min
		160	2136	35.5 kg/sec
Toxic area of vapor cloud, Flammable area of vapor cloud, Blast area of vapor cloud				
331 (Modified Plant 2)	Methanol	10	4648	160 kg/min
		75	5757	4490 kg/min
		160	5757	95.9 kg/sec
Thermal radiation from jet fire				
331 (Modified Plant 2)	Methanol	10	4648	206 kg/min
		75	5757	11600 kg/min
		160	5757	878 kg/sec

B. Day & night, 20 m^3

Pressure (Bar)	Chemical	Leak size (mm)	Total amount release (kg)	Release rate
Toxic area of vapor cloud				
76 (Modified Plant 3)	Carbon Dioxide	10	448	39.9 kg/min
		75	448	7.47 kg/sec
		160	448	7.47 kg/sec
184 (Modified Plant 4)	Carbon Dioxide	10	1017	98 kg/min
		75	1017	16.9 kg/sec
		160	1017	16.9 kg/sec
Toxic area of vapor cloud, Flammable area of vapor cloud, Blast area of vapor cloud				
331 (Modified Plant 5)	Methanol	10	2705	150 kg/min
		75	2741	2690 kg/min
		160	2741	45.7 kg/sec
Thermal radiation from jet fire				
331 (Modified Plant 5)	Methanol	10	2705	206 kg/min
		75	2741	11600 kg/min
		160	2741	878 kg/sec

C. Day & night, 5 m^3

Pressure (Bar)	Chemical	Leak size(mm)	Total amount release (kg)	Release rate
Toxic area of vapor cloud				
76 (Modified Plant 6)	Carbon Dioxide	10	112	36.6 kg/min
		75	112	1.87 kg/sec
		160	112	1.87 kg/sec
184 (Modified Plant 7)	Carbon Dioxide	10	254	88.3 kg/min
		75	254	4.23 kg/sec
		160	254	4.23 kg/sec
Toxic area of vapor cloud, Flammable area of vapor cloud, Blast area of vapor cloud				
331 (Modified Plant 8)	Methanol	10	685	146 kg/min
		75	685	11.4 kg/sec
		160	685	11.4 kg/sec
Thermal radiation from jet fire				
331 (Modified Plant 8)	Methanol	10	685	206 kg/min
		75	685	193 kg/sec
		160	685	878 kg/sec