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Molar ratio variation on high pressure methanol production: Quantitative safety analysis

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Abstract

The objective of this research was to conduct a quantitative safety analysis as well as estimate the possible risk of deaths due to methanol reactors at the Labuan process facility in Malaysia. The gathered outcomes included scenarios that occurred, such as toxicity, thermal radiation, and overpressure. The percentage of mortality was determined when a chemical mixture was discharged from nine plants in varying ratios of 1:3, 1:7, and 1:10, and at different operating pressures of 76, 184, and 331 bar, resulting in the occurrence of various events. ASPEN Hysys software was used to compute the mass and volume fraction of a chemical mixture. ALOHA and MARPLOT were also used to gather data on toxicity, thermal radiation, overpressure, and impacted zones. The quantity of chemicals emitted was calculated for three distinct leakage sizes (10 mm, 75 mm, and 160 mm). The findings showed that the plant with 331 bars at a ratio of 1:3 had the highest fatality rate of 16.07 %, which was caused by methanol leakage at night for a leakage size of 160 mm. This work has the potential to lower the number of deaths caused by methanol plants.

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1.0 Introduction

The principle of Carbon Capture and Utilisation (CCU) gradually gained popularity. The intention of CCU is just to employ carbon dioxide as a substrate for numerous fields and it could be seen as a potential feedstock that could minimise the need for and exploitation of natural resources. CCU has the ability to cut CO_2 emissions and reduce dependency on fossil fuels. As a result, emissions might be cut by half according to Becattini et al. (2021). Directly use, mineralization, biological conversion, and chemical conversion are the four major CO_2 usage pathways. Methanation, Methanol Synthesis, and Olefin Synthesis are processes that use renewable energy to produce hydrogen, and they are among the most frequently used methods for converting carbon dioxide conversions (Ho et al., 2019).

Back in 2011, the George Olah Renewable Methanol Plant was the world's first industrial-scale methanol manufacturing plant to use carbon dioxide waste gas as a feedstock. The industrial amount of methanol increased from 1300 to 4000 tonnes per year, resulting in carbon dioxide emissions being recovered by 5500 tonnes (Jiang et al, 2020).

Methanol production is one of the primary products in the research of CCU. In the past, process-based simulations of methanol (MeOH) synthesis from CO_2 and H_2 were reported (Gabrielli et al., 2020). Fig. 1 provides an illustration of technology methanol production based on CCU- Direct Air Capture (DAC). They are composed of various basic elements, which are starting with hydrogen production contribute to methanol production.

Gaikwad et al. (2016) recently studied methanol production which uses high pressure with different Gas Hourly Space Velocity (GHSV) and molar ratios. To achieve high conversion of carbon monoxide to methanol, high pressure is necessary which could compromise safety. Thus, few past 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 very high selectivity for the temperature range (>99.9% at 220 °C and 99.0% at 300 °C) (Gaikwad et al., 2016).

Ahmad et al. (2021a) proposed the expected number of fatalities due to a methanol reactor event at a newly planned facility in Perak, Malaysia. This research examined the impact of carbon dioxide-hydrogen-methanol-carbon monoxide-water mixture discharge from a methanol reactor in respect of expected fatality percentage, considering several events with varying reactor pressure settings. The leakage sizes ranged from low to high are 10 mm, 25 mm, and 160 mm. The analysis revealed that CO_2 and CO contributed to one incidence, H_2 caused four occurrences, and MeOH released ten scenes. Furthermore, the biggest percentage of deaths was due to CO_2 from 160 mm leaking size, which is 15.7% during the night.

However, according to Ahmad et al. (2022), the results on various mixture's leakage could be influenced by various variables such as pressure, mass, volume, size of the leak, wind direction, and wind speed. To evaluate the rate of death, all such aspects must be simulated. A MeOH plant running at pressures of 76, 100, 150, 200, 250, 300, 350, 400, 450, and 500 bar was chosen as the case study to be used in this study. The lowest pressure of 76 bar was determined based on the normal working pressure of a commercial MeOH. As an outcome, the mass and volume of CO_2, H_2, CO, and MeOH diverse at each operating pressure from 76 to 500 bar, influencing the mass release and total amount burned for the toxicity and jet-fire occurrences and, as a matter of fact, generating a different red region area footprint.

Moreover, for molar ratio variation, hydrogen gas might 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 release, fire, and explosion. Enhancing the weight fraction, as mentioned by Rashid et al. (2021), led to a rise in massive release when subjected to leakage, which might also contribute to an increased discharge rate due to the increment in methanol mass in the reactor. The flammability of methanol and hydrogen, among some of the outputs to be consumed in the plant, should be addressed. At standard temperature and pressure, methanol and hydrogen gas are extremely flammable substances. As it generates a pale blue flame, hydrogen is almost undetectable. The exposure of carbon monoxide to the environment for a long term is surely very deadly while carbon dioxide is an asphyxiant gas when working in enclosed areas and poses a serious threat. These gases can replace the oxygen in the air and leads to hypoxemia which is low level of oxygen in the blood.

According to Gupta & Edwards (2002), the inclusion of safety in the process design phase could benefit from studying the inherent safety characteristics of the process, which provided a suitable framework for its integration. According to Ortiz-Espinoza et al. (2017), the primary goal of inherent safety was to eliminate or minimise risks in a processing facility, thus reflecting considerably fewer levels and protective attachments such as substitution, moderation, and simplicity. Both temperature and pressure have been utilised to demonstrate the inherent safety of a system. This could be attributed to the reason that temperature is a direct measure of the heat energy present at the time of emission. Meanwhile, pressure could indicate both the amount of energy available for discharge and the energy necessary to initiate a rupture. The probable reactiveness was measured by chemical interaction in conjunction with the heat of the side reaction. The generation of flammable or toxic gas was 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 impact on total risk. This was designed to show that the suitability criteria were satisfied and that the residual hazards were 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 (Di Domenico et al, 2014).

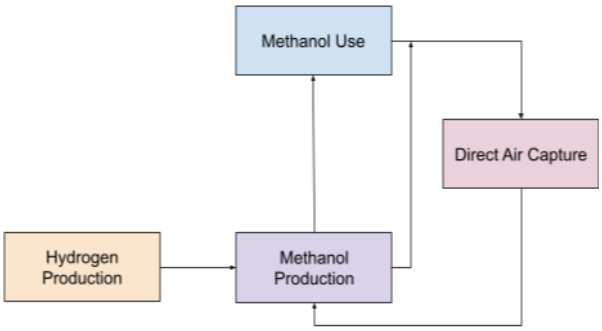

Fig. 1: Flow for CCU route

Recent research into sulfuric acid production facilities, employing threat zone analysis as a component of Quantitative Risk Assessment, has shown significant effectiveness in carrying out consequence assessments (Ahmad et al., 2021b). The paper investigated the effects of each major piece of equipment in the sulphuric acid plants such as drying tower, sulphur burner, multi-bed reactor, absorber tower, and electrostatic precipitator if the major chemical existed inside it, particularly regarding sulphuric acid, sulphur, sulphur trioxide, and hydrogen sulphide. The recorded distance of the affected region accelerates from 10 mm diameter leakage to 150 mm diameter leakage. The wider the diameter of the equipment leaks, the longer the distance of the region affected by the scenario.

The main purpose of this research is to identify the chemical component's mass fraction in the mixture for molar ratio variation in methanol production and chemical potential hazard scenarios. Next, to quantify the safety of methanol plants using distance and area plot threat analysis with a variation of inlet molar ratio.

2.0 Methodology

2.1 Reference plant for case studies

This study used a methanol synthesis route simulation done by Van-Dal & Bouallou, (2013) and further simulated by Pérez-Fortes et al. (2016) as shown in Fig. 2, as a reference plant in which the main focus is the methanol reactor. The pressure and temperature used are at 76 bar and 288 ℃ respectively. The fed of CO_2 at a pressure of 1 bar was compressed up until a four-stage compressor. Upon entering the reactor, the pressure increases to 78 bar as each compressor adds pressure three times that from the inlet. Moreover, the hydrogen was delivered at a pressure of 3 bar and compacted until the exit stream achieved 76 bar. The outlet stream of CO_2 and H_2 are mixed before entering the methanol reactor.

2.2 Molar ratio variation

The assessment is conducted using simulation ASPEN Hysys at various molar ratios where pressure will change at 184 bar and 331 bar with a constant temperature which is 288 ℃, as tabulated in Table 1. The total inlet flow rate used is 467,600 kg/h where the molar ratio is carbon dioxide to hydrogen. Chemical components and their weightage inside the reactor will be observed by using ASPEN Hysys.

2.3 Process plant location and weather condition

Weather information such as temperature, relative humidity, and atmospheric stability, are critical for atmospheric modelling dispersion and, hence, Fig. 3 is the reference plant location that has been available in Labuan, Malaysia. The area is approximately 139,000 m2 based on Google Earth reading. The coordinate of the reactor should be identified to simulate in ALOHA which is 5°14'41"N, 115°14'27" E. Both data are important when simulating ALOHA to assess the

Table 1: A case study of molar ratio variation

Molar Ratio	Pressure (bar)	Plant (Number)
1:3	76	1
	184	2
	331	3
1:7	76	4
	184	5
	331	6
1:10	76	7
	184	8
	331	9

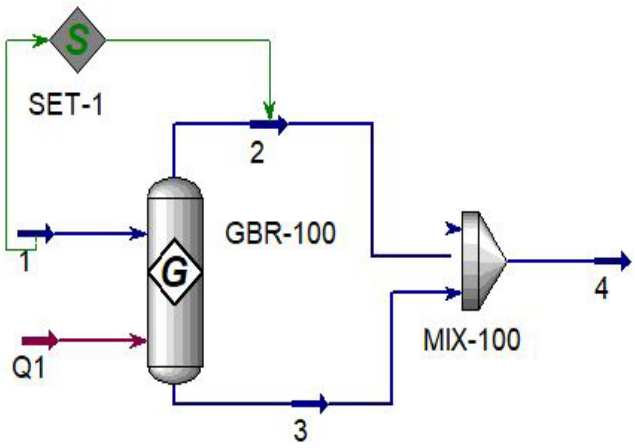

Fig. 2: Process flow diagram using ASPEN Hysys

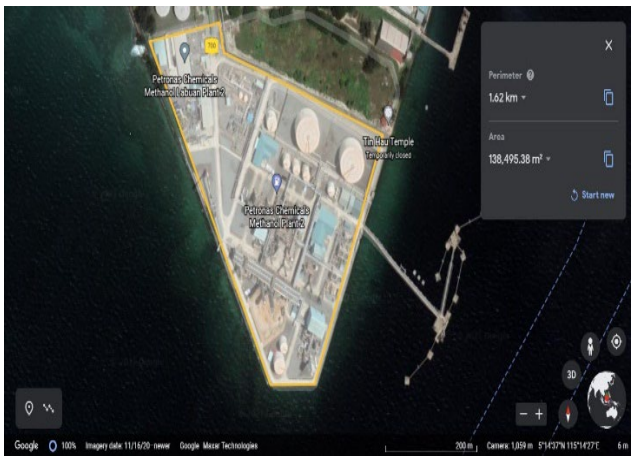

Fig. 3: Plant location of methanol production at Labuan (Google Earth)

percentage of fatalities of the plant. The weather condition can be found using any forecast application such as WINDFINDER. The information that is needed is the most dominant wind directions, average wind speed, and the average temperature during daytime and night-time. The most dominant wind directions in 2021 are West-Northwest (WNW). Moreover, the average wind speed recorded is 4 m/s and 2 m/s during day and night respectively. Lastly, average temperatures during the day time are 28 °C while at night-time 27 °C.

2.4 Plant layout facilities

The structure of the process units and supporting units must be constructed to provide the most effective flows of materials and employees around the site. Hazardous activities must be retained at a safe distance from other facilities. The site's possible development must also be considered. Based on Towler & Sinnott, (2021) an idea of a typical site layout is illustrated in Fig. 4.

2.5 Number of people in the plant and surrounding

Aziz (2018) reported that the total number of employees working at Labuan Methanol is 474. It covers both operational and non-operational employees. If there is a maintenance shutdown, there would be a rise in the number of employees working on the site, involving third-party contractors. This number might increase or decrease over the years.

On the east, south, and west of the methanol plant, it is surrounded by the sea while the north consists mostly of factory buildings including the administration office.

2.6 Determination of chemical hazardous and consequence scenario

The chemical hazard can be identified when simulation using ASPEN Hysys has been done where only one dominant chemical is chosen to study the worst-case scenario. If the dominating components are methanol and hydrogen, the possible hazard is it is extremely flammable where it could be ignited easily in ambient temperature and pressure. Meanwhile, carbon monoxide has the potential to be toxic and highly flammable. Its features are somewhat lighter than air, thus if a leak occurs, the flame will quickly flashback to the site of the leak. Carbon dioxide, a significant amount can replace oxygen in the air and trigger suffocating in low-lying regions, especially inside enclosed spaces where high concentrations might cause asphyxia. After that, the consequence scenario for this case study is leakage sizes which are 10 mm, 75 mm, and 160 mm. Must also consider the day and night condition scenario including the dominant wind directions at the Labuan plant.

2.7 Theory of consequences scenario

Toxic compounds could be emitted speedily and can create harmful clouds that spread over a plant site and the surrounding population. During a discharge, the toxic substance in the environment is driven out as a noticeable plume or puff. Due to the diffusion of the toxic chemical with airflow, the largest concentration of dangerous material occurs near the release site, whereas concentrations downwind are lower. Eq. (1) in Supplementary Materials is the fundamental basis for dispersion modeling (Crowl & Louvar, 2001).

The triangle illustrated in Fig. 5 comprises of three ingredients required for a flame to ignite: heat, fuel, and an oxidising agent (usually oxygen). A spark is usually seen as the ignition source (for gaseous fuels, or liquids with high vapor pressure, the ignition source can be a spark initiated by friction). The source of ignition leads to the thermal degradation of a solid into

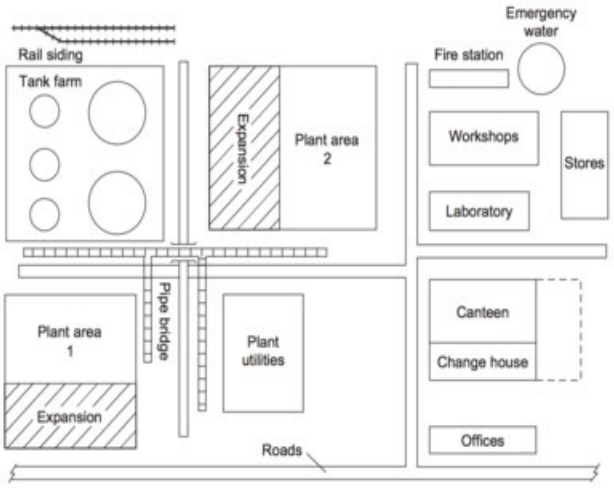

Fig. 4: A common site layout

Fig. 5: The fire triangle

combustible gases, and the interaction of those gases with oxygen in the outer atmosphere, as in the scenario of solids burning. People normally think of small ignition sources like a match or a spark, but for compounds that are not ordinarily flammable, a huge flame can function as an ignition source. A strong ignition source would help a solid that isn't generally combusted to contribute to the fire. The calculation for flammability can be determined using Eq. 2, 3, 4, and 5 in Supplementary Materials (Crowl & Louvar, 2001).

The most damaging blast is a vapor cloud explosion (VCE). These explosions happen in a series of processes that include a huge amount of flammable vapor being released suddenly, the vapor being dispersed around the plant site while mixing with air, and the vapor cloud being ignited. Certain requirements must be satisfied for an explosion to occur. To start, the chemical emitted must be flammable, and ignition should happen after a specific period has passed since instant ignition leads to another event (a jet fire). A sufficiently huge cloud of a fuel-air combination will likely form if there's a lengthy delay (Oran et al., 2020). VCE is influenced by a range of factors, including confinement, congestion, wind, and leakage conditions, any of which must be considered when assessing the amount of overpressure induced by VCE. Quantity of material released, the fraction of material vaporised, probability of cloud ignition, distance traveled by a cloud before ignition, the time delay before cloud ignition, probability of explosion rather than fire, the existence of a threshold quantity of material, explosion efficiency, and location of ignition source concerning release have been some of the elements that determine VCE actions (Baron et. al, 2017). Experiments with explosives have shown that the overpressure could be determined using Eq. (6), (7), and (8) in the Supplementary Materials.

2.8 Structure Operations

Fig. 6 shows the process flow conducted during an assessment. It is the first approach to conduct this assessment by using ASPEN Hysys as a process simulation tool. The Peng Robinson equation of state has been an appropriate fluid package for methanol (Rashid et al., 2021). The information of temperature at 288 °C, pressure at 76, 184, and 331 bar, and molar flowrate based on ratio variation which are 1:3, 1:7, and 1:10 are incorporated in HYSYS. The ASPEN Hysys data comprises the mass fraction and volume fraction of substances in the solution. The results will then be applied as parameters of source data in ALOHA software to calculate the amount of toxicity, thermal radiation, and overpressure of the chemicals. Moreover, the input that needs to be inserted in ALOHA are chemical and atmospheric data. Atmospheric data such as wind speed, wind direction, elevation, ground roughness, cloud cover, air temperature and humidity are needed in order to generate ALOHA. ALOHA results will be shown in the graphical structure whereas MARPLOT is present in the map view. Finally, using MARPLOT software, this information will be generated into an area footprint based on distance and threat zone. It will determine the exact area of the plant. The three coloured regions that will be displayed are red, orange, and yellow. The red color will be labeled as a hazard area. As a result, the percentage of fatalities will be calculated by dividing the area footprints by the total area.

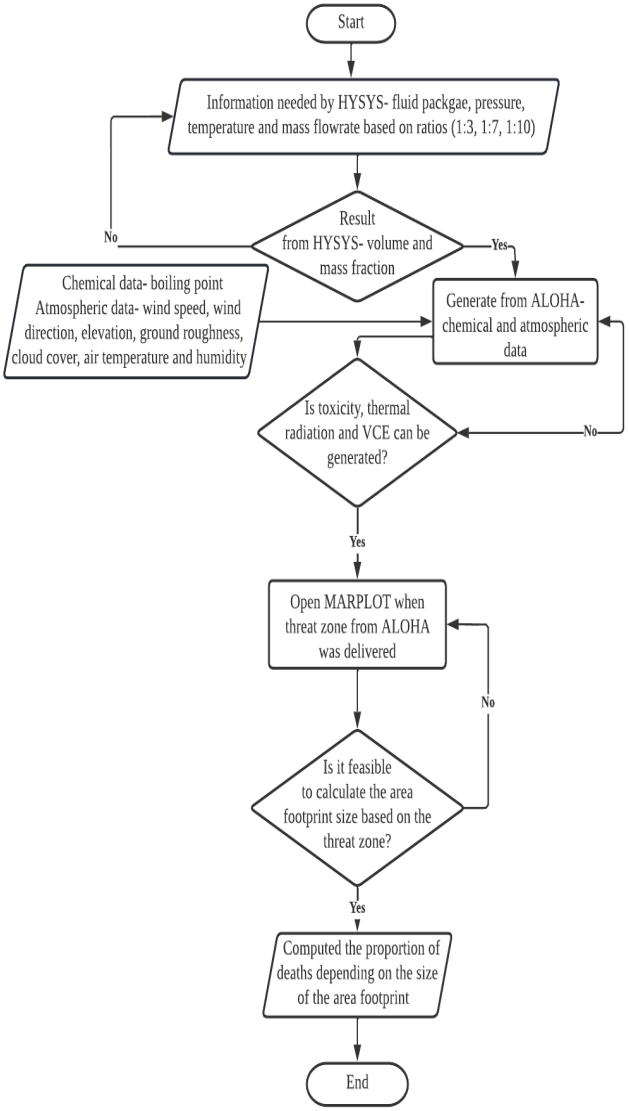

Fig. 6: The flowchart for the process output

3.0 Results and discussion

3.1 Nine plants scenarios

ASPEN Hysys simulations are utilised to obtain the mass fraction and volume fraction of the three plants. Plant 1's specifications are based on the reference plant, which has a pressure of 76 bar and a temperature of 288 °C. Next, Plant 2 raises the pressure to 184 bar while maintaining the temperature same, whereas Plant 3 uses a pressure of 331 bar. From Plant 1 until Plant 3, the input ratio is 1:3. However, Plant 4, 5, and 6 operate at 76, 184, and 331 bar respectively at a molar ratio of 1:7. In addition, at a molar ratio of 1:10, Plant 7 runs at 76 bar, Plant 8 at 184 bar, and Plant 9 at 331 bar. All of these plants used the same temperature as a reference plant. Table SM 1 and SM 2 summarise the results for each plant in terms of mass and volume fraction, respectively.

For every plant, the data for mass and volume fractions are diverse. According to the results of Plant 1, 2, 4, and 7 carbon dioxides is the major chemical component at 0.6306, 0.4699, 0.4252, and 0.333 accordingly. Meanwhile, the remaining Plant 3, 5, 6, 8, and 9, shows methanol as a dominant chemical which is 0.4678, 0.3553, 0.4866, 0.3584, and 0.4538 respectively. In contrast with mass fraction, the dominant chemical that exists for volume fraction is mostly hydrogen for all plant except for Plant 3 display methanol as the dominant chemical.

3.2 Percentage fatalities of all leakage size

The entire amount of data for all scenarios, including toxic, flammable, VCE, and jet fire, for a 10mm leaking size is 45. Only 40% of those will end in fatalities, resulting in 18 incidents. Following, for the 75 mm and 160 mm leakage sizes, there have been 46 incidents, both deadly and non-fatal, with 70% of them resulting in plant death. Table SM 3 in Supplementary Materials shows all significant incidents that will result in deaths.

Plant 1 seemed to have no deaths during any carbon dioxide release for all leakage sizes, both during the day and at night. Carbon dioxide has mainly toxic behavior, but methanol generates four consequences: toxic, flash fire, VCE, and jet fire. There have been no fatalities in any case for VCE of methanol. Leakage sizes of 75 mm and 160 mm in Plant 2 only lead to a percentage of fatalities due to toxicity by carbon dioxide. For 75 mm, during daytime has 0.98% while at night increase by 10% which is 9.95%. But, for 160 mm daytime contributes 1.09% of fatalities while nighttime inclines to 11.14%. Furthermore, Plant 3 has one of the worst situations for methanol toxicity at a leakage size of 160 mm, with 16.07% fatalities throughout the night. In the case of flash fire, 3.58% are caused by a 160 mm leakage size at night, but for jet fire, the worst case is during daylight for the same leakage size which is 9.17%. Next, Plant 4 achieves the same outcome as plant 1, namely 0% deaths due to carbon dioxide. Plant 5 had the highest rate of deaths at 75 mm and 160 mm leakage sizes, with 6.13% occurring at night for toxic cases and 1.33% occurring at night for flash fire cases. However, due to the 160 mm leaking size, jet fire causes 2.15% of fatalities during the day. In-Plant 6 throughout the night, the worst fatality for methanol components are 9.97%, and 2.21% in toxic and flash fire situations, respectively. Meanwhile, during the day, the percentage of fatalities caused by jet fire is 3.92%. All worst cases for Plant 6 happened at leakage size 160 mm. Furthermore, as the results of Plants 1 and 4, Plant 7 yields 0% deaths due to carbon dioxide exposure.

The leak of methanol at Plant 8 can result in a toxic release, flash fire, and jet fire occurrences. Plant 8, methanol leakage can create toxically and flash fire incidents with the same percentage of fatalities for both leakage sizes of 75 mm and 160 mm at 5.11% and 1.1% deaths at night accordingly. The situation for jet fire in Plant 8 produces the worst scenario during the night which is 1.66% at 160 mm leakage. Finally, the worst proportion of fatalities that occurred in Plant 9 is the same as in Plant 8, but in toxic cases, it increased to 7.07%. Cases of flash fire and jet fire rise to 1.15% and 3.74%, respectively.

Fig. 7 illustrates the worst impacted footprint from MARPLOT when the wind direction is WNW. The leaking size of 160mm is responsible for all of the outcomes, whether during the day and at night. Fig. 7(a) depicts the release of methanol partly due to jet fire, with a footprint of roughly 12740 m^2 surrounding the processing area during the day, and Fig. 7(b) represents the case based on methanol toxicity, with a footprint of 22335 m^2 during the night. Both are derived from a 1:3 input molar ratio. Fig. 7(c) and 7(d) indicate the effect of an input ratio of 1:7. Based on the footprint, the impacted area for Fig. 7(c) is 5455 m^2 during the day due to a methanol jet fire. Fig. 7(d) shows that it is caused by methanol toxicity, with an impacted area of 13865 m^2 at night. Finally, the molar ratio in Fig. 7(e) and 7(f) is 1:7. The situation for these two figures will be the same as the previous ratio for

both day and night. Fig.7(e) has an impacted area of 3967 m^2 during the day and 9833 m^2 at night for Fig. 7(f). It is shown that whenever the molar ratio increases, the impacted area decreases during both day and night.

3.3 Results analysis

3.3.1 Comparison between pressure

Three plants perform at various pressures: 76 bar (Plant 1), 184 bar (Plant 2), and 331 bar (Plant 3). The quantity of CO_2 emitted by Plant 1 leakage diameters of 10 mm, 75 mm, and 160 mm is 893 kg, 951 kg, and 951 kg, respectively. However, in this situation, the proportion of fatalities caused by the poisonous CO_2 emitted is 0% for both conditions, day and night. This is due to the fact that the distance is less than 10 m, making it less reliable over short distances. Following that, Plant 2 emitted CO_2 at 2009 kg, 2121 kg, and 21211 kg for leakage sizes of 10 mm, 75 mm, and 160 mm, sequentially. However, because the distance is shorter than 10 m, the likelihood of death drops to 0% for leakage sizes of 10 mm. However, the deaths for 75 mm and 160 mm leak sizes are 0.98% and 1.09%, respectively, during the day, and 9.95% and 11.14%, respectively, during the night. Considering leak sizes of 10 mm, 75 mm, and 160 mm, the amounts of methanol emitted in Plant 3 are 4656 kg, 5776 kg, and 5776 kg, accordingly. Once the size of the leak increases, the percentage of deaths increases from 0% to 4.32% to 5.55% during the day. Meanwhile, during the night, the percentage of fatalities increases from 1.23% to 16.07% for leak sizes ranging from 10 mm to 160 mm. From Table 2, the worst mortality occurs when the leak size is 160 mm at a pressure of 331 bar. Furthermore, as pressure increases, so does the amount of chemicals released and the percentage of deaths. As a result, greater pressure situation has a significantly greater influence as pressure increased since the amount of mass and volume fraction also rises.

3.3.2 Comparison between molar ratio

At the same pressure setting of 331 bar, raising the input molar ratio results in a much-reduced mortality percentage. The percentage of deaths drops from 16.07% to 7.07% when such leak size is 160 mm. Table 3 provides a quick comparison of molar ratio fluctuation. When such leak size is 160 mm and the molar ratio is 1:3, the quantity of methanol released is 5776 kg, whereas the amounts released at ratios 1:7 and 1:10 are 3047 kg and 2128 kg, correspondingly. Next, according to the ratios 1:3, 1:7, and 1:10, the value of methanol released for the leak size 75 mm is the same as in the leak size 160 mm.

Table 2: Comparison of percentage fatalities under various pressures

Pressure (bar)	Fatalities (%)
76 (Plant 1, 4, 7)	no worst cases
184 (Plant 2)	11.14
331(Plant 3)	16.07

Table 3: Comparison of percentage fatalities under various molar ratio

Ratio	Fatalities (%)
1:3	16.07
1:7	9.97
1:10	7.07

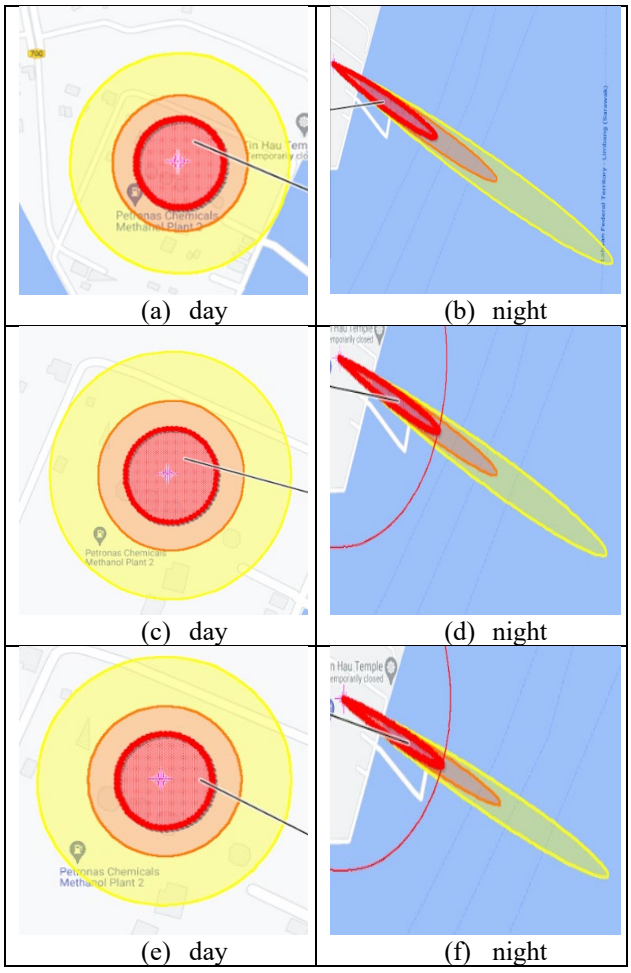

Fig. 7: The trace of methanol dispersed in the ratios of 1:3,1:7, and 1:10 throughout the day and night out from the WNW direction of the wind; (a) 1:3, day, jet fire, (b) 1:3, night, toxic, (c) 1:7, day, jet fire, (d) 1:7, night, toxic, (e) 1:10, day, jet fire, (f) 1:10, night, toxic

Nevertheless, the quantity of methanol emission with a leakage size of 10 mm is 4656 kg, 2976 kg, and 2126 kg from a ratio of 1:3 to 1:10. So, when the molar ratio increases, the number of chemicals released and the proportion of mortality reduces. This is because raising the input molar ratio decreases the mass and volume fraction. It demonstrates that when the molar ratio increases, the harm of methanol on individuals becomes less severe.

4.0 Conclusions

Finally, the possible hazards of methanol production for molar ratio modification at high-pressure settings of 76, 184, and 331 bar were evaluated. The mass and volume fraction of the chemical mixture in the reactor vessel was estimated using ASPEN Hysys simulation software. The outputs will now be considered a valuable parameter in ALOHA software to calculate the chemicals' toxicity, thermal radiation, and overpressure. Then, this information is converted into a region footprint focused on distance and threat zone using MARPLOT software. The percentage mortality may be calculated using MARPLOT by dividing the impacted area by the overall area of the plant. Plant 3 has the most fatalities case, which were also triggered by methanol toxicity at a leakage diameter of 160 mm. The incident occurred during the night, while the wind was blowing from the WNW. The mortality rate as a consequence is 16.07%. Methanol is by far the most harmful chemical in the process area, followed by carbon dioxide, carbon monoxide, and hydrogen. In comparison to other molar ratios, an input molar ratio of 1:3 at pressure 331 bar resulted in higher deaths. The important finding of the study is that it would give greater precise predictions of potential threats. Additionally, since there is limited space for misinterpretation, the thoroughness of this analysis may give more assurance. It can offer a more secure conclusion about the idea by presenting a clear amount concerning potential risk. increase the yield of bioethanol production.

Contribution statement

Mohd Aizad Ahmad: Conceptualization, experimental design, methodology, investigation, contributed reagents and materials, data analysis and interpretation, and writing/review-original draft; **Anis Syamimi Abd Rashid:** Conceptualization, 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 Materials

Table SM 1: Summary for mass fraction for 9 plants

RATIO	PRESSURE (BAR)	MASS FRACTION				
		CO_2	H_2	CH_3OH	H_2O	CO
1:3	76 (Plant 1)	0.6306	0.0969	0.0994	0.1017	0.0713
	184 (Plant 2)	0.4699	0.0686	0.2658	0.1675	0.0281
	331 (Plant 3)	0.2261	0.032	0.4678	0.2673	0.0067
1:7	76 (Plant 4)	0.4252	0.2081	0.1545	0.1359	0.0762
	184 (Plant 5)	0.2298	0.1739	0.3553	0.2159	0.0251
	331 (Plant 6)	0.0776	0.1504	0.4866	0.2782	0.0072
1:10	76 (Plant 7)	0.333	0.2793	0.1689	0.1434	0.0754
	184 (Plant 8)	0.1547	0.2472	0.3584	0.2165	0.0232
	331 (Plant 9)	0.0495	0.2304	0.4538	0.2595	0.0068

Table SM 2: Summary for volume fraction from 9 plants

RATIO	PRESSURE (BAR)	VOLUME FRACTION				
		CO_2	H_2	CH_3OH	H_2O	CO
1:3	76 (Plant 1)	0.3097	0.5623	0.0506	0.0413	0.0361
	184 (Plant 2)	0.2726	0.4703	0.1599	0.0804	0.0168
	331 (Plant 3)	0.1716	0.2872	0.3682	0.1678	0.0052
1:7	76 (Plant 4)	0.1314	0.76	0.0495	0.0347	0.0243
	184 (Plant 5)	0.0804	0.7191	0.129	0.065	0.0091
	331 (Plant 6)	0.0299	0.6844	0.1943	0.0886	0.0028
1:10	76 (Plant 7)	0.0832	0.824	0.0437	0.0296	0.0194
	184 (Plant 8)	0.0424	0.8002	0.1019	0.049	0.0066
	331 (Plant 9)	0.0143	0.7859	0.1359	0.062	0.002

Table SM 3: Summary of percentage fatalities in every plant

Ratio	Pressure - Plant	Chemical-event	Percentage Fatalitites - 0.01m		Percentage Fatalitites - 0.075m		Percentage Fatalitites - 0.16m	
			DAY	NIGHT	DAY	NIGHT	DAY	NIGHT
1 to 3	76– Plant 1	CO_2 - Toxic	0.00	0.00	0.00	0.00	0.00	0.00
	184– Plant 2	CO_2 - Toxic	0.00	0.00	0.98	9.95	1.09	11.14
	331– Plant 3	MeOH - Toxic	0.00	1.23	4.32	15.15	5.55	16.07
		MeOH - Flammable			0.72	3.24	0.92	3.58
		MeOH - Jet Fire	0.22	0.22	3.86	2.89	9.17	6.73
1 to 7	76– Plant 4	CO_2 - Toxic	0.00	0.00	0.00	0.00	0.00	0.00
	184– Plant 5	MeOH - Toxic	0.00	0.86	1.69	6.13	1.69	6.13
		MeOH - Flammable	0.00	0.14	0.28	1.33	0.28	1.33
		MeOH - Jet Fire	0.22	0.22	1.80	1.75	2.15	2.09
	331– Plant 6	MeOH - Toxic	0.00	1.16	2.82	9.89	2.92	9.97
		MeOH - Flammable	0.00		0.47	2.18	0.49	2.21
		MeOH - Jet Fire	0.22	0.22	3.22	2.41	3.92	3.82
1 to 10	76– Plant 7	CO_2 - Toxic	0.00	0.00	0.00	0.00	0.00	0.00
	184– Plant 8	MeOH - Toxic	0.00	0.85	1.32	5.11	1.32	5.11
		MeOH - Flammable	0.00	0.14	0.22	1.10	0.22	1.10
		MeOH - Jet Fire	0.22	0.22	1.57	1.52	1.71	1.66
	331– Plant 9	MeOH - Toxic	0.00	1.02	2.26	7.07	2.27	7.07
		MeOH - Flammable	0.00	0.16	0.38	1.55	0.38	1.55
		MeOH - Jet Fire	0.22	0.22	2.18	2.81	2.85	3.74

List of equations

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

Flashpoint temperatures for pure substances of liquid:

$$T_f = a\frac{b(c/T_b)^2 e^{-c/T_b}}{\left(1-e^{-c/T_b}\right)^2} \quad (2)$$

For a mixture, LFL and UFL are using the equation below:

$$LFL = \frac{0.55(100)}{4.76m+1.19x-2.38y+1} \quad (3)$$

$$UFL = \frac{3.5(100)}{4.76m+1.19x-2.38y+1} \quad (4)$$

LOC is estimated using stoichiometry of the combustion reaction and the LFL:

$$LOC = Z(LFL) \quad (5)$$

$$z_e = \frac{r}{m_{TNT}^{1/3}} \quad (6)$$

$$m_{TNT} = \frac{hmDH_c}{E_{TNT}} \quad (7)$$

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