Severity Effect of Methanol Toxicity from High Pressure Reactor

Z A Rashid, M A Subri, M A Ahmad, M F I Ahmad Fuad, N S Japperi*
Faculty of Chemical Engineering, Universiti Teknologi MARA,
40450 Shah Alam, Selangor, Malaysia
**zulkifli466@uitm.edu.my*

ABSTRACT

CO_2 hydrogenation to methanol synthesis is one of the effective solutions to mitigate the climate changes and the greenhouse gas emissions. However, the drawbacks of this process needed it to operate at high pressure condition where the possibility of leakage and fatality occur is possible. The simulation of this process was simulated using Aspen HYSYS, ALOHA and Google Earth to analyse the methanol toxicity severity from the high-pressure reactor. The probit will determine the level of the severity. It shows that higher pressure with bigger leakage size may experience high severity for the methanol is achieved the highest severity at 400 bar with the bigger leakage size. As the leakage size and pressure is increasing the exposure of the chemical is increasing, thus increasing the severity to the surrounding.

Keywords: *Risk Assessment; Severity; Consequence Modelling; Toxicity*

Introduction

Methanol has a characteristic which are very toxic and very flammable. Methanol is toxic when it enters the body by ingestion, inhalation, or absorption through the skin and can be fatal due to depression of the central nervous system which can lead to decreased respiratory rate, decreased heart rate, and suppressed brain activity [1]. Methanol has colourless appearance, hygroscopic and methanol is miscible or mixable with water completely. The demand of methanol has increasing as fuel at global competition where the needs to search the new alternatives of producing the chemical bulk is varied [2]. Methanol is a feasible substitute for the energy source which offering a suitable solution on large scale for the efficient energy storage, while it plays a significant part in economy and sustainability by captured the carbon dioxide from power plant and convert it into the methanol [3]. One of the alternatives

ISSN 1823-5514, eISSN 2550-164X

Received for review: 2020-09-16
Accepted for publication: 2021-03-18
Published: 2021-04-15

is the methanol synthesis from hydrogen (H_2) and carbon dioxide where carbon dioxide is hydrogenated to methanol which has greater attention recently because of the global warming such as greenhouse gas emission from the industrial activities [4]. The importance of CO_2 hydrogenation to methanol was highlighted in the work using electricity and electrolysis for methanol production [5], and study on power to fuel technologies [6].

Since 1920's until 1960's the methanol synthesis from syngas was operated at pressure range from 250 bar to 350 bar and 320 ^oC to 450 ^oC. Then, at 1970 the reaction operating condition switched to 50–100 bar and 200–300 ^oC due to present catalyst that more active [7]. However, the methanol conversion percentage is still low (less 60%). Recently, advantage of using high pressure has been discovered by several researchers [8]–[11]. In 2016, based on experiment done by Gaikward et. al, have shown that under high-pressure condition above a threshold temperature, the reaction overcomes kinetic control, entering thermodynamically controlled regime. 90% CO_2 conversion and >95% methanol selectivity was achieved with a very good yield (0.9-2.4 gMeOH gcat $^{-1}$h^{-1}) at 442 bar [10]. In view of this fact, it can be concluded that CO_2 hydrogenation methanol synthesis process introduced is operated at the high-pressure condition which is more than 100 bars, when the experimental results show a 76.4 bar with recycle pressurized CO_2 hydrogenation reactor, at a temperature of 288 ^oC, is able to produce a conversion to methanol product of 24%. This methanol conversion percentage increased to 35% (200 bar), 54% (300 bar), 87% (400 bar) and exceeded 90% (500bar). However, this condition is possibly can lead to the leaking of the reactor due to the high-pressure condition [12]. Furthermore, high temperature combine with high pressure have more energy, lead to higher risk compare to lower pressure [13]. The exposure of chemical from the reactor such as methanol may lead to fatality to the human and environment. Based on past incident, methanol has poison effect that can cause severe metabolic disturbances, loss of sight, permanent neurologic dysfunction and also lead to death [14]. This study aims to analyse the leakage from CO_2 hydrogenation to methanol synthesis reactor that operating at high pressure and determine the severity effect from the CO_2 hydrogenation to methanol synthesis process which is methanol toxicity. The risk assessment analyses the severity of the incident towards the human and environment if the methanol leakage occurred in the plant. Currently, only few author works on high-pressure methanol plant such as study on fatalities comparing pressure 76 bar and 442 bar [15], work using artificial intelligent to predict percentage fatalities for methanol jet fire [16], where other works not focus on risk assessment study for CO_2 hydrogenation to methanol such as study on energy analysis for methanol plant up to 950 bar and 1000 bar [17, 18], study on the thermodynamic equilibrium using high-pressure methanol process [19], design and simulation CO_2 hydrogenation to produce methanol for CO_2 capture and energy analysis [20], works on CO_2 and H_2 different ratio to produce high yield methanol [21, 22], works on CO_2 and H_2 1:3 ratio at high-pressure as high as 442 bar to produce more methanol [10] [23].

Methodology

The assessment is focussed on severity effect of methanol plant in high pressure condition. The reactor of the methanol is modelled to determine the methanol produce based on 100, 200, 300, 400 and 500 bar. The volume of reactor used was 7.6 m^3, refer to the work by Mar Perez-Fortes et al. [24]. In this study, mass flow rate into reactor was 91,500 kg/h, combining 80,500 kg/h of CO_2 and 11,000 kg/h of H_2, while simulation study by Mar Perez-Fortes et al. used 91,500 kg/h at inlet combined with recycle flow rate of 376, 200 kg/h, to have 467,600 kg/h flow rate into reactor. Mar Perez-Fortes et al. using 42 m^3 to contain 515 gas hourly space volume (GHSV), then this GHSV value was used to get reactor volume of 7.6 m^3 for this study. The severity effects of methanol are determined based on the leakages and pressure simulations.

Modelling simulation

The study is conducted by using the computer aided such as Aspen HYSYS, ALOHA and Google Earth. The suitable fluid package for carbon dioxide (CO_2) process used is The Peng-Robinson equation of state. Peng Robinson equation is suitable for mixtures of nonpolar and slightly polar compounds and most widely used thermodynamic package as it applies to all applications involving hydrocarbons [25]. The ALOHA is simulated to determine the radius affected and downwind concentration which the location is located at Port Kalama, WA. The coordinate location is 46^o 01'18" N 122^o 51' 30.07" and has elevation about 8 meters. The windspeed modelled is 1.6 m/s, temperature is 51.5 ^{o}F, surface roughness is 1 meter, class B, no inversion and humidity level at 71%. All these data extracted from QRA report on Methanol Plant produced by AcuTech Consulting Group [26]. The Google Earth is applied in order to get affected mapping areas from consequence simulation. Figure 1 shows the process diagram of reactor modelled in this analysis.

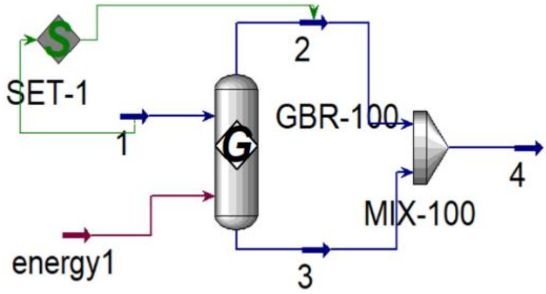

Figure 1: Reactor's process flow diagram.

Release rate formulation

The choked pressure is the maximum downstream pressure resulting in maximum flow through the hole or pipe.

$$\frac{P_{choked}}{P_1} = \left(\frac{2}{\gamma+1}\right)^{\left(\gamma/\gamma-1\right)} \tag{1}$$

Where P_{choked} is maximum downstream pressure resulting in maximum flow, P_1 is upstream pressure (bar abs) and k is heat capacity ratio (1.2 for methanol).

$$Q_{m,choked} = C_o A P_o \sqrt{\frac{\gamma g_c M}{R_g T_o}\left(\frac{2}{\gamma+1}\right)^{(\gamma+1)(\gamma-1)}} \tag{2}$$

Where $Q_{m,choked}$ is gas discharge rate, choked flow (kg/s) ,C_o is discharge coefficient (approximately 1.0 for gases) , A is hole cross-section area (m^2), P_o is upstream pressure (N/m^2), M is molecular weight (kg/kg-mol) (for methanol 1.2), R_g is gas constant (8314 J/kg-mole/°K) and T is upstream temperature (K). Equation (1) and Equation (2) is referred in published Purple book [27].

$$Y = K_1 + K_2 \ln V \tag{3}$$

Where V is dose and Y is probit variable. Equation (3) provided by author in QRA book [28].

Results and Discussion

Methanol vapour discharge rate

Simulation of methanol plant was conducted using HYSYS software, where density of mixture in reactor was increase with 30, 71, 148, 387 and 433 kg/m^3 for plant 100, 200, 300, 400 and 500 bar respectively. The simulation also observed increasing of weight fraction for methanol which were 0.14, 0.29, 0.44, 0.59 and 0.61 for plant 100, 200, 300, 400 and 500 bar respectively. The increasing of density and weight fraction lead to increasing mass of methanol in the reactor, which were 32, 155, 492, 1753 and 1990 kg for plant 100, 200, 300, 400 and 500 bar respectively. The increasing amount of methanol mass cause increasing amount of mass release when subjected to leakage, thus, higher discharge rate was observed. Figure 2 shows the gas discharge rate (mchoked) in relation with the pressure operated for methanol at opening of 10 mm, 25 mm and 160 mm with different pressures of 100, 200, 300, 400 and 500 bar. The lowest gas discharge rate is at pressure 100 bar for all leakages. As the pressure increases, the gas discharge rate increases and the highest mchoked is at 500 bar. The mchoked values for leak sizes are 5.45x10-5 kg/s (10 mm), 0.000341 kg/s (25 mm) and 0.0139 kg/s (160 mm). The leak sizes affect the gas discharge rate (mchoked) where the larger the leak size, the higher the gas discharge rate (mchoked). Gas discharge rate (mchoked) will determine the radius of areas affected. The choked pressure is the maximum downstream pressure that will results in maximum flow through the leakage and caused the choked flow or sonic flow.

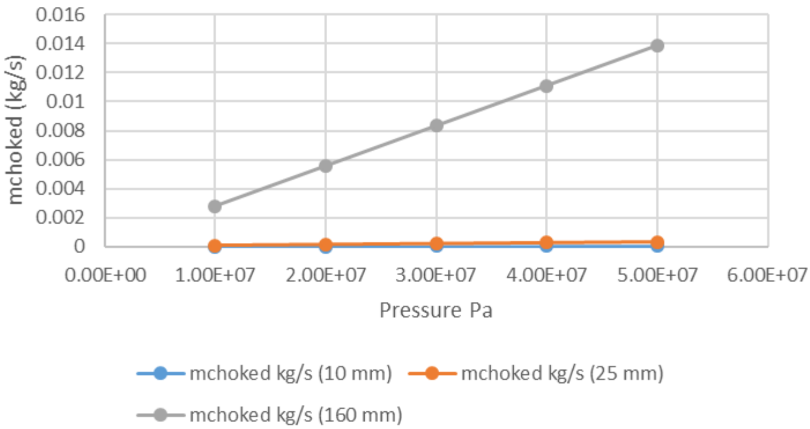

Figure 2: Methanol vapour discharge rate.

Consequence analysis

Figure 4 - 8 show the areas affected by methanol dispersion at 10 mm leakage size where the operating pressures are varied from 100 bar to 500 bar. Wind speed is simulated at 1.6 m/s with three wind directions, which of NNW, NW, and WNW. The duration simulated is 60 minutes, which is the maximum duration of release. Figure 3 shows the dispersion areas at a pressure of 100 bar, which has the lowest distance of area affected. The affected areas are at 34 yards (red zone), 64 yards (orange zone), and 128 yards (yellow zone). Figure 7 shows that at 400 bar of pressure, yield the highest distance where the red zone is affected at 58 yards, the orange zone at 108 yards, and the yellow zone is affected at 216 yards. Figure 8 shows the affected area at 500 bar of pressure yields the highest gas discharge rate but has a lower distance. The affected areas are at 56 yards (red zone), 103 yards (orange zone), and 205 yards (yellow zone). The distance of affected areas increased at 100 bar until 400 bar and decreasing back when the pressure reached 500 bar. At 500 bar of pressure, the affected distance is higher than 300 bar of pressure, as shown in Figure 13. The maximum area affected due to 10 mm of leak size is predicted at 400 bar, and the minimum area affected is predicted at 100 bar. In the red zone, the person exposed may have life-threatening health effects or mortality at a distance of 58 yards. In comparison, at 108 yards, the person may experience injury or disability, and at 216 yards, the person may experience discomfort or irritation of breathing.

Figure 9-13 shows that the areas affected by 25 mm leakage of the methanol reactor, where the wind speed simulated is 1.6 m/s at three wind direction of NNW, NW, and WNW. The 25 mm leakage shows the increase in distance of area affected compared to the 10 mm leakage, where the lowest area affected leakage occurs at 100 bar, as shown in Figure 8. The affected distances are 83 yards at the red zone, 154 yards at the orange zone, and 305 yards at the yellow zone. Figure 12 shows the highest area affected has occurred at 400 bar. The affected areas are at 134 yards (red zone), 249 yards (orange zone), and 474 yards (yellow zone).

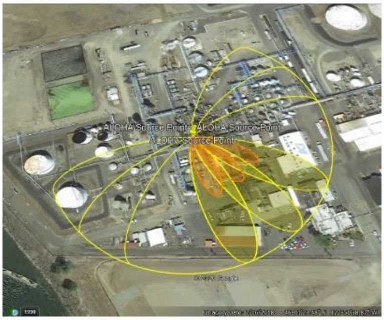

Figure 4: Area affected at 100 bar from 10 mm leakage.

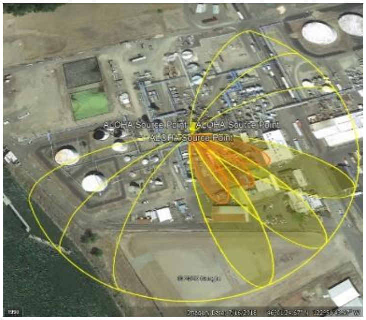

Figure 5: Area affected at 200 bar from 10 mm leakage.

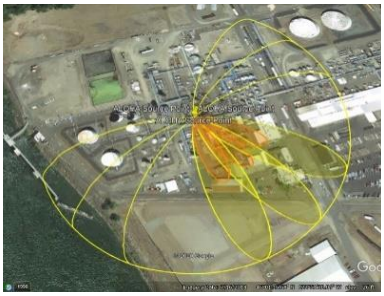

Figure 6: Area affected at 300 bar from 10 mm leakage.

Figure 7: Area affected at 400 bar from 10 mm leakage.

Figure 8: Area affected at 500 bar from 10 mm leakage.

Figure 9: Area affected at 100 bar from 25 mm leakage.

Figure 10: Area affected at 200 bar from 25 mm leakage.

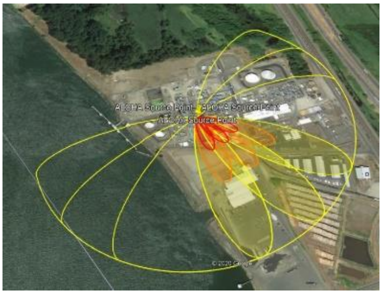

Figure 11: Area affected at 300 bar from 25 mm leakage.

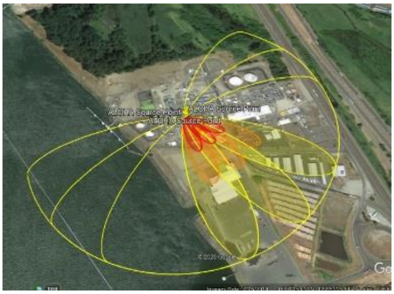

Figure 12: Area affected at 400 bar from 25 mm leakage.

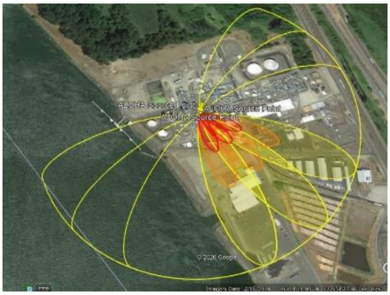

Figure 13: Area affected at 500 bar from 25 mm leakage.

Then, the affected areas are decreasing at 500 bar, as shown in Figure 13, where the red zone is at 129 yards, the orange zone at 240 yards, and the yellow zone at 458 yards. The affected areas at 500 bar are quite similar to the affected areas at 300 bar, as shown in Figure 11. The trend of affected areas at 25 mm leakage size shows the increase of the affected areas from 100 bar to 400 bar and decreasing between 400 bar and 500 bar. It is simulated at 400 bar has a higher severity followed by 500 bar, 300 bar, 200 bar, and 100 bar. At 134 yards, there will be a life-threatening effect on the person in the area distance. In contrast, at 249 yards, the person may experience severe or irreversible and long-lasting adverse health effects or an impaired ability to escape the area. At 458 yards, the person may experience the discomfort of irritation of breathing.

Figure 14 - 18 show the affected areas at 160 mm leakage of the methanol reactor. The wind speed is 1.6 m/s at three different directions: NNW, NW, and WNW. The 160 mm leakage size is simulated to yield the

highest affected areas compared to the other two leak sizes (10 mm and 25 mm). The lowest area affected is shown in Figure 14 at the distance of 137 yards for the red zone, 254 yards for the orange zone, and the 471 yards for the yellow zone. The highest affected area is shown in Figure 17 at the distance of 251 yards for the red zone, the orange zone at 440 yards, and the yellow zone is at 731 yards. It is predicted that the methanol reactor with bigger leak size may have a longer distance of area compared to the smaller leak size. The maximum pressure that yields higher severity is 400 bar for all the leak sizes. The severity percentage is calculated based on the probit percentage studied and discussed in the next section.

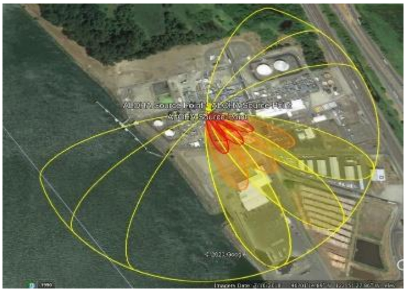

Figure 14: Area affected at 100 bar from 160 mm leakage.

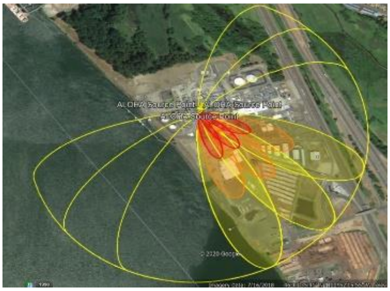

Figure 15: Area affected at 200 bar from 160 mm leakage.

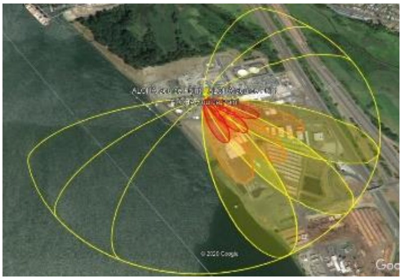

Figure 16: Area affected at 300 bar from 160 mm leakage.

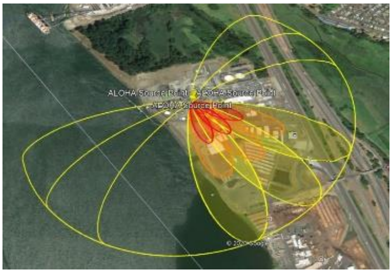

Figure 17: Area affected at 400 bar from 160 mm leakage.

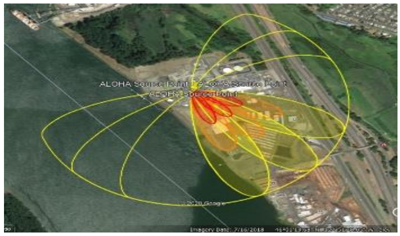

Figure 18: Area affected at 500 bar from 160 mm leakage.

Methanol probit toxic release

Table 1 shows the value of probit for each duration, from 10 minutes to 60 minutes, and categorized by three different types of exposure-response of Acute Exposure Guideline Levels for Airborne Chemicals (AEGL). Each level of AEGL has each concentration limit to methanol exposure, AEGL-3 at 7200 ppm, AEGL-2 at 2100 ppm, and AEGL-1 at 530 ppm. The severity of methanol from the exposure of 10 minutes is 1.1% of people will suffer to the exposure of AEGL-1, 0.3% of people will suffer to the exposure of AEGL-2, and there will be no injury or exposure to people in AEGL-3 as the probit is negative in values. At a duration of 20 minutes, the exposure from AEGL-1 will suffer about 1.5%, whereas AEGL-2 will expose the chemical to people about 0.7% and no injury or any suffering at AEGL-3. At the duration of 30 minutes, the probit percentage increases, where about 1.8% of people will suffer from exposure to AEGL-1. While 1% of people will experience at AEGL-2, and 0.08% will suffer life-threatening effects at AEGL-3. As the duration reached 40 minutes, 2% of people will suffer from AEGL-1, 1.2% will suffer from AEGL-2, and 0.3% will suffer at an exposure of AEGL-3, which can lead to mortality. In the duration of 50 minutes, the severity increases as the people will experience 2.1% from AEGL-1, 1.3% will suffer from the AEGL-2, and 0.4% will be exposed to AEGL-3. The highest score of probit will be at duration 60 minutes, where 2.3% of people will suffer irritation or discomfort of breathing, while 1.5% of people will suffer long-lasting adverse health effects or an impaired ability to escape and 0.5% of people surrounding may suffer which can lead to mortality. Figure 19 shows most of the people surrounding will have higher exposure from AEGL-1.

Table 1: Probit percentage of methanol

Duration	10	20	30	40	50	60
AEGL-1	1.079456	1.539706	1.808934	1.999955	2.148123	2.269184
AEGL-2	0.261312	0.721562	0.990791	1.181812	1.329979	1.451041
AEGL-3	-0.65289	-0.19264	0.076585	0.267606	0.415774	0.536835

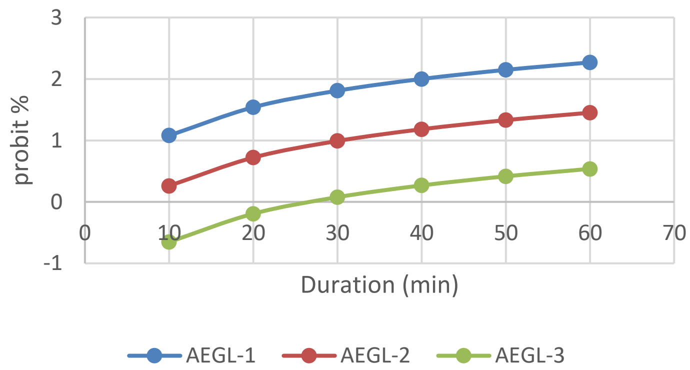

Figure 19: Duration vs probit for Methanol.

Conclusion

This study analyses the severity of methanol with various high pressure and three different leakages. The gas release from methanol is causing the severity of such toxicity towards the surroundings. The gas discharge rate from methanol is increasing as the pressure operated is increasing. While the affected areas from methanol exposure are achieved, the highest at 400 bar for all leakages and increasing as the pressure increases for all leak sizes simulated. Probit equation is added to determine the percentage from the general population to the surrounding, which methanol yield cause bigger severity for catastrophic leakages.

Acknowledgment

The authors would like to acknowledge 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.

References

[1] J. V Ashurst and T. M. Nappe, "Methanol toxicity," *StatPearls [Internet]*, 2019.
[2] R. Kajaste, M. Hurme, and P. Oinas, "Methanol-Managing greenhouse gas emissions in the production chain by optimizing the resource base," *AIMS Energy*, vol. 6, no. 6, pp. 1074–1102, 2018.
[3] A. A. Kiss, J. J. Pragt, H. J. Vos, G. Bargeman, and M. T. De Groot, "Novel efficient process for methanol synthesis by CO_2 hydrogenation," *Chem. Eng. J.*, vol. 284, pp. 260–269, 2016.
[4] T. Kakumoto and T. Watanabe, "A theoretical study for methanol synthesis by CO_2 hydrogenation," *Catal. today*, vol. 36, no. 1, pp. 39–44, 1997.
[5] C. Bergins, K. C. Tran, E. I. Koytsoumpa, E. Kakaras, T. Buddenberg, and Ó. Sigurbjörnsson, "Power to methanol solutions for flexible and sustainable operations in power and process industries," *Power-Gen Eur*, 2015.
[6] S. Schemme, R. C. Samsun, R. Peters, and D. Stolten, "Power-to-fuel as a key to sustainable transport systems–An analysis of diesel fuels produced from CO_2 and renewable electricity," *Fuel*, vol. 205, pp. 198–221, 2017.
[7] B. Tidona, C. Koppold, A. Bansode, A. Urakawa, and P. R. von Rohr, "CO_2 hydrogenation to methanol at pressures up to 950 bar," *J. Supercrit. Fluids*, vol. 78, pp. 70–77, 2013.
[8] R. Gaikwad, A. Bansode, and A. Urakawa, "High-pressure advantages in stoichiometric hydrogenation of carbon dioxide to methanol," *J. Catal.*, vol. 343, pp. 127–132, 2016.
[9] S. Li, L. Guo, and T. Ishihara, "Hydrogenation of CO_2 to methanol over Cu/AlCeO catalyst," *Catal. Today*, vol. 339, pp. 352–361, 2020.
[10] R. Gaikwad, A. Bansode, and A. Urakawa, "High-pressure advantages in stoichiometric hydrogenation of carbon dioxide to methanol," *J. Catal.*, vol. 343, no. April, pp. 127–132, 2016.
[11] R. Gaikwad, H. Reymond, N. Phongprueksathat, P. R. von Rohr, and A. Urakawa, "From CO or CO_2?: space-resolved insights into high-pressure CO_2 hydrogenation to methanol over $Cu/ZnO/Al_2O_3$," *Catal. Sci. Technol.*, vol. 10, no. 9, pp. 2763–2768, 2020.
[12] A.-M. Heikkilä, "Inherent safety in process plant design," *VTT Publ*, pp. 1–132, 1999.
[13] R. Srinivasan and N. T. Nhan, "A statistical approach for evaluating inherent benign-ness of chemical process routes in early design stages," *Process Saf. Environ. Prot.*, vol. 86, no. 3, pp. 163–174, 2008.
[14] N. Yayci, H. Ağritmiş, A. Turla, and S. Koç, "Fatalities due to methyl alcohol intoxication in Turkey: an 8-year study," *Forensic Sci. Int.*, vol.

131, no. 1, pp. 36–41, 2003.

[15] M. Aizad and A. Rashid, "Fatality assessment for high pressure reactor of methanol production plants from CO_2 hydrogenation," *Malaysian J. Chem. Eng. Technol.*, vol. 2, pp. 26–40, 2019.

[16] M. A. Ahmad and Z. A. Rashid, "Adaptive neuro-fuzzy inference system prediction method for percentage fatalities of jet fire incident in methanol production plant," *Int. J. Eng. Adv. Technol.*, vol. 9, no. 1, pp. 5766–5772, 2019.

[17] P. R. Tidona, B., Koppold, C., Bansode, A., Urakawa, A., & von Rohr, "CO_2 hydrogenation to methanol at pressures up to 950 bar," *J. Supercrit. Fluids*, vol. 78, pp. 70–77, 2013.

[18] B. Tidona, "Hydrogenation of carbon dioxide in a flow microreactor at pressures up to 1000 bar." *ETH Zurich*, 2013.

[19] J. G. Van Bennekom *et al.*, "Methanol synthesis beyond chemical equilibrium," *Chem. Eng. Sci.*, vol. 87, pp. 204–208, 2013.

[20] É. S. Van-Dal and C. Bouallou, "Design and simulation of a methanol production plant from CO_2 hydrogenation," *J. Clean. Prod.*, vol. 57, pp. 38–45, 2013.

[21] A. B. Bansode, "Exploiting high pressure advantages in catalytic hydrogenation of carbon dioxide to methanol." *Universitat Rovira i Virgili*, 2014.

[22] A. Bansode and A. Urakawa, "Towards full one-pass conversion of carbon dioxide to methanol and methanol-derived products," *J. Catal.*, vol. 309, pp. 66–70, 2014.

[23] R. Gaikwad, "Carbon dioxide to methanol: stoichiometric catalytic hydrogenation under high pressure conditions." *Universitat Rovira i Virgili*, 2018.

[24] M. Pérez-Fortes, J. C. Schöneberger, A. Boulamanti, and E. Tzimas, "Methanol synthesis using captured CO_2 as raw material: Techno-economic and environmental assessment," *Appl. Energy*, vol. 161, pp. 718–732, 2016.

[25] R. Stryjek and J. H. Vera, "PRSV: An improved Peng—Robinson equation of state for pure compounds and mixtures," *Can. J. Chem. Eng.*, vol. 64, no. 2, pp. 323–333, 1986.

[26] AcuTech Consulting Group, "Quantitative risk assessment final report prepared for : NW Innovation Works, Port of Kalama," February, 2016.

[27] P. G. Stoffen, "Guidelines for quantitative risk assessment," *Minist. van Volkshuisv. Ruimtelijke Ordening en Milieu. CPR E*, vol. 18, 2005.

[28] J. Casal, 2nd Ed., Evaluation of the effects and consequences of major accidents in industrial plants. Amsterdam: Elsevier, 2017.