Quantitative Risk Assessment for Two-Step Process Route of MeOH Production Plant Using Recycled CO_2 with HYSYS

Zulkifli Abdul Rashid, Mohd Aizad Ahmad, Mohd Azahar Mohd Ariff , Muhd Nizam Marzuki

Abstract*: A new technology of methanol (MeOH) production by using carbon dioxide CO2 has changed world prospective regarding methanol production. These will contribute to the mitigation of CO2 which become the major gas in greenhouse gas. The study of this paper is to use quantitative risk assessment (QRA) for this process route to determine the risk tolerance levels, it acceptability in methanol production region and comparing to the old process route which used synthesis of natural gases. With the help of process simulators HYSYS, it can provide precise information regarding the process route at any given time. ALOHA software is implanted in this case study to help in identify the safe zone and vulnerability mapping of each of the process route. Lastly, by comparing the tolerance levels between new and old process route, it can determine which is more preferable to implemented in industrial production.

***Keywords* : Quantitative Risk Assessment (QRA), Methanol Production, HYSYS, Process Route, Carbon Dioxide Recycled.**

I. INTRODUCTION

The quantitative risk assessment (QRA) is used to determine the risk existing of an installation of industrial plant to provide the data for their acceptance, as well as helping to assist decisions and prioritization of choices in order to reduce unacceptable ones [1]. This method is determining the risk due to use, transport, manipulation or storage of hazardous substances during the production. This will show the result of the risk caused by the activity present in the plant and gives important information regarding the acceptability of the activity to the relevant authorities [9].

QRA is one of the important methods to use to give priori evaluation of the safety of the plant before the plant being built. Most of QRA was implemented to existing facilities which is not advisable. Although, this method can calculate the risk safety of the plant but it is difficult to apply it as it is already built. With the integration of process simulator such as HYSYS, it can provide further information to be used in the QRA calculation to determine better result of the risk safety.

Nowadays, QRA work basically focusing on the new methodological aspects which allow the integrated use of QRA and process design simulator. This lead to a topic of ; the assessment of risk and comparing the risk of methanol production plant by using recycle CO_2 and synthesis of natural gases

For a non-existing plant, the risk is assessed in order to determine its acceptability for each region in the plant. The application considered is the production of methanol via hydrogenation of carbon dioxide and via synthesis of natural gases. In this modern era, greenhouses effect is a common environmental impact from the production of side product such as carbon dioxide. This carbon dioxide is the main gases in greenhouse effect. To reduce the environmental impact, the CO_2 is converted into useful fuel in the methanol production. Most of studies based on the methanol production via hydrogenation of CO_2 are on the economical, mitigation of CO_2 and lacking on the safety itself.

Based on this, the QRA is fundamental for this process as it based on technology which is still under improvement and in the chemical route considered here, demands stringent operational conditions (high pressures and temperatures; catalytic process) and involves of hazardous material [1]. Information mainly is available about industrial plants (e.g. Mitsui Chemicals, in Japan) that really implement this process, making its simulation mandatory for any risk analysis [10].

Based on the [9], the methodology of QRA can be divided into five steps; (i) identification and characterization of the installation and system to be analysed; (ii) hazardous identification of the accidental scenario; (iii) estimation of the accidental consequences with vulnerability analysis and physical effects and (iv) estimation and evaluation of the risks.

After all the methodology, it is necessary to analyse the risk and conclude whether it is tolerable or not based on the safety regulation. The risk acceptability criterion is usually based on the NIOSH regulation.

II. METHODOLOGY

A. Description of the Installation

For this case study of a methanol production plant was considered. The production of methanol was based on the process route of Everton S. [5] and Y.H. Hu. [4]. With the help of HYSYS, the simulation can be run and the value of process can be obtained.

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B. Location

The methanol production plant is assumed to be located in Pulau Labuan, Labuan Federal Territory, Malaysia. Methanol plant Labuan was chosen as the study area since it was the most suitable area for the methanol production based on the factors that made it a safe location for methanol operations based on a Detailed Environmental Impact Risk Assessment (DEIA) report in 2006. However, the current technology used in Labuan, does not reuse CO_2-emitted at atmosphere. Therefore, this study is to see the potential of utilization of CO_2 in the plant help minimize the green house effect.

Meteorological data region for the area are the keys in atmospheric modeling dispersion which will be using in QRA. Atmospheric stability is a measure of detecting vertical turbulence in the atmosphere near the earth's surface, if Turbulence tends to increase mixing and diffusion rates, so unstable conditions encourage short vapor clouds and stable conditions encourage long vapor clouds. All the meteorological data was obtained from Malaysia Meteorological Department (MMD) in the year of 2019. Based on the MMD, it can concluded that the most suitable classification of stability at Labuan site is class B, since that the average wind speed at that site is less than 2.5 m / s.

FIG. 1: MAPPING OF METHANOL PLANT LOCATION

C. Process Description

The methanol production process via CO2 was based in the study of Everton S. (2013) [5]. The main reaction occur in the process is where;

$$CO_2 + 3H_2 \rightarrow CH\neg 3OH + H_2O \quad (1)$$

Carbon dioxide and hydrogen gas react to produce methanol and water. The temperature and pressure of the reaction are at 205.2oC and 7.8 atm respectively. The process flow can be seen in the Fig. 2(A) with the help of HYSYS simulation program. The methanol production process via synthesis of natural gases was based on the study of Y.H Hu (2004) [4]. This process flow was used old technology which required high pressure for the reaction to achieve in making the desired product.

$$CH_4 + H_2O \rightarrow CO + 3\,H_2 \quad (2)$$

$$CO + 2H_2 \leftrightarrow CH_3OH \quad (3)$$

The temperature and pressure of the main reaction in this process are at 150oC and 110 atm respectively. The catalyst presence in the reaction is copper, zinc oxide, or aluminium oxide to promote the production of product. The process flow can be seen in the Fig. 2(B) with the help of HYSYS simulation program.

The similarities between both of the process route are that the production rate is set at the range of 2500kg/h of methanol. Besides that, the number of major equipment used in both process are similar such as one reactor, one distillation column and two separator.

Meanwhile, the differences between these process routes are their operating condition in each of the equipment. For example, the condition in reactor at new technology is 205.2oC and 7.8 atm while old technology is at 150oC and 110 atm. The reactant used in both process routes are different and by comparing economically and safety, is in favor of new technology.

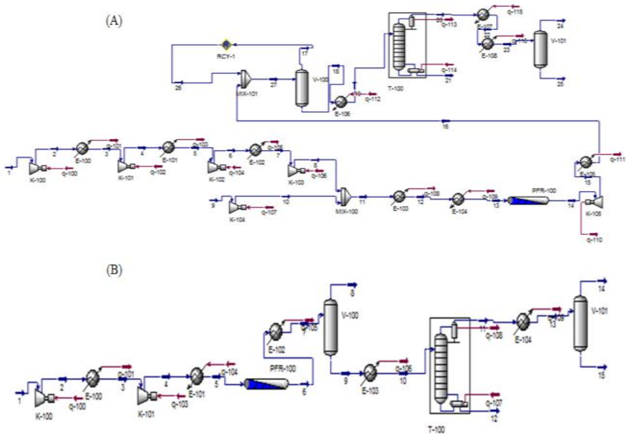

Fig. 2: 2(A) Simulation of process flow of methanol production via CO2 recycle and 2(B) methanol production via synthesis of natural gases

D. Chemical Involved in the Process

In order to complete the risk assessment of this process route, it requires determining the assessment of chemical used in the process route. Based on those two process route, the main chemical presence are methanol, hydrogen and carbon dioxide. The assessments are focusing on to the physical, toxicology and flammability state of the chemical used in the production plant. Methanol and hydrogen gas will be assessing on the flammability while carbon dioxide will focusing on the toxicology.

Methanol and hydrogen gas are extremely flammable chemical at standard temperature and pressure. When these chemical leak from any piping and mix with the atmosphere, it will form vapor cloud which can explode with any ignition present in the situation. Thus, it is necessary to install gas chemical detector in the plant to detect any gas leak occurred.

Carbon dioxide is a toxic gas at high concentration, as well as an asphyxiant gas due to reduction of oxygen [2]. When the carbon dioxide gas leak occurs for long period of time, it will increase the concentration of the gas and harm the surrounding. For the early period, it will causes irritation of the eyes, nose and throat while it will cause lethal for further period of time. By installing a gas detector, this event can be prevented in the early period of time.

Water does not include in this assessment as it a neutral based, not flammable and not toxic chemical.

E. Hazards Identifications

In this case of study, the preliminary risk analysis (PRA) is the technique used to determine any possible hazardous event occurs in an industrial production plant. For this case of study, it divided into two group assessment which is flammability of leak gases and toxicology of leak gases. There are three locations chosen to do flammability assessment based on gas leak from piping. These locations are piping before entering reactor, distillation column, and final separator. While for toxicology, the location chosen is piping entering the mixer. Based on these case study, the result for both process route will be compared and determine which is safer compare to others.

F. Procedure of Consequences and Vulnerability analysis

The objectives of these are to assess of any possible damage to equipment and structure, estimation of social risk and/or individual risk for populations subject to harmful physical effects, mapping of vulnerable areas to determine safe zone and much more [9].

The base quantification of this case study is of exposure to the effect of the hazardous event in death probability. In other words, it only noted the lethal effect from the hazardous events. The possibility of injuries and fatalities that occur to a population impacting from blast wave or release of toxic substance is represented by a Probit function [11]. HYSYS simulation program was used to determine the exact data value for any given time for the probit function assessment. With the precise data, it can be process by ALOHA simulation program which can calculate and mapping the hazardous area from the source. ALOHA simulation program has the function to simulate the progress of hazardous incident from its initial leakage through the formation of a cloud or puddle until its dispersion, and automatically applying the dispersion model suitable to the event analyzed. To complete the calculation and determining the damage structure and social risk, certain assumption and formula was used:-

- Probit function for explosion/impact from blast wave
  The probit function was obtained from G.Opschoor [3]. Whereby Ps is the peak overpressure in Pa unit while Pi is the impulse of the shock wave Pa.s.

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$$Pr = 5-2.44 \ln[7380/Ps + 1.3x109/Pi] \quad (4)$$

- Probit function for toxicology of leakage gas
  The probit function was calculated and obtained the value of constant from HSE. (2008). Whereby C is the concentration of gases, ppm while t is the period of time of gas leakage from the source, s.

$$Pr = -90.8 + 1.01 \ln (C_{nt}) \quad (5)$$

Fig. 3 shows the steps in getting the probit result and comparing between both of the process route.

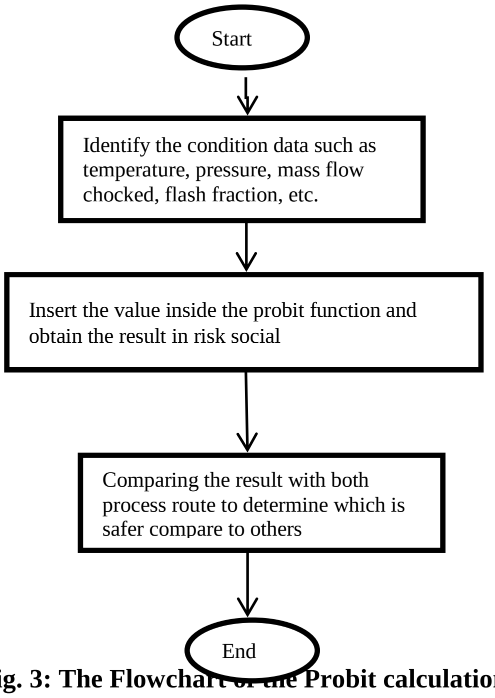

Fig. 3: The Flowchart of the Probit calculation

III. RESULTS AND DICUSSIONS

Once the procedure is follow and the result was obtained based on the data and calculation given. The result obtained in categorised into two segment which are explosion and toxicology result. These results will be used to determine the safety hazardous level between the two process routes. By comparing both of the process routes, it can identify which is more practicable to implement in the industrial plant worldwide.For the explosion result, it divided into three locations which are:-

A. *Gas leakage at piping before entering reactor*

Table 1:Probit calculation for gas leakage before entering reactor

Gas Leakage through 25 mm Hole for 5 minutes				
Technology	Distance, m	peak overpressure	probit	%
Via Carbon dioxide	50	58097.83	9.93	100%
	100	19877.21	7.30	99%
	200	8752.71	5.29	62%
	500	3367.074	2.94	2%
	1000	1673.944	1.21	0%
	2000	835.7722	-0.49	0%
Via Synthesis of natural gases	50	77892.42	10.65	100%
	100	24554.48	7.827	100%
	200	10394.5	5.716	76%
	500	3944.359	3.331	5%
	1000	1956.887	1.603	0%
	2000	976.5312	-0.11	0%

Based on the Table I, it can be seen that methanol production via synthesis of natural gases has high probit value compare to the other technology method. This is due to high peak overpressure obtain from the calculation. Both of this technology production has almost the same probit value and the safe zone is more than 500m.

B. *Gas leakage at piping before distillation column*

Table II: Probit calculation for gas leakage before entering distillation column

Gas Leakage through 25 mm Hole for 5 minutes				
Technology	Distance, m	peak overpressure	probit	%
Via Carbon dioxide	50	35075.16	8.701679	100%
	100	13707.6	6.39623	92%
	200	6365.886	4.510175	31%
	500	2491.438	2.199138	0%
	1000	1241.791	0.481041	0%
	2000	620.4046	-1.23361	0%
Via Synthesis of natural gases	50	802775.3	16.36361	100%
	100	162872.7	12.46152	100%
	200	42182.09	9.153854	100%
	500	12061.83	6.081959	86%
	1000	5678.821	4.229047	22%
	2000	2795.227	2.482805	1%

From the Table II, it shows that the methanol production via synthesis of natural gases is far more dangerous. The safe distance for new technology is at 500m while old technology requires about 2000m to be safe for any hazardous event.

C. *Gas leakage at piping before entering final separator*

Table III: Probit Calculation for gas leakage before entering final separator

Gas Leakage through 25 mm Hole for 5 minutes				
Technology	Distance, m	peak overpressure	probit	%
Via Carbon dioxide	50	36813.58	8.82	100%
	100	14216.3	6.49	93%
	200	6573.687	4.58923	34%
	500	2569.3	2.275017	0%
	1000	1280.346	5.57E-01	0%
	2000	639.6349	-1.15813	0%
Via Synthesis of natural gases	50	32877.65	8.543076	100%
	100	13050.78	6.275595	90%
	200	6094.417	4.40291	28%
	500	2389.278	2.095894	0%
	1000	1191.171	0.378277	0%
	2000	595.1522	-1.33637	0%

Based on the Table III, it can say that both of the probit value are almost the same but for this location, the new technology considered to be more harmful compared to other location. Same as the first location, the safe distance for both technology is at 500m. For toxicology, it only calculates for the new technology via CO_2 production to do risk assessment on it. The probit calculation at gas leakage at piping before entering mixer.

Table IV: Probit calculation for gas leakage before entering mixer

Gas Leakage through 25 mm Hole for 5 minutes				
Size of Hole	Distance,m	Concentration (ppm)	Probit	%
5mm	50	5.993856	-18.4543	0%
	100	16.64678	22.81357	100%
	200	7.91638	-7.21507	0%
	500	1.666065	-70.1772	0%
	1000	0.495671	-119.154	0%
	2000	0.160608	-164.683	0%
25mm	50	149.8464	111.5883	100%
	100	416.1696	152.8562	100%
	200	197.9095	122.8275	100%
	500	41.65162	59.86534	100%
	1000	12.39178	10.88814	100%
	2000	4.015199	-34.6405	0%

This Table IV show the toxicology of gas leakage of carbon dioxide. The result show lethality for 25mm hole around 1000m while only 100m for 5mm hole. Fig. 4 show the vulnerability mapping of probit value from 25mm holes gas leakage at piping before entering the reactor.

Fig. 4: vulnerability mapping

IV. CONCLUSION

The use of process simulator such as HYSYS and ALOHA can help with risk analysis and assessment methods by reducing the expert time and large volume of result and data. This work showing that by applying QRA to a new technology process can help determine the safety and risk by comparing to old technology. Both of these process technologies were run in simulator to obtain data in different operating condition. Based on the result, it can conclude that the new technology; methanol production via CO2 recycle are much more safer compare to old technology; methanol production via synthesis of natural gases in terms of social risk and damages to structure surrounding. Besides that, the safe zone for both process route can be determine by the result value for example, the safe zone of Fig. 4 is at 500m away from production plant.

From these three locations, two of them in favor of new technology which is safer process route compare to old technology. It can conclude that, the new technology is more practicable in terms of safety and economical. Gas detector plays a major role in avoiding these hazardous events and should be compulsory to install in the production plant. Besides that, a relief valve also can be install to minimize the chances of incident to occurs. This result however, should be further studied in order to obtain the mitigation measured that will reduce the risk.

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