CHEMICAL ENGINEERING TRANSACTIONS

VOL. 77, 2019

A publication of
AIDIC
The Italian Association
of Chemical Engineering
Online at www.cetjournal.it

Guest Editors: Genserik Reniers, Bruno Fabiano

ISBN 978-88-95608-74-7; **ISSN** 2283-9216

DOI: 10.3303/CET1977125

Inherently Safer Design of Carbon-Neutral Methanol Production

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In the present framework of global energy transition, a significant increase in the use of carbon-neutral synthetic fuels as renewable energy carriers is expected in the next years. Renewable resources are huge even though scarcely exploitable due to aleatory availability and costs of transportation when produced in remote areas and offshore. Thus, the synergy of methanol production with oil & gas activities represents a beneficial opportunity to share infrastructures and convert renewable energy in a synthetic liquid fuel which can be easily stored and transported. Renewable methanol is a valuable chemical and an energy transition fuel with several applications, in particular in the mobility sector. Moreover, the use of carbon dioxide as raw material for the methanol synthesis could have a positive impact on the global carbon balance, valorising the attractive "Carbon Capture and Utilization (CCU)" concept. However, the novelty of renewable methanol process technologies in the renewable energy context requires a thorough investigation of the critical concerns of the possible routes, among which the safety challenges are prominent. The application of the inherent safety approach can play a paramount role for orienting choices in the preliminary design phases of safer methanol production processes. In the present study, reference schemes for processes proposed for renewable synthetic methanol production were defined. The expected inherent safety performance of the alternative processes were assessed by a specific system of multi-criteria key performance indicators (KPIs), based on the consequence simulation of potential accident scenarios affecting different targets (i.e. humans, assets, environment) both onshore and offshore. The results of the applied methodology allowed a preliminary screening of the hazard level of the alternative process routes, as well as the identification of the key safety issues that need to be addressed in the further development of inherently safer methanol production technologies.

1. Introduction

Nowadays the electricity produced of the entire world still comes from fossil fuels, such as oil, natural gas and coal (BP, 2018), which are unavoidably limited and not environmental friendly. The deployment of sustainable free-emissions renewables plays an important role for decarbonising the energy supply, even though it is often considered technically and economically infeasible to transport discontinuous renewable power for long distances and integrate it into the electricity grid (Zahedi, 2011). One solution consists of converting the excess power into chemical storage media at the production site. In contrast to hydrogen raising serious safety and infrastructure problems, liquid methanol was proposed as a more convenient energy carrier (Olah, 2005). Methanol is already a key compound widely used to produce intermediates or synthetic hydrocarbons in industry and as fuel for heating and automobiles. Moreover, different green processes for methanol production have been recently investigated instead of the traditional method via syngas (Bozzano and Manenti, 2016). These routes can be based on the direct partial oxidation of methane valorising the exploitation of natural gas or can use carbon dioxide (CO_2) as input source in order to promote the "Carbon Capture and Utilization (CCU)" schemes. Even though highly promising for the global future energy transition,

Paper Received: 31 December 2018; Revised: 27 May 2019; Accepted: 3 July 2019

Please cite this article as: Crivellari A., Moreno V., Tugnoli A., Salzano E., Bonvicini S., Cozzani V., 2019, Inherently Safer Design of Carbon-Neutral Methanol Production, Chemical Engineering Transactions, 77, 745-750 DOI:10.3303/CET1977125

these relatively new process technologies should be properly analysed to capture their critical issues, among which safety challenges are crucial.

An inherent safety approach was recognized as a successful way to compare the safety performance of conventional methanol production processes during the early design stages (Ortiz-Espinoza et al., 2017). A method based on inherent safety Key Performance Indicators (KPIs) (Tugnoli et al., 2010) was adapted to identify emerging risks of innovative alternatives in biogas upgrading (Scarponi et al., 2016) and offshore oil production (Crivellari et al., 2018). In the present study, the KPIs framework was preliminarily applied to the possible routes for the renewable production of methanol. Reference process schemes were defined for the most efficient solutions proposed in the existing technical literature. Specific scale-up approaches were adopted to allow the comparison of different scale technologies. The potential hazards associated to them were evaluated by the identification of the dangerous scenarios derived from reference releases for each unit. The expected accident consequences for the human target were analyzed by using conventional simulation tools. The final ranking of inherently safer solutions was obtained by means of proper KPIs assessing the potential hazard level of single units and the overall process with respect to humans.

2. Description of the proposed inherent safety KPIs methodology

Figure 1 illustrates a flow chart of the methodology specifically applied to the present evaluation of innovative methanol production technologies. As shown in this figure, a preliminary step (step 0) consists in the definition of the process schemes to analyze specifying the global material balance and operation mode of the process. In order to perform a consistent assessment, proper assumptions should be applied to convert the processes from batch and fed-bath operation to more productive and commercial continuous mode. In addition, a reference production of methanol should be chosen and all the options should be refer to this by scaling up the global input flowrates with respect to the desired methanol output.

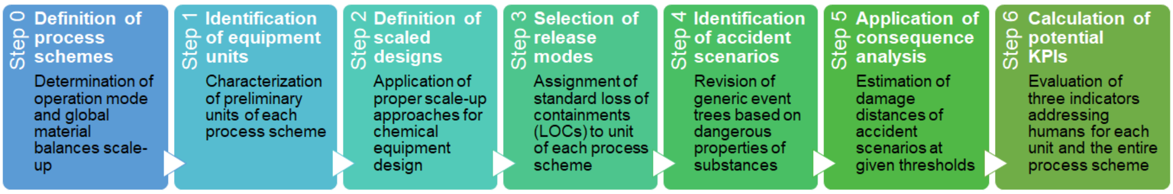

Figure 1: Flow chart of the inherent safety method applied to alternative processes for methanol production

Once the reference schemes were defined, the procedure is carried out for each scheme through six main steps. According to step 1, equipment units were identified and characterized in terms of key substances, operating conditions, material flows, inventory and general technical specifications. Successively, in step 2 specific scale-up design approaches based on dimensionless variables were applied in order to identify the final number of units required for the target methanol productivity. After that, during step 3 loss of containment modes (LOCs) (Purple Book, Uijt de Haag and Ale, 2005) were assigned to each unit according to the approach adopted by Scarponi et al. (2016). In the fourth step of the methodology, event tree analysis was used to identify the possible accident scenarios related to every LOC assigned to each process unit.

Since the proposed KPIs method is a consequence-based approach, damage distances ($d_{i,j,k}$) were estimated for the j-th accident scenario following the i-th LOC of the k-th unit by adopting well-known consequence simulation models (Van Den Bosch and Weterings, 2005) and standard damage thresholds for human target (Crivellari et al., 2018). A height of 1 m was assumed as representative elevation for the estimation of these distances. Finally, the unit potential hazard index (UPI) is calculated as a measure of the maximum damage area which may derived from the worst-case accident scenario for the k-th unit:

$$UPI_k = \pi \, max_i \left(max_j d_{i,j,k}^2 \right) \qquad (1)$$

Moreover, two other indicators were defined within the present methodology, i.e. the flammability potential hazard index (UFPI) and the toxicity potential hazard index (UTPI), by considering only the damage distances for fire/explosion and toxic dispersion, respectively, in Eq(1). The inherent safety performance of the process scheme is then evaluated by summing up KPIs of single units into the overall potential hazard index (PI), the overall flammability potential hazard index (FPI) and the overall toxicity potential hazard index (TPI).

3. Definition and characterization of the process schemes

An extensive survey regarding the state of the art on the alternative processes for methanol production led to the identification of 11 main routes, among which two are the catalytic hydrogenation and the electrochemical reduction of CO_2 (Olah et al., 2009) while the others concern different technologies for the direct conversion of methane to methanol, i.e. conventional catalytic processes, photo- and bio-catalysis, supercritical water oxidation and others (Zakaria and Kamarudin, 2016). In the present study, two of such alternatives were considered for the proposed inherent safety assessment as they currently demonstrate the highest technological maturity in terms of mass and volumetric productivity of methanol.

The first process scheme analysed was the synthesis of relatively pure liquid methanol (CH_3OH) by using renewable electrolytic hydrogen (H_2) and recycled CO_2 in a thermo-catalytic plant (Matzen et al., 2015). As illustrated in Figure 2a, H_2 requires to be compressed in the multi-stage compressor (K01) and then mixed with raw CO_2 and with a recycle stream previously compressed in a dedicated unit (K02). In order to reach the appropriate temperature for the catalytic hydrogenation reaction, the stream is heated (heat exchanger H01) and then fed to the multi-tube reactor (R01). The reactor output is separated into liquid and gas streams in a flash drum (V01). The liquid phase, mainly composed of CH_3OH and water, is separated in a tray distillation column (C01) and finally the produced CH_3OH is cooled down to ambient conditions (heat exchanger H02).

The second scheme selected for the present analysis was the high-temperature partial oxidation of methane (CH_4) based on homogeneous radical gas phase reactions (Yarlagadda et al., 1988). According to this process, gaseous CH_3OH is produced in a flow tubular reactor (R02 in Figure 2b) with other sub-products.

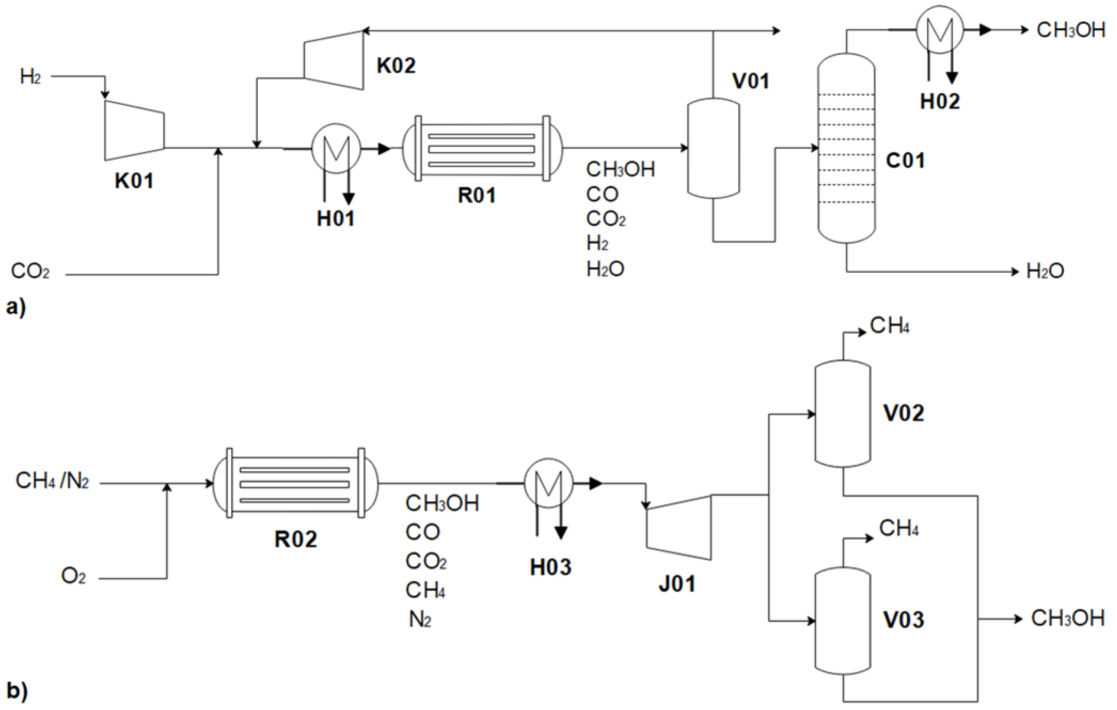

Figure 2: Simplified process flow diagrams of (a) catalytic hydrogenation and (b) radical gas oxidation

Even though these two processes were designed to operate in continuous mode, the radical gas oxidation gives a CH_3OH output flowrate which is seven orders of magnitude lower than that of the catalytic hydrogenation (4.15 t/h). Therefore, this latter rate was fixed as benchmark production in the present analysis and the original inputs of the least performing process were rescaled accordingly.

According to step 1 of the displayed procedure in Figure 1, the preliminary units of the catalytic hydrogenation process were considered equal to those of the original scheme reported in the technical literature (Figure 2a), while conventional scale-up procedures for tubular reactors (Nauman, 2008) were applied to R02 resulting in one multi-tubular reactor of 100 tubes. Moreover, following step 2 of the proposed method, some new units were added to the scaled design of the radical gas oxidation process in order to obtain liquid methanol at high purity. As shown in Figure 2b, a cooler (H03), an expander (J01) and two flash drums (V02-V03) were introduced by adopting basic notions of chemical engineering equipment designs. Table 1 reports the key substances, reference operating conditions and equipment data assumed for the final units of the process schemes.

Table 1: Main input data of process units considered in the present study

Unit	Key substance	Pressure (bar)	Temperature (°C)	Pipe/tube diameter (mm)	Pumped flowrate (kg/s)	Inventory (kg)
K01	H_2	50	25.0	85.7	0.22	-
H01	H_2	50	235.0	133.3	0.23	-
R01	9.4 $\%_{vol}$ H_2 + 90.62 $\%_{vol}$ CH_3OH	50	235.0	127.0	0.08	0.90 (H_2) 12.77 (CH_3OH)
V01	H_2; CH_3OH	1	73.0	136.5; 49.0	0.008;1.16	0.06;161.40
K02	H_2	50	120.6	49.0	0.007	-
C01	CH_3OH	1	64.5	49.0	1.15	482.36
H02	CH_3OH	1	25.0	49.0	1.15	-
R02	92.6 $\%_{vol}$ CH_4 + 7.4 $\%_{vol}$ CH_3OH	50	451.0	39.2	0.08	8.25 (CH_4) 1.33 (CH_3OH)
H03	CH_4; CH_3OH	50	87.5	161.9	9.09	2725.56
J01	92.6 $\%_{vol}$ CH_4 + 7.4 $\%_{vol}$ CH_3OH	1	-26.8	797	8.34	-
V02-V03	CH_4; CH_3OH	1	-26.8	603.6; 49.0	4.00; 0.55	2.47; 98.62

4. Results and discussions

The data reported in Table 1 were used to assign LOCs to the analyzed units as proposed in the Purple Book (Uijt de Haag and Ale, 2005):

- LOC 1 (small leak, continuous release from a 10 mm equivalent diameter hole);
- LOC2 (catastrophic rupture, release of the entire inventory in 600 s) and
- LOC3 (catastrophic rupture, instantaneous release of the entire inventory)

were assumed when unit inventory is the most relevant hazard factor than inlet/outlet streams, whereas

- LOC4 (pipe leak, continuous release from a hole having 10 % of pipe diameter) and
- LOC5 (pipe rupture, continuous release from the full-bore pipe)

were considered. For these LOCs, accident scenarios causing damage only to human targets (flash fire, jet fire, pool fire, fireball, toxic cloud, vapour cloud explosion or VCE, physical explosion, toxic cloud) were identified from standard event trees by considering the flammable properties of H_2 and CH_4, and the flammable/toxic properties of CH_3OH. Two examples of revised event trees are reported in Figure 3.

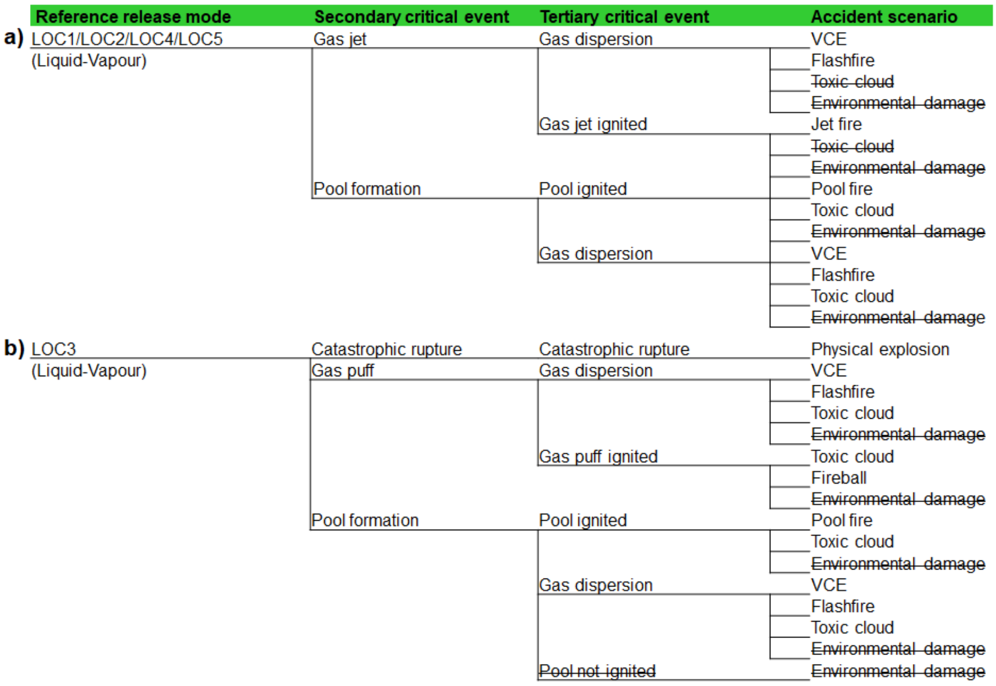

Figure 3: Event trees for (a) continuous release and (b) instantaneous release of CH_3OH-H_2/CH_4 mixture

For the purpose of accident consequences modelling, the most conservative environmental conditions of the industrial plant were assumed in the present study, i.e. average wind speed of 2 m/s, Pasquill category F (night time), air temperature of 20 °C (70 % relative humidity), surface temperature of 20 °C. The damage distances derived from the consequence analysis allowed to directly calculate UFPI, UTPI and UPI, according to Eq(1). Figure 4 summarizes the results for all the units of the two process schemes.

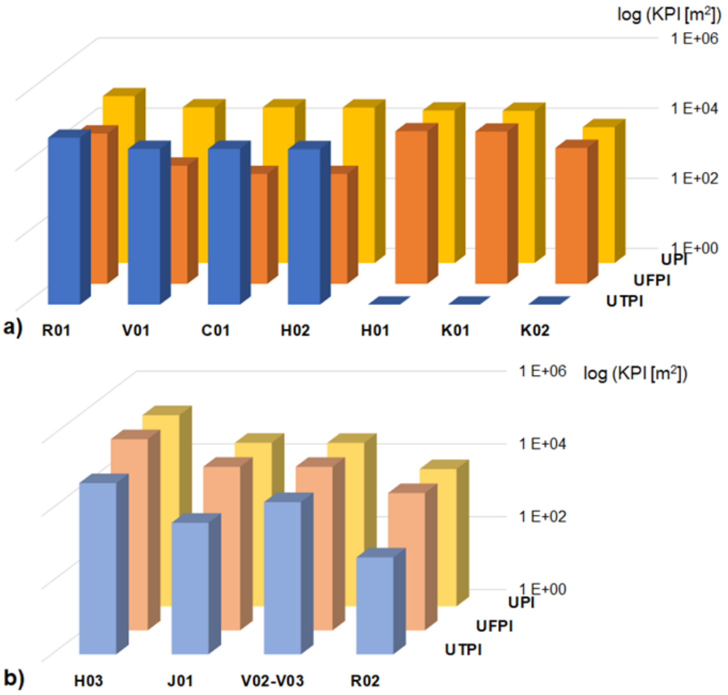

Figure 4: UTPI, UFPI and UPI for (a) catalytic hydrogenation and (b) radical gas oxidation

As shown in Figure 4a, UPI results evidence that the most critical unit of the catalytic hydrogenation process is the reactor (R01). This is further confirmed also by the UTPI values since toxic cloud from CH_3OH releases is the worst-case accident scenario. However, looking at the UFPI outcomes, the most dangerous units are those involving only H_2 (H01 and K01) due to its highly explosive effects. Focusing on the radical gas oxidation process (Figure 4b), the cooler H03 was the equipment with the highest value of all three KPIs due to larger inventory of CH_4 and CH_3OH (Table 1) causing severe fireball and toxic cloud after LOC3.

Figure 5 illustrates the overall KPIs calculated for the two process schemes from the summation of KPIs addressing single units. As evident from the figure, PI have essentially the same order of magnitude of TPI in case of the catalytic hydrogenation, thus indicating that the contribution of toxicity hazards to the overall hazards of this process is prevailing. An opposite finding was instead obtained for the radical gas oxidation as flammability hazard plays the most relevant role in all the units of the scheme. Finally, the results in Figure 5 suggest that the radical gas oxidation process gives the worst inherent safety performance by means of PI and FPI compared to the other alternative because of greater size of critical equipment required to produce the target methanol (Figure 4b). Whereas, TPI penalized the catalytic hydrogenation due to the presence of more units containing mainly methanol (Table 1).

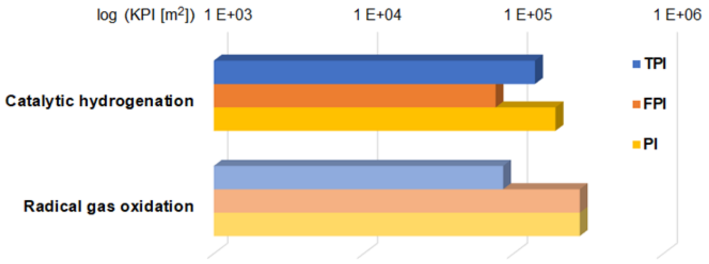

Figure 5: Overall KPIs for (a) catalytic hydrogenation and (b) radical gas oxidation

5. Conclusions

A methodology for the identification of inherently safer solutions in alternative process designs for methanol production was developed. Two reference process schemes were selected and defined among the possible emerging routes, namely catalytic hydrogenation of CO_2 and radical gas oxidation of CH_4. A benchmark productivity of methanol was fixed for the comparison of alternatives and the global material balances were thus rescaled properly. The final number of units of the processes required to produce liquid methanol were identified by adopting conventional scale-up procedures. After that, the inherent safety assessment including the assignment of reference release modes, identification of accident scenarios for human targets and estimation of damages distances through conventional consequences models was applied to all the units of the processes. KPIs were finally calculated addressing the flammability, toxicity and overall hazard levels of each unit and of the entire process schemes. The findings obtained from the analysis evidenced that the reactor for the catalytic hydrogenation is the most critical with respect to both overall and toxicity unit KPIs, while the equipment involving large amounts of H_2 was identified as the most dangerous by means of the flammability hazard KPIs. On other hand, the post-reaction cooler in the radical gas oxidation process demonstrated the highest values of all three KPIs. Finally, the method allowed to identify that, for the given methanol benchmark (4.15 t/h), the catalytic hydrogenation process is the inherently safer in the overall and flammability hazard analysis but demonstrates the worst inherent safety performance in the toxicity hazard assessment compared to the radical gas oxidation.

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