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# Incorporation of Safety Evaluation in Techno-economic Analysis of DMC and EG Production from $CO_2$

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For a new carbonylation technology using ionic liquid as catalyst to produce DMC (dimethyl carbonate) and EG (ethylene glycol) by $CO_2$ and EO (ethylene oxide), ROI (Return on Investment) was chosen to evaluate the economic efficiency with the raw material and product price fluctuation. Meanwhile, ROI can be helpful to select suitable catalysts as a reasonable economic assessment method. Based on tech-economic analysis, inherent safety assessment was performed using the combination chemical safety index relying on physical properties and process safety index relying on operating condition. Finally, when conflicts with economic and safety metrics were observed, a new approach compromising the economic efficiency and safety to determine profitable mole ratio of ethanol to ethylene carbonate is presented based on SWROI.

## 1. Introduction

Climate change and its adverse impacts have been threatening the living of human kind. Fossil fuel will continue play very important role in the foreseeable future.The $CO_2$ management is therefore looking at “curing” the problem rather than “preventing” it. By putting the captured $CO_2$ to use, CCUS (Carbon Capture Utilization and Storage) provides an additional business and market case for companies or organizations to pursue the environmental benefits of CCS (Carbon Capture Storage). Chemical conversion of $CO_2$ into fuels or chemicals can actualize its recycling utilization as resources, which is one of the potential technological solutions to current carbon capture utilization issue. An interesting option is the production carbonates, such as ethylene carbonate, propylene carbonate and dimethyl carbonate (Vooradi et al., 2018). We need the method to highlight the synthesis, design and analysis of sustainable chemical processing in the areas of carbon-capture and utilization to produce value added chemicals. Direct synthesis of dimethyl carbonate (DMC) from methanol and $CO_2$ is one of the most preferable reactions. Unfortunately, the yield of DMC is far from satisfactory because of thermodynamic limitations. Kongpanna et al. found that the ethylene carbonate route was the most promising process alternative for DMC production and presented the sustainable process design considering economics, sustainability and LCA factors. But catalyst performance improvement have not been considered.

The National Key Research and Development Program of China initiated the “Clean and efficient utilization of coal and new energy saving technology” Program. In the innovation chain “carbon dioxide capture utilization and storage”, The carbonylation technology was presented to convert $CO_2$ to DMC and ethylene glycol (EG) using ionic liquid as catalyst by a two-step reaction (ILC process) in Eq. (1) and (2).

$$C_2H_4O+CO_2 \rightarrow C_3H_4O_3 \quad (1)$$

$$C_3H_4O_3+2CH_3OH \rightarrow C_3H_6O_3+C_2H_6O_2 \quad (2)$$

As a unique new process, the carbonylation technology with high concentration ethylene oxide (EO) can greatly improve the reaction efficiency and simplify the subsequent treatment process, reduce energy consumption and increase economical efficiency. Undeniably, the process was environmental friendly and atomic economy is 100%. In ranking and selecting process improvement projects, the decision makers typically use economic profitability criteria such as return on investment, payback period, and net present

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value (El-Halwagi, 2017). But as a kind of hazardous chemical material, ethylene oxide is flammable and explosive, it is necessary to take mild operating condition against autopolymerization. All these contribute to the relative safety of the process. In order to choose from a number of alternatives, it is essential that the inherent safety to be quantified. Many researchers have developed a series of inherent safety assessment tools by combining inherent safety principles with safety assessment methods. We called them inherent safety indexes first presented by Edwards and Lawrence. The indexes were grouped into two categories: chemical and process safety. Heikkila added new parameters and set the score between 0-4. Inherent safety index are computed as the sum of the chemical and process safety subindexes. Gangadharan et al. improved the chemical safety index through the score of each chemical in the unit multiplied by their flow rate through the unit plus the score of the reactions of these chemicals when present together multiplied by the total flow rate. Ahmad et al. used this inherent safety assessment for solvent alternatives in palm oil recovery.

When safety issues are introduced into the process improvement projects, the decision makers should consider more than just economic viability (Vianelloa et al., 2019). Recently, El-Halwagi introduced a new metric referred to as a safety and sustainability weighted return on investment metric (SASWROIM) for use in process integration and improvement projects. In this paper, ROI was chosen to evaluate economic efficiency and catalyst of the process. And safety weighted return on investment (SWROI) was used to determine the key mole ratio of methanol to EC.

## 2. Methodology

### 2.1 Tech-economic analysis through ROI

The economic efficiency of DMC production by transesterification technology is controlled by the price of EO and EG. So ROI is selected to evaluate the economic efficiency of the process. The conventional economic ROI is calculated through the following expression.

$$ROI_p=AEP_p/TCI_p \qquad TCI_p=FCI_p/0.85 \tag{3}$$

where AEPp, TCIp and $FCI_p$ are, respectively, the annual after-tax economic profit, the total capital investment and the fixed capital investment.

$$FCI_p=FCI_{reference}(capacity_p/capacity_{reference})^{0.6} \tag{4}$$

$$AEP_p=(\text{Annual income-Annual operating cost-Annual depreciation})*(1\text{-Tax rate})+\text{Annual depreciation} \tag{5}$$

$$\text{Annual income=price of product}\times\text{capacity of product} \tag{6}$$

$$\text{Annual operating cost=annual raw materals cost}/0.7 \tag{7}$$

$$\text{Annual depreciation}=FCI_p/10 \tag{8}$$

2.2 Safety evaluation through Inherent safety index

Usually, inherent safety indexes rank chemical process units mainly in terms of the hazardous substances and operating conditions associated with the concerned units. The steps are taken from Gangadharan et al.

2.3 Safety weighted ROI

When safety issues are introduced into the process improvement projects and the trend of safety change is not the same with economic viability. The decision maker needs a new metric incorporating safety to evaluate process improvement projects. Halwagi [8] extended ROI incorporating sustainability. But safety targets are not absolute and safety metrics are not conserved compared to sustainability. The new formation of The Safety Weighted Return on Investment “SWROI” can better represent the safety metric just as in Guillen-Cuevas et al.

$$SWROI_p=AEP_p/FCI_p\{1+\omega[(ISI_{base}-ISI_p)/(ISI_{base}-ISI_{target})]\} \tag{9}$$

Where $\omega$ is a weighting factor in the form of a ratio representing the relative importance of safety indicator compared to the annual net economic profit. ISIp is the value of the safety indicator associated with the pth design. The denominator ISIBase – ISITarget represents the maximum desired improvement. The numerator ISIBase − ISIp is the improvement (when the difference is positive) or deterioration (when the difference is negative) associated with the pth design option. Therefore, the ratio represents the fractional contribution of the pth design option toward meeting the target performance associated with the safety.

This generalized profit term is enhanced when there is an improvement in safety compared to the base-case design, and its value is reduced when the specific alternate design option results in a deterioration of the safety-relevant performance when compared to those associated with the base-case project.

## 3. Results and discussion

### 3.1 DMC production process description

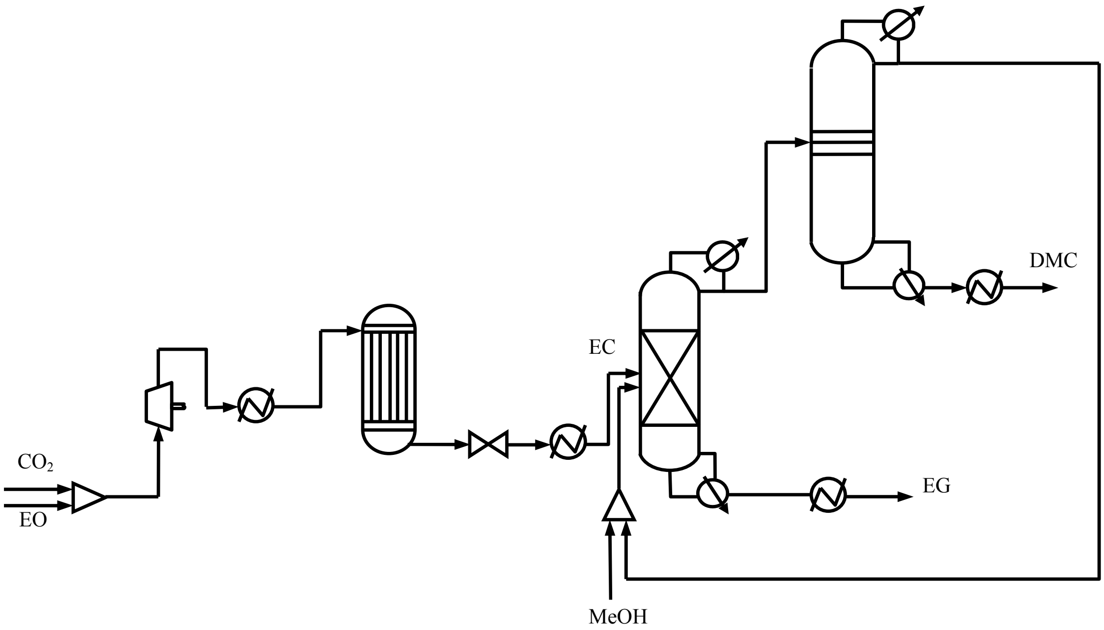


*Figure 1. The simplified flowsheet of DMC production from $CO_2$ catalysted by ionic liquid (ILS process).*

Figure 1 showed a simplified process flow diagram of synthesis of DMC from $CO_2$, MeOH and EO by a two-step transesterification process in a well-designed trickled bed reactor avoiding the use of solvent. DMC and EG was produced via transesterification of MeOH and EC in reactive distillation. The extractive separation of DMC/ MeOH can be used to separate azeotropic mixture of DMC/MeOH.

*Table 1 Flow rate of chemicals through equipment in ILS process*

| Equipment name | EO | CO2 | EC | MeOH | DMC | EG | total |
|---|---|---|---|---|---|---|---|
| Carbonylation reactor | （2513） | 2513 （2513） | 5026 | | | | 7539 |
| Transesterification reactor | | | （4121） 902 | 15278 （2998） | 4215 | 2904 | 23302 |
| Extractive distillation | | | | 15278 | 4215 | | 19493 |

The data in the bracket represented the consumption of reactants

Near 100% conversion of EO and 82% conversion of EC were obtained under mind reaction conditions using ionic liquid as catalyst. In this base-case design for 3M ton DMC every year, the temperature and pressure were 120°C and 2MPa at the first step of EC generation from EO, the mole ratio of $CO_2$/EO is 2. The second step of transesterification reaction temperature and pressure were 110°C and 1MPa, the mole ratio of methanol/EC was 10. Based on above conversion, the overall mass balance calculation was performed and the flow rates of chemicals in equipments are summarized in Table 1. Provided by the flow rate in Table 1 and price of the raw material and product, ROI calculation can finish. In which the capital investment can be estimated through the 2.6 billion for 12M ton DMC production. The flow rates of chemicals in equipments for Texaco process for 3M ton DMC were shown in Table 2 (Kongpanna et al., 2015).

Through comparison between the ILS process and Texaco process to produce DMC and EG in Table 3, we can see economic efficiency and safety were improved greatly through the flowsheet simplification and catalyst modification (make operating condition mild). And the ROI of Texaco only attained $4.82yr^{-1}$. Just as Maria-Ona Bertran et al. said, In order to make profit ($ROI>10yr^{-1}$), the dimethyl carbonate needs to be sold at least 2.30 USD per kilogram. Due to the usage of ionic liquid catalyst, the conversion ratio of EO at the first stage and the yield of DMC at the second stage were increased in ILC process. Which lead to the decrease of raw material cost especially for EO consumption. Meanwhile, inherent safety index were declined because of the moderate operating condition and simplified flowsheet of the new process compared with Texaco process. But we found the inherent safety index only had a subtle advantage of ILS process over Texaco process. That was because the large amout MeOH was used and recycled in the system for ILS process. So the ratio of MeOH/EC is the important factor to consider in the process improvement.

*Table 2 Flow rate of chemicals through equipment in Texaco process (Kongpanna et al., 2015)*

| | Carbonylation reactor | Transesterificatio n reactor | Conventional Distillation DMC,EG, MeOH, EC | Extractive distillation | Conventional distillation EG, EC |
|---|---|---|---|---|---|
| Temperature/□ | 588.7 | 154.9 | 160 | 111.2 | 306.1 |
| Pressure/MPa | 12.5 | 1 | 1 | 1 | 1 |
| CO2 | 7921.76 | | | | |
| EO | 3348.04 | | | | |
| EC | 5724.09 | 1602.74 | 1602.74 | | 1602.74 |
| MeOH | | 1807.17 | 1807.17 | 1807.17 | |
| DMC | | 4215.69 | 4215.69 | 4215.69 | |
| EG | | 2904.8 | 2904.8 | | 2904.8 |
| total | 16993 | 10528 | 10528 | 6022 | 4506 |

*Table 3 Comparison of ROI and inherent safety between ILC process and Texaco process*

| | ROI/%$yr^{-1}$ | ISI |
|---|---|---|
| ILC process | 11.00 | 704.44 |
| Texaco process | 4.82 | 751.44 |

### 3.2 ROI and inherent safety analysis

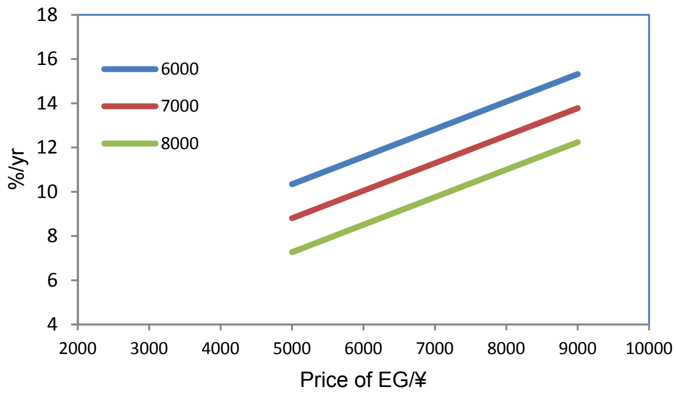


*Figure 2. The effect of EG and EO price on ROI.*

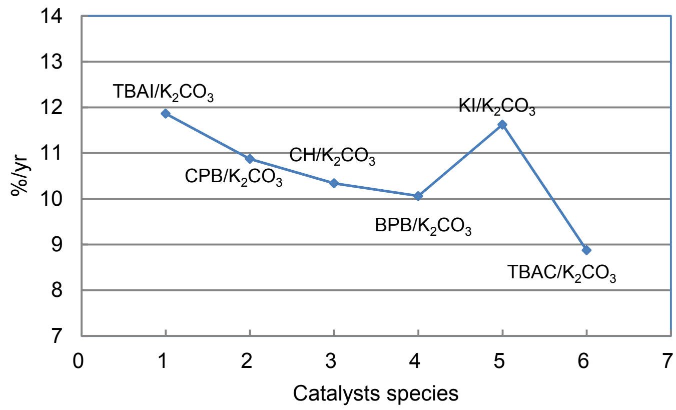


*Figure 3. The effect of catalysts species in ILC on ROI.*

The company uses a minimum ROI value of 10 $yr^{-1}$%. The ILC process was an economically attractive option because it offered a ROI value of 11 $yr^{-1}$%. The sensitivity analysis in Figure 2 showed that the ROI depended much more heavily on the purchase price of EO than on the selling price of EG. If the EO can be self-supply by 8000¥/ton, the results showed a profitable process above a EG selling price of approximately 7000¥/ton. With the price fluctuation of EO and EG, the conversion ratio of EC should be increased through the appropriate selection of catalysts. From Figure 3, we can see TBAI/$K_2CO_3$(83), CH/$K_2CO_3$(79) , CPB/$K_2CO_3$(77), BPB/$K_2CO_3$(76) and KI/$K_2CO_3$ (82)were economic and effective candidate binary catalysts for two-step synthesis of DMC just as Wang et al. cited.

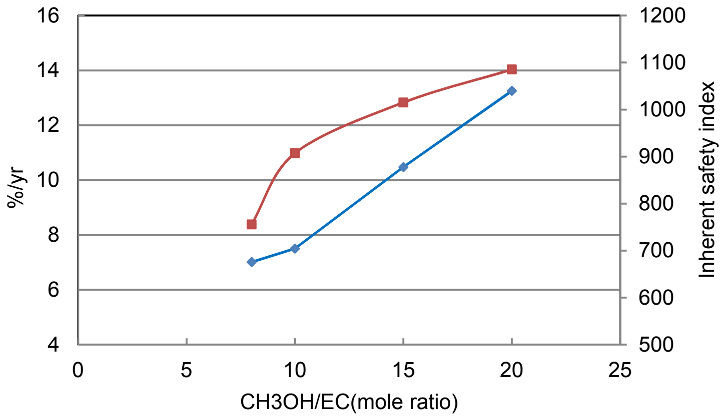


*Figure 4. The effect of the mole ratio of methanol to EC on ROI and inherent safety index.*

In addition to select high-effective catalyst, other method to further improve conversion was to increase the ratio of methanol to EC on the second step. We found the economic and safety objectives may contradict each other over certain ranges. The higher the ratio was, the higher the ROI was (because of lower yield). But, higher ratio led to a un-safer operation shown in Figure 4. SWROI was used to trade off economic and safety effect.

**3.3 Optimization of the mole ratio of methanol to EC by SWROI**

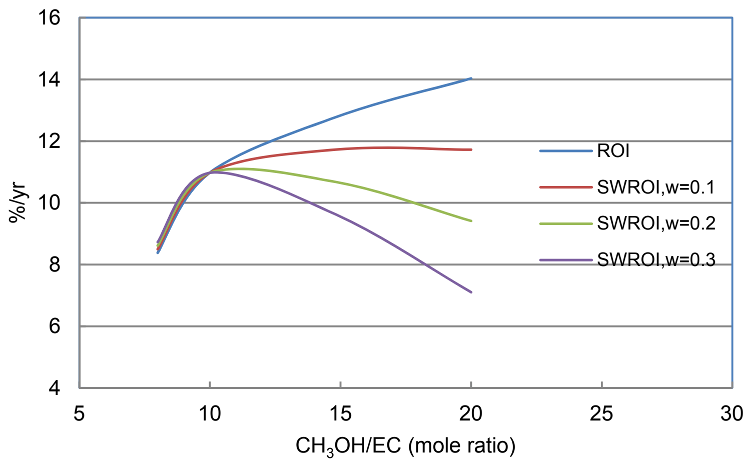


*Figure 5. The effect of the ratio of methanol to EC on SWROI at different weighting factor of safety.*

In eq.(9) to evaluate SWROI, weighting factor of safety reflects the company's core values relative to profit. According to a sensitivity analysis in Figure 5, if the weighting factor for safety was set as 0.1, inherent safety index didn't have effect on the selection of a higher ratio. When we put more attention on safety, we find SWROI decreased rapidly with the rising of mole ratio. Therefore, the moderate mole ratio of methanol to EC 10 offered attractive values of ROI and SWROI.

## 4. Conclusions

An approach including inherent safety at the design stage of production of DMC and EG through ionic liquid catalyst has been presented. ROI and inherent safety index were applied to demonstrate its advantages compared with Texaco process. The results indicated that catalyst evaluation were consistent with the experiments using ROI as an effective tool. When conflicts with economic efficiency and safety assessment were observed, SWROI was presented to compromise between economic efficiency and safety, and the optimal ratio of methanol/EC was determined. The results also provided an opportunity to formulate multi-objective optimization models in order to systematically identify designs when economic efficiency and safety was simultaneously considered in the process.

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