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# COMPARATIVE ANALYSIS OF CARBON DIOXIDE BASED FORMIC ACID PRODUCTION PROCESS ALTERNATIVES

Dongin Kim[1] and Jeehoon Han[1,2,*]

1 School of Semiconductor and Chemical Engineering, Chonbuk National University, Jeonju 54896, Korea

2 School of Chemical Engineering, Chonbuk National University, Jeonju 54896, Korea (Corresponding Author)
* Corresponding author. Tel.: +82-63-270-4039; Fax: +82-63-270-2306
E-mail address: jhhan@jbnu.ac.kr

## ABSTRACT

This study presents two commercial scale processes for producing formic acid (FA) using $CO_2$ captured from the power plant and conducts economic, energy and environmental analysis of the processes. The process is designed conceptually based on experimental data to produce high purity of FA. For the comparative analysis the FA production amount is set to 12,000 t/y. As a result of the process analysis, the process 1 considering amine shift reaction shows better results. The energy efficiency of the process 1 is 60.9%, the minimum selling price of produced FA is US$ 1,422/$t_{FA}$ and the $CO_2$ emissions is 0.07 $t_{CO2}/t_{FA}$.

**Keywords:** carbon utilization process, formic acid production, energy analysis, economic analysis, environmental analysis.

## NONMENCLATURE

| | |
|---|---|
| *Abbreviations* | |
| BIZ | Butylimidazole |
| CCS | Carbon capture and storage |
| CCU | Carbon capture and utilization |
| FA | Formic acid |
| FCI | Fixed capital investment |
| MSP | Minimum selling price |
| $Net_3$ | Triethylamine |
| *Symbols* | |
| $\eta$ | Energy efficiency |
| $\Sigma$ | Sum |
| hr | Hour |
| M | Million |
| Y | Year |

## 1. INTORDUCTION

Currently, greenhouse gas (GHG) emission is the major problem of global warming. The GHG includes $CO_2$, $CH_4$, and $NO_2$, and more than 60% of total GHG is $CO_2$ [1]. The methods of $CO_2$ reduction have been suggested as follows: system improvement, carbon capture and storage (CCS), carbon capture and utilization (CCU). System improvement is an indirect method for $CO_2$ reduction by improving process and reducing the requirements of fossil fuels. However, the indirect method have a limitation to $CO_2$ reduction because $CO_2$ must emit to produce the target material and energy [2]. CCS and CCU are direct methods to reduce $CO_2$ emissions. CCS sequestrates $CO_2$ over a long time in underground and offshore. CCU uses $CO_2$ as a feedstock to produce high value-added products such as dimethyl ether, methanol, dimethyl carbonate and formic acid (FA) [3].

FA is the simplest carboxylic acid and an important material used in various industries. Also, FA is receiving increasing attention as a $H_2$ career. FA is mainly produced by the hydrolysis of methyl formate in commercial plants, which is not environmentally friendly [4]. In this study, we have applied an amine shift reaction to design an effective separation process, not a conventional separation process [5]. We present two processes for FA production from $CO_2$ and conduct energy, economic and environmental analysis to show the feasibility of the processes. Based on the experimental investigation, we design conceptually the process including conversion and separation subsystems. We calculate energy efficiency by taking into account the material and energy balance of the process. We calculate the minimum selling price (MSP) of FA based on process simulation and

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energy analysis. Also, we also calculated the $CO_2$ emissions not only from the direct emissions from the process, but indirect emissions from the energy used in the process.

## 2. METHODS

This section presents two processes about $CO_2$ to FA production and methods for energy, economic and environmental analysis of the process.

### 2.1 Process alternatives

Two process alternatives to produce FA from $CO_2$ are presented and compared with commercial petroleum based process. In process 1 (Fig. 1. (a)), a FA (85wt%) can be produced from $CO_2$, $H_2$, triethylamine ($Net_3$) and butylimidazole (BIZ). The process is divided into four stages as follows: (1) compression stage, (2) FA-$Net_3$ adduct production, (3) amine shift reaction and (4) FA recovery. First, $CO_2$, $H_2$ and $Net_3$ are pressurized and cooled under the experimentally optimized reaction conditions (180bar, 313K) through a multi-compressor. Then, $CO_2$, $H_2$ and $Net_3$ are hydrogenated to FA-$Net_3$ adducts with a high conversion over a commercial Au/TiO2 catalyst [5]. After that, FA and $Net_3$ were separated by amine shift reaction, which takes place between BIZ and $Net_3$ of FA-$NEt_3$ adduct in the reactive distillation column (1bar, 451K) and produced to FA-BIZ adduct [6]. Last, a high-purity of FA is recovered in the distillation column.

In process 2 (Fig. 1. (a)), a high purity FA (85wt%) can be produced from $CO_2$, $H_2$, and trihexylamine ($NHeX_3$). The process is divided into three stage as follows: (1) compression stage, (2) FA-$Net_3$ adduct production, (3) FA recovery. In the first process stage, as in strategy 1, $CO_2$, $H_2$ and $NHeX_3$ is first pressurized and cooled under the condition (105bar, 313K) through a compressor and cooler. Then, $CO_2$, $H_2$ and $NHeX_3$ are hydrogenated to FA-$NHeX_3$ adducts over ruthenium- and phosphino-based catalysts. Finally, a high-purity of FA is recovered, which is thermally separated in the distillation column.

### 2.2. Energy analysis

The energy efficiency ($\eta$) is a major criterion to evaluate process. It is defined as the ratio of total output energy ($\Sigma E_{out}$) to the total input energy ($\Sigma E_{in}$) as 100 times:

$$\eta = \frac{\Sigma E_{out}}{\Sigma E_{in}} \times 100\% = \frac{E_{FA}}{E_{H_2} + E_{Net3} + E_{BIZ} + E_{H} + E_{Elec}} \times 100\% \quad (1)$$

where $\Sigma E_{in}$ is the sum of higher heating values (HHVs) of the feed streams such as $H_2$, $Net_3$, BIZ and required energy for the process such as heating energy, electricity, $\Sigma E_{out}$ is the HHVs of the product FA stream.

To minimize the energy requirements of the whole process, heat exchanger network was designed by Aspen plus Energy Analyzer v10 to transfer heat between process streams. We assumed that a minimum allowable temperature difference is 10K, the minimum heating and cooling energy requirements were determined and the heat exchange area and cost were then estimated.

### 2.3 Economic analysis

We adopted several economic assumptions (Table 1) to analysis the economics of FA production process from $CO_2$. Total cost was the sum of total annualized capital cost and total operating cost. The total annualized capital cost was calculated from capital charge rate and total capital investment using discount rate.

Total capital investment of the process was the sum of direct costs (e.g., yard improvement, equipment cost), indirect costs (e.g., construction expenses and contingencies) and working capital. Total operating cost was the sum of variable operating costs (e.g., raw materials and utility costs) and fixed operating costs (e.g., operating and maintenance costs). To evaluate the economic feasibility of the proposed process, MSP of FA, which is equal to total revenue and the total cost, was calculated as US$/$t_{FA}$.

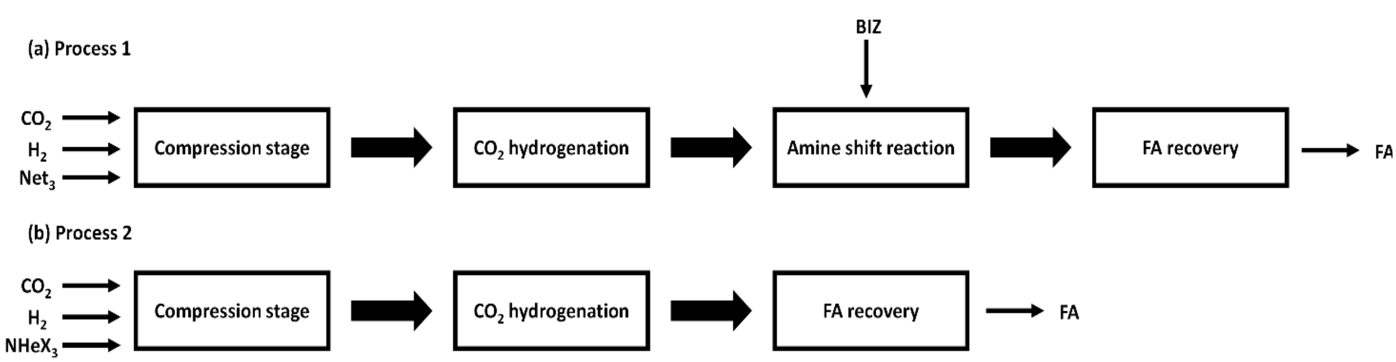


Fig. 1. Process flow diagram of producing FA from $CO_2$ of each strategy

Table 1. Economic analysis assumptions.

| Economic assumption | Value |
|---|---|
| Base year | 2018 |
| Plant lifetime | 20y |
| Plant uptime | 8000hr/y |
| Construction period | 3 y |
| Capital distribution | (1st 30%, 2nd 60%, 3rd 10%) |
| On stream factor of each year | (1st 30%, 2nd 70%, 3rd-20th 100%) |
| Discount rate | 8% |
| Tax rate | 35 % |

### 2.4 Environmental analysis

We conducted an environmental analysis with cradle to gate approach. This study assessed the net $CO_2$ emission ($CO_{2\ net\ emission}$) of the process as an environmental impact indicator. $CO_{2\ net\ emission}$ is the difference between the amount of $CO_2$ output ($CO_{2\ out}$) and the amount of $CO_2$ input ($CO_{2\ in}$) (Eq. 2) [7]. The $CO_{2\ out}$ is the sum of direct $CO_2$ emission ($CO_{2\ direct}$) and indirect $CO_2$ emission ($CO_{2\ indirect}$) (Eq. 3). $CO_{2\ direct}$ is emitted by the process, such as purge and flue gas, and $CO_{2\ indirect}$ is emitted by energy consumption of electricity ($CO_{2\ electricity}$) and heat ($CO_{2\ heat}$) for the whole process (Eq. 4). The $CO_2$ emissions from energy consumption are 0.47 $t_{CO2}$/MWh for natural gas-based electricity and 0.093 $tCO_2$/MMBtu for heat. The $CO_2$ emissions of the conventional FA production process are assumed to 2.18 $t_{CO2}/t_{FA}$ [7].

$$CO_{2\ \text{net emission}} = CO_{2\ \text{out}} - CO_{2\ \text{in}} \quad (2)$$

$$CO_{2\ \text{out}} = CO_{2\ \text{direct}} + CO_{2\ \text{indirect}} \quad (3)$$

$$CO_{2\ \text{indirect}} = CO_{2\ \text{electricity}} + CO_{2\ \text{heat}} \quad (4)$$

## 3. Results and Discussion

### 3.1 Process simulation

Large scale process alternatives that produce FA from $CO_2$ captured at the power plant was designed based on the experimental data, by using the Aspen Plus Process Simulator v10. The annual production of FA is set to 12,000 tons. The mass balance of each process is summarized in Table 2. In processes 1 and 2, $H_2$ and $CO_2$ inputs for FA production are similar at 0.04 $t/t_{FA}$ and 0.83 $t/t_{FA}$, respectively. This is because the conversion rates of $CO_2$ for the entire process are similar to 98% and 96%, and the most unreacted materials are recycled.

Table 2. Mass balance of each processes.

| Mass balance | Process 1 | Process 2 |
|---|---|---|
| Inlet ($t/t_{FA}$) | | |
| $CO_2$ | 0.83 | 0.83 |
| $H_2$ | 0.04 | 0.03 |
| Make up | 0.16 | 0.27 |
| Outlet ($t/t_{FA}$) | | |
| FA | 1 | 1 |
| Off gas | 0.01 | 0.16 |
| Conversion (%) | | |
| $CO_2$ – reactor | 84 | 81 |
| $CO_2$ – process | 98 | 96 |

### 3.2 Energy analysis

We have considered the amine shift reaction to reduce the energy required for FA separation and summarized in Table 3. The η of the processes are 61% and 21%, respectively. There are two reasons for this difference. First, there is a difference in the amount of unreacted materials recycled. In order to increase the conversion rate of the whole process, the more unreacted materials are recycled, the more energy is consumed to pressurize and heat the unreacted materials. The second is the boiling point difference of the amines forming the adducts in the final FA recovery process. In FA recovery process, FA is recovered by thermal decomposition. At this time, the boiling points of the $Net_3$ and $NHex_3$ are 508K and 428K, respectively, and the smaller the difference in boiling point between FA (374K) and amines, the more energy is required to recover FA of high purity.

Table 3. Energy balance of each processes

| Energy balance ($MWh/t_{FA}$) | Process 1 | Process 2 |
|---|---|---|
| Electricity | 0.16 | 0.30 |
| Heating | 0.70 | 2.78 |
| Cooling | 0.98 | 2.96 |
| Energy efficiency (%) | 61 | 21 |

### 3.3 Economic analysis

Economic analysis was conducted based on the results of process simulation and energy analysis. The MSP of the each processes were calculated to US\$ 1,422/$t_{FA}$ and US\$ 1,584/$t_{FA}$, respectively, which are 1.5 times and 1.7 times higher than the market price. The capital cost and consumable cost were the major component of the MSP on the process 1 and consumable cost was the major components of the MSP on the process 2. In process 2, the higher contribution of consumables is due to the use of expensive catalysts such as ruthenium- and phosphino-based catalysts.

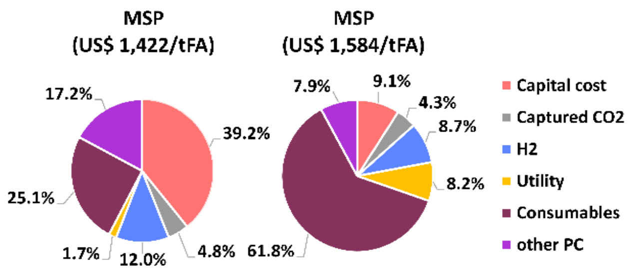


Fig. 2. The MSP of FA and cost contribution on the MSP

### 3.4 Environmental analysis

Based on the results of process simulation and energy analysis, an environmental analysis was conducted. The environmental analysis using the system boundary is cradle-to-gate shows that the $CO_2$ emissions of the processes 1 and 2 are 0.07 $t_{CO2}/t_{FA}$ and 0.36 $t_{CO2}/t_{FA}$, which are 3% and 16% of the conventional process $CO_2$ emissions, and the environmental impacts of the processes are much better comparing conventional process. In the environmental point of view, process 2 is less favorable than process 1 because of the higher amount of $CO_2$ emitted and the large amount of energy consumed in the process.

Table 4. Environmental analysis results of each processes.

| $(t_{CO2}/t_{FA})$ | process 1 | process 2 |
|---|---|---|
| $CO_{2\ in}$ | 0.83 | 0.83 |
| $CO_{2\ out}$ | | |
| $CO_{2\ direct}$ | 0.01 | 0.17 |
| $CO_{2\ indirect}$ | 0.88 | 1.03 |
| $CO_{2\ net\ emission}$ | 0.07 | 0.36 |

## 4. Conclusions

This paper has presented two CCU process alternatives for producing FA from the captured $CO_2$ at a power plant and compared with other conventional petroleum based process to produce FA from CO. Simulation considered $CO_2$ hydrogenation reaction and amine shift reaction for producing high purity of FA. The process was consisted of conversion and separation subsystems at a large scale and explored the economic, energy and environmental feasibility.

The simulation results show that processes 1 and 2 have a $CO_2$ input of 0.83 $t_{CO2}/t_{FA}$ and an FA production of 12,000t/y. Process 1 reduces the amount of energy required for FA recovery by considering the amine shift reaction. As a result, process 1 showed favorable results in energy, economic, and environmental analysis compared to process 2. Compared with process 2, process 1 has a high energy efficiency of 60.9%, MSP of FA is US$ 1,422/$t_{FA}$, which is 1.5 times the market price, and $CO_2$ emission of process is 0.07$t_{CO2}/t_{FA}$, which is more suitable for environment.

The study has developed CU process to produce FA and conducted comparative analysis of FA production processes. While this study has no economic advantages over commercial processes, it demonstrates the energy and environmental benefits of $CO_2$ based FA production processes.


## ACKNOWLEDGEMENT

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