Utilizing carbon dioxide from refinery for methanol and electricity co-production: system design and economic assessment

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Abstract. Mitigating greenhouse gas (GHG) emissions to curb climate change has become a consensus among international community. Refining is one of the major industries with high energy consumption and high emissions, which is responsible for 4-10% of global carbon dioxide (CO₂) emissions and approximately 25% is generated by fluid catalytic cracking (FCC) units. The flue gas discharged from FCC units has a high CO₂ content, presenting potential for methanol and electricity co-production production when the methane in the dry gas is considered. To unlock this green chance for enterprises, we designed a methanol production system that uses the CO₂ recovered from the flue gas of fluid catalytic cracking (FCC) unit in a refinery and the CH4 separated from dry gas as feed stock (hydrogen to be added from an internal hydrogen production unit of the refinery). We analyzed economic feasibility of the process, the results show that the developed system is economically feasible for annual methanol yields of 1.0–2.5 Mt and the internal rate of return increases by 8.3%.

1. Introduction

As the world's largest emitter of CO₂, China has made a commitment to become carbon neutral by 2060 and to begin cutting its CO₂ emissions within the coming decades. China's ambitious plan to meet the goal of carbon neutrality requires a set of diversified emission reduction strategy, which has become a long-term strategy to ensure the achievement of China's carbon neutral goal[1]. With the rapid urbanization and economic development of national economy, environmental problems caused by carbon emissions have attracted more and more attention. Refining and chemical industry is one of the main industries represents a significant source of China's GHG emissions^[2]. In the face of increasingly severe environmental protection requirements, bear the corresponding responsibility for emission reduction and strategies to work toward the develop deep decarbonization of the refineries are critical to meet the goal of carbon neutrality.

Studies on low-carbon refinery development are not rare. Johansson et al. [3] concluded that fuel substitution helps to reduce short-term CO_2 emissions in a refinery. Zhang improved refinery energy efficiency by recovering low temperature waste heat through Organic Rankine Cycle power generation[4]. Thus, previous studies primarily focused on improving the energy efficiency of refineries, whereas endeavors to direct GHG emission reduction via CO_2 capture and utilization are usually lacking.

In addition to improve refinery energy efficiency, CO₂ is a valuable C1 raw material. It offers a good opportunity for refineries to improve decarbonization while to improve CO₂'s economic value through chemical conversion[5]. Fernández-Dacosta C used Aspen to simulate CO₂ capture from a hydrogen production unit to co-produce dimethyl-ether (DME) and polyols, providing refineries with an approach to mitigate CO₂ emissions [6]. Through carbon capture technology to recover CO₂ from flue gas, and then realizing its utilization by chemical reaction promises an optimistic outlook for lowcarbon refineries. In addition to environmental benefits, converting CO₂ into high added value chemicals can also bring considerable economic benefits[7]. At present, Chinese petrochemical enterprises are facing the dual pressure of increasing oil-gas supply and the reduction of CO_2 emissions. How to balance this dilemma, this is the significance of this study.

We developed a novel CO_2 utilization process in refinery using Aspen Plus. Specifically,we designed a process turning "waste" into wealth in refinery that uses the CO_2 recovered from the flue gas of an FCC unit and the CH_4 separated from dry gas as feedstock for producing methanol, Fig. 1 displays the conceptual design of this study.

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Fig.1. System design of the FCC co-production

2. Methodology of economic evaluation

In this study, several key indicators, such as the total capital cost (TCI), the total product cost of methanol (TPC), the accumulative net present value (NPV) and internal rate of return (IRR) were calculated for economic evaluation due to their wide application in economics [8,9,10]. TCI mainly includes fixed asset investments and fluid capital. Peters proposed that the fixed asset investments of general chemical plants account for approximately 85% of the total project investment. He also proposed that there is an exponential relationship between the cost of similar chemical process equipment and scale rather than a simple linear relationship. In this paper, the scaling factor method is used to estimate the purchased equipment cost [11], which is expressed as

$$C_B = C_A \times \left(\frac{s_B}{s_A}\right)^n \quad , \tag{1}$$

where C_A and C_B are the equipment cost of the reference scale and the required scale to be estimated, respectively; S_A and S_B denote the scale of A and B, respectively; and *n* is the equipment scale factor. The TCI is the sum of all purchased equipment investment and fixed investment (instrument and control, pipeline, installation costs, etc.), and its calculation equation is expressed as

where I is the total purchased equipment investment, F_i is the ratio of the other purchased equipment cost to the total equipment investment, and i is the components of investment.

TPC is all the costs generated in the process of producing products, which is divided into two parts: operation $\cos \frac{1}{2}$ and general expense. It is determined by Eq. (3).

 $T_{TPC} = C_{RM} + C_U + C_{0\&M} + C_{P\&R} + C_D + C_{T\&I} + C_{PO} + C_{GE}$ (3) where C_{RM} , C_U , $C_{0\&M}$, $C_{P\&R}$, C_D , $C_{T\&I}$, C_{PO} and C_{GE} denote raw materials, utilities, operation and maintenance costs, patents and royalties, depreciation, taxes and insurance, plant overhead and general expenses, respectively. Among these, the depreciation cost adopts the average life method with an assumption of a 20-year plant life and 5% salvage value.

is given by
$$TCI = I \times (1 + \sum F_i)$$
 (2)
 $\sum_{i=1}^{t} CI - CO$

$$NPV = f(t, n) = \sum_{t=0}^{\infty} \frac{1}{[1+i]^t} , \qquad (4)$$

$$\sum_{t=0}^{NPV} \frac{NPV}{[1+IRR]^t} = 0 \qquad , \tag{5}$$

where CI and CO denotes the inflow cash and outflow of cash, t is the cash flow year, i is the discount rate and n is the total number of years.

3. Results and discussion

Fig. 3 displays the IRR, TCI and constitution of costs with methanol production ranging from 0.35 Mt/yr to 3.5 Mt/yr. From the point of view of IRR, it is economically infeasible when the capacity is less than 0.7Mt/yr, which is lower than the value specified in the industry standard of China (12%). As can be seen, the value of IRR increases with increasing methanol capacity, which is similar to the effect of plant scale on capital investment. Compared with the traditional process, the IRR increases by 8.25 at the production of 1.8 Mt/yr [12]. With production changes in the scope of 3.5-2.45 Mt/yr, the TCI and constituent costs increase exponentially with increasing production. It is obvious that production of 2.45Mt/yr is a threshold, and increasing production beyond this point leads to significant increases in TCI. This bottleneck implies that there is a requirement for more processing units and power consumption to meet the higher capacities of methanol. The unit investment (TCI divided by production) decreases dramatically when the production is no more than 1.5 million tons. In general, the TCI for fixed asset investments is dominant, followed by working capital and equipment investment.



Fig. 3 Variations in total capital and constituent costs with changing methanol production

Fig. 4a shows the production cost distribution with different levels of methanol production. It is obvious that TPC increases were gradually caused by increasing production. Moreover, the raw material costs as well as O&M costs and utilities occupy the greatest portion of the TPC, which means the TPC seems to be highly affected by the prices of raw materials, O&M and utilities costs, which is consistent with the sensitivity analysis of methanol production cost. To obtain a better understanding of the economic performance, the unit product cost of methanol was evaluated (see Fig. 4b). Obviously, when the yield is within 145 t, the unit product cost drops conspicuously. Then the downward trend flattens until it reached a minimum of 1690 Yuan/t at 2.45 Mt/yr, after which the trend goes up for methanol production over 245 t. This indicates that the optimal methanol production is approximately 125-325 t from the perspective of production cost. Fig. 5 shows the comparison of accumulative NPV under different methanol production levels. As shown in the enlarged part

of the red circle, the longest payback period is 7 years, while the capacity is 0.35 Mt/yr. When the capacity is in the range 1.05–3.15 Mt/yr, the payback period is 4 years.



Fig.4 Variations in the TPC and unit product cost at different methanol production (Mt/yr)



Fig. 5 Cumulative cash flow of the CO2–dry gas methanol production process



Fig.6 Sensitivity analysis of the most influential parameters on unit production cost of methanol

Finally, a sensitivity analysis was conducted to evaluate the effects of uncertainties of some important factors. It can be seen from Fig. 6 that the raw materials, O&M and utilities costs are the three main factors that affect the unit of methanol cost. Among these, raw materials comprise the principal sensitive factor, while the O&M and utilities costs are less so. When the price of raw materials fluctuates by $\pm 30\%$, the variation range of unit product cost can reach 11.4%, followed by O&M and utilities costs with variations of 6.4% and 6.1%, respectively. Finally, reasonable changes in depreciation and local taxes and insurance have little impact on the methanol product cost.

Considering the above analysis results of TPI, TPC and NPV, when the production scale of methanol is within approximately 100–250 million, the economic performance of the CTM process is better.

4. Conclusion

In this study, we proposed a promising way to reduce greenhouse gas emissions in the petrochemical field by recovering the CO2 in the flue gas of the FCC unit and the methane in dry gas to unlock a solution for green refinery development. Specifically, a CO₂-dry gas to methanol production process was modeled based on Aspen Plus. The techno-economic and environmental performance of the system was analyzed. The results show that the proposed process could not only demonstrate excellent performance in mitigating carbon emissions in refineries but also make it possible to make good use of the methane in dry gas compared to the traditional methods. With the aid of economic analysis, the economic performance of the CTM process is better considering the annual production capacity within 100-300 million and compared with the conventional technique of methanol production, IRR increases by 8.3%. In addition, sensitivity analysis shows that the raw materials, O&M and utilities costs are the three main factors that affect the unit of methanol cost.

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