Utilizing CO_2 from refinery for methanol and electricity co-production: system assessment

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Abstract. As one of the major energy-consuming and high-emission industries, the refineries account for 10% of global industrial carbon emissions, of which about 25% is emitted by fluid catalytic cracking (FCC) process. Therefore, CO_2 capture from FCC flue gas create the possibility for low-carbon refineries. We developed a novel CO_2 utilization process to methanol production modeling using Aspen Plus. Meanwhile, organic Rankine Cycle (ORC) power generation technology was coupled to recover the waste heat of the system. A five-million-ton FCC unit in China was selected as a case study. We conducted some analysis for the process, the results show that the developed system boosts the energy efficiency of the FCC unit by 2.8%. The annual capacity of the waste heat power generation unit is 4.8 GWh, with a thermal efficiency of 5.9%.

1. Introduction

Globally, annual carbon dioxide (CO_2) emissions have increased sharply during past few decades.The increasing greenhouse gas emissions exacerbate climate change and leads to various extreme weather events[1].Thus, the consensus on CO_2 reduction has prompted most countries to make commitments and put them into action.China also put forward the strategic goal of achieving carbon peak by 2030 and carbon neutrality by 2060 in 2020.

The chemical industry is one of the industries with high energy consumption and high emissions. Refineries, as a major contributor to the chemical industry, occupy 10% of the global industrial carbon emissions [2]. Although the energy structure is gradually transforming, driven by the rapid economic development , the carbon emissions caused by energy use are still rising , increasing by about 7% by 2040[3]. In the face of “double carbon target”, refineries must assume corresponding responsibility to contribute to China’s transition toward a lower carbon future. Many refineries’ units emit CO_2, Given the FCC process has a high CO_2 emissions, accounting for 20-35% of the total carbon emissions of the refinery[4].Therefore, capturing CO_2 from FCC flue gas will be an important step to reduce the total CO_2 emissions of refineries. Meanwhile, the dry gas of refinery is rich in hydrogen, methane, nitrogen, ethylene, ethane, etc., and the production of dry gas in FCC is the largest[5-6]. But at present, the dry gas in domestic refineries is not well used that used as fuel gas or torch. Therefore, the utilization of dry gas in refinery promises an optimistic outlook for decarbonization.

In this study, we designed a methanol production system that uses the CO_2 recovered from the flue gas of FCC unit and the CH_4 and H_2 separated from dry gas as feedstock. A 5-million-tons FCC unit in China was selected for case study. Fig.1 shows the conceptual design of the hybrid system, including carbon capture, methane dry reforming, methanol synthesis, methanol distillation, and ORC units. To be specific, the CO_2 in the FCC flue gas was captured by carbon capture unit using monoethanolamine (MEA) , followed by syngas generation. Then the reaction of syngas with hydrogen via methanol synthesis unit to produce crude methanol, which sent to distillation unit to purify. After the optimization of HEN, the low-grade waste heat derived from methanol distillation unit was utilized by ORC unit for electricity generation.

Methanol, as a chemical intermediate, has attracted much attention. China is the world's largest producer and consumer of methanol. Based on the essential situation, the domestic methanol production is mainly from coal-to-methanol, which is characterized of high energy consumption and high carbon emission intensity [7]. It is not conducive to the low-carbon development of China's economy. Natural gas is the most ideal raw material for methanol synthesis. However, at the restrictions of region, it doesn't work in China based on the current energy structure that rich in coal, insufficient oil and limited natural gas supply.

Meanwhile, the generated low-grade waste heat was also recovered and utilized by coupling with Organic Rankine Cycle (ORC) power generation technology. The ORC is a state-of-the-art technology that combines the main process system with power generation system [8]. Although energy use has been optimized under the heat exchanger network , some low-grade heat has still not been well utilized. Thus, we deployed ORC system to recover the waste heat from the methanol distillation unit, converting the low-grade waste heat into electricity.

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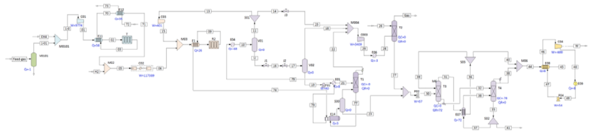

Fig.1. Aspen model diagram of the FCC co-production

2. Methodology

2.1 Overall energy efficiency calculation

According to the First Law of Thermodynamics, the overall energy efficiency of the methanol production system is calculated as Eq 1.

$$\eta = \frac{\sum E_o}{\sum E_i} \times 100\% \qquad (1)$$

where, ŋ denotes the energy efficiency of the methanol production system, Eo denotes the energy output of the system , and Ei denotes all the input energy of the system.

2.2 Sustainability evaluation

The pros and cons of the new process system are affected by various factors. In order to evaluate the new process more comprehensively, we assessed the sustainability of the CTM from a multi-dimensional perspective. In general, the four main aspects of technology, environment, economy and society contained 12 sub-indicators are considered respectively. To evaluate and compare sustainability of different alternatives more reasonably and scientifically, a further processing of these indicators is adopted by use of normalization method, according to eq. (12). In addition, the setting of some sub-indicators such as technical maturity refers to a previous study of Huang[9].

$$x_{ij} = \frac{x_{ij} - worst(x_i)}{best(x_i) - worst(x_i)} \qquad (2)$$

where xij is the indicator j for process i ; best(xj) is the assumed best case of indicator j; worst(xj) is the assumed worst case of indicator j; xij, which varies in the range [0,1], is the normalized indicator j for process i.

3. Results and discussion

3.1 Energy efficiency of the CO_2–dry gas to methanol production system

Based on the Aspen simulation tool and theoretical calculations, the input and output energy of the CO2–dry gas to methanol production system are summarized in Table 1. It can be seen that the system's energy input mainly derives from the feedstock, fuel gas, and electricity, with a total energy input of 36815 TJ, while the total energy output was estimated to be 28958 TJ . According to Eq (1), the overall energy efficiency of the CO_2–dry gas to methanol production system was 78.6%.

Table 1 Input and output energy of the"CO2-dry gas" methanol production system

Input		Export	
Material	Energy (TJ)	Material	Energy (TJ)
methane	18900	Methanol	28933
H_2	14.8	3.5Mpa Steam	7.47
Fule gas	10400	Electricity	17.3
Electricity	7500		
Sum	36815	28958	
Overall energy efficiency		78. 6%	

Fig. 2 compares the energy efficiency of the FCC process, the CO_2–dry gas to methanol production process (CTM), and the FCC combined with the CO_2–dry gas to methanol process (FCC+ CTM). As for the FCC unit, its energy efficiency is relatively lower than CTM process (78.6%), which is only 57.9%. With the co-production of the process, the energy efficiency of FCC increased from 57.9% to 60.7%, prompting a 2.8% energy efficiency improvement.It can be seen that through carbon recovery and recycling can effectively improve the energy utilization efficiency of the original FCC unit.

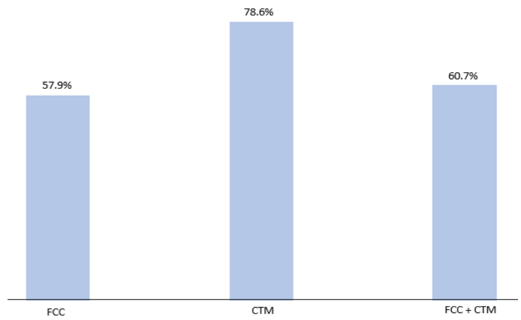

Fig. 2 Energy efficiency comparison of process integration

3.2 Electricity generation analysis based on ORC

There is a large quantity of low-grade heat in the methanol production system, and this waste heat is difficult to use for heat exchange. However, the ORC process enables efficient utilization of these energies for electricity generation. Waste heat mainly derives from the cooling process of the methanol product. Considering the impacts of the working fluid temperature and expansion ratio on the ORC process, we selected R290 as the working fluid for ORC power generation. For the designed system with an annual production capacity of 1.45 million tons of methanol, the net output power was 4798 MW, and the annual power generation capacity was 4.798M kWh. The thermal efficiency of the ORC unit was calculated to be 5.9%.

3.3 Sustainability analysis

To evaluate the CTM process more conveniently and intuitively, sustainability evaluation was developed that enable to identified advantages and drawbacks of new process compared with original unit (FCC) and traditional technology. The specific setting values of different indicators are listed in Table 2 and the results (Fig.7) show that CTM brings more environmental benefits in comparison to FCC and traditional process. However, it also has some weak points, such as low energy security. Besides, the technology is still immature and needs further study and improvement. In short, because of its good carbon utilization and high internal recovery rate, and it also shows outstanding advantages in energy efficiency. Therefore, It is a step closer to the realization of urban low-carbon refineries.

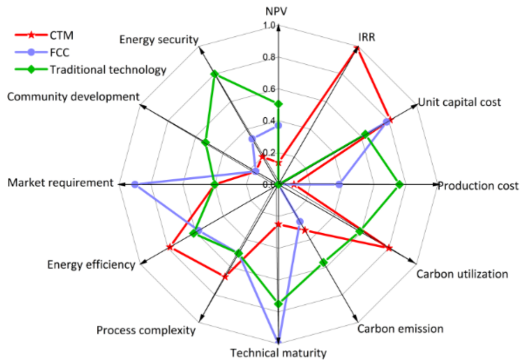

Fig.3 Sustainability comparison of CTM, FCC and Traditional

Table 2 Comparison of Indicators for CTM, FCC and Traditional technology

Indicator (subindicator)	CTM	FCC [12,13]	Traditional technology [10,11,16]	Reference value	
				Best	Worst
Economic					
NPV (RMB/B Yuan)	12.74	17.33	20.1	30	10[14]
IRR (%)	22.6	14.9	17.15	22.65	17.15[11]
Unit capital cost (RMB/M Yuan)	17.16	17.8	21.76	12.4	37.4[11]
Production cost (RMB/Yuan)	1690	1511	1323	1204	1700[11]
Technical					
Technical maturity	0.250	1.00	0.750	1	0[14]
Process complexity (%)	20	40	40	30	50[11]
Energy efficiency (%)	0.787	0.507	0.614	100	0[14]
Environmental					
Carbon utilization (t/t production)	0.75	0.00	0.55	0.93	0[14]
Carbon emission (t/t production)	0.333	0.27	0.566	0	2.99[14]
Social					
Market requirement (%)	40	90	40	100	0[11]
Community development (staff/1000t)	5	5	16	30.3	0[15]
Energy security (%)	20	33	8	100	0[15]

4. Conclusion

Implementation of the new process, not only can energy efficiency of original FCC unit be improved, but the GHG can also be utilized. In other words, it has obvious net carbon emission reduction potential for refinery. The energy efficiency analysis showed that the energy efficiencies of the original FCC process, the CO_2–dry gas methanol production process in the basic case, and the integrated FCC process with the CO_2–dry gas methanol production process were 57.9%, 78.6% and 60.7%, respectively, illustrating a 2.8% energy efficiency improvement, which was attributed to the process integration. Moreover, reuse or make full use of methane in dry gas is a new thinking of promote production while reducing emissions, which CH4 and CO2 are the main GHG. The design ingeniously saves raw materials and turn “waste” into a benefit. Also, it is necessary to apply the new system in other carbon capture and utilization industries that can achieve a beneficial effect on GHG abatement for future sustainable energy systems.
To completely understand the sustainable performance of the CO_2–dry gas to methanol production system, other environmental footprints (such as the water and environmental footprints) should be further quantified, which are directions for future studies.

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