Novel Process for Carbon Cycle Utilization from Industrial Flue Gas into Methanol

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Abstract. Reduction of greenhouse gas (GHG) emissions for mitigating climate changes is globally necessary. As a major GHG emitter, refinery sector is responsible for 14.1% of China's CO_2 emission in 2019. The flue gas associated with petroleum refining has high CO_2 content, presenting potentials for methanol and electricity co-production when the methane and hydrogen in dry gas are considered. To unlock the green opportunity for refineries, in this study we employed Aspen Plus to develop the process of methanol synthesis by recovering CO_2 in the flue gas of fluid catalytic cracking (FCC) unit and the methane and hydrogen in dry gas. The results show that the new co-production process increases the energy efficiency of the FCC unit by 2.4%. Compared with traditionally natural gas-based methanol production, the developed process enables annual CO_2 mitigation of 1.3 million tons.

1 Introduction

Globally, the annual carbon dioxide (CO_2) emissions dramatically increased during past decades, from 2.215 billion tons in 1990 to 3.389 billion tons in 2018 [1-2], and this number is predicted to reach 3.6 billion tons by 2040. With the continuous attention of the international community to the issue of climate change, it has become an indisputable fact that CO_2 causes global warming and lead to human dangers and soaring financial costs [3]. Thus, climate scientists have reached a consensus that containing carbon emissions will have a host of benefits.

Currently, refining industry is one of the key energy consumers and GHG emitters. During the 14th Five-Year Plan (2021-25) period, China's crude oil processing is expected to account for more than 16 % of energy consumption and 22% of the CO_2 emissions[4]. Driven by rapid development of economy and transportation, a greater demand for petrochemical is an inevitability in the foreseeable future for China , necessarily increasing the energy consumption and environmental emissions of refineries [5]. However, as China pledges to become carbon neutral before 2060, more initiatives and actions about low-carbon refineries are urgent needed. As such, unlocking the facility-wide green opportunities help refineries ease energy and environmental challenges, contributing to the cleaner and lower-carbon transition of the country's chemical industry.

Studies on refinery carbon reduction are not rare. Sardari et al. studied refinery's CO_2 reduction through process improvement of hydrogenation unit[6]. Qian et al. improved the efficiency by recovering waste heat in refinery, which contribute to carbon abatement indirectly[7]. Posada and Kreutz proposed the conceptual design of CO_2 recycle in the flue gas from CO_2-intensive industries in the perspective of biological utilization[8-9].All these previous carbon mitigation studies primarily either focused on improving the energy efficiency or specific unit process improvement, which can't solve the problem of carbon recycle utilization. Although as a way of carbon dioxide recycling, there is a huge bottleneck in biological utilization for the restrictions of geographic location and high economic costs[10-11]. In general, endeavors to direct GHG emission reduction via CO_2 capture and utilization are usually focused on generating station and cement plant, while in petrochemical industry was typically lacking.

To fill the above-mentioned research gap, in this study, we used Aspen to simulate a system of methanol synthesization that utilizes the CO_2 captured from FCC flue gas and the CH_4 and H_2 separated from dry gas. We select a refinery factory in China as a case to evaluate the energy efficiency and CO_2 reduction effect of the developed system. We aim to provide refineries with a path to simultaneously abate CO_2 and produce a high-added-value chemical product(methanol), reduce the trade-off between refineries' environmental and economic benefits, and shed light on directions for urban type low-carbon refinery development.

2 Research boundaries , methodology and system validation

2.1 Research boundaries

In this study, CO_2 was recovered by adding CO_2 absorber

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and desorber. The syngas was synthesized by dry reforming of methane separated from dry gas and high concentration CO_2 product gas, and methanol was obtained by further reaction. The overall process includes: CO_2 capture, methane dry reforming, methanol synthesis, methanol distillation, organic Rankine cycle power generation units. The conceptual design of CO_2-dry gas to methanol production system coupled with waste heat power generation is shown in the figure 1.

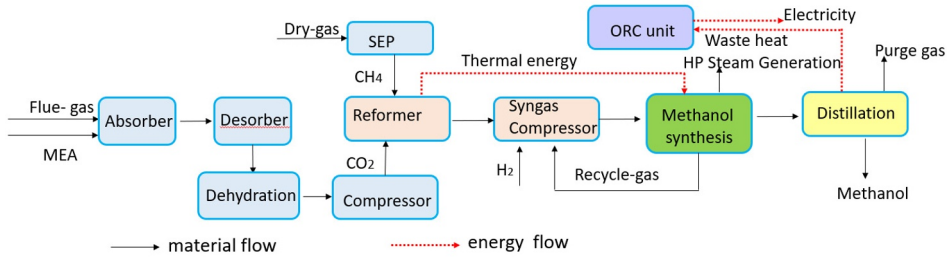

Figure 1. CO_2-dry gas to Methanol System Coupled with Waste Heat Power Generation

2.2 Methodology and validation

2.2.1 Energy Efficiency

In this study, there are two main types of feedstocks, the first is as raw materials, the second is as fuel consumption to provide energy or direct power consumption; products refer to effective products, mainly including main products and by-products, FCC process main products are catalytic gasoline, catalytic diesel and so on, by-products are fuel gas and other substances, in which all fuel gas is used for production or plant living facilities, the self-use products participate in the internal energy cycle of the process, so they are not included in the output. The standard energy efficiency can not only qualitatively reflect the energy efficiency level of the process, but also objectively reflect the situation of chemical energy conversion. The change of energy efficiency between 0 and 1, the best ideal case when the energy efficiency is 1, which means all the energy of the feed is completely converted into products, and the worst case when the energy efficiency is 0, which indicates all the transformations are ineffective. The energy efficiency formula is shown in Formula 1:

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

Among them, E_0 represents the energy of the main and by-products of the process; E_i represents the energy of all input systems.

2.2.2 CO_2 abatement

In the process of methanol production, a large amount of CO_2 will be consumed. However, the production process will also relies on energy, resulting in non negligible carbon emissions. In the analysis of process carbon abatement effect, CO_2 utilization, CO_2 production and product substitution emission reduction should be considered. Consequently, the calculation of carbon emission reduction is as follows:

$$ER_{total} = ER_{utilization} + ER_{substiution} - ER_{emission} \quad (2)$$

Among them, ER_{total} is the total CO_2 reduction of industrial chain; $ER_{utilization}$ is the amount of CO_2 utilized in the process; $ER_{substitution}$ is the CO_2 abatement compared with the conventional methanol production pathway; $ER_{emission}$ is CO_2 emitted in the production process.Specifically, the utilization of CO_2 is the CO_2 consumed as raw materials. The CO_2 emission mainly comes from three aspects: process emissions, fuel emissions and indirect power emissions. The process emission is CO_2 purge gas, which can be obtained from Aspen simulation data. Fuel and power emissions are calculated according to the corresponding emission factors [12]. The substitution reduction caused by the difference of carbon emission intensity between this process and traditional methanol production way, which Qin's research as a reference[13]. The results showed that the carbon emission intensity of conventional methanol production path was 1.783 t CO_2/t methanol.

2.3 System validation

After the establishment of the process simulation by Aspen, a very powerful tool for designing, simulating and optimizing the chemical engineering process [14,15], to accurately evaluate the process performance before scaling-up the model process for integrating it on a commercial scale, the key units are validated against experimental data from the perspective of dynamics. Table 1 showed the comparison of simulation results with reference data. It is noted that the simulation results are in good agreement with the literature and experimental data, implying the developed model is reliable for the system.

Table 1 Comparison between simulation results and experimental data of key units

Units	Items	Components				
		H_2	CH_4	CO_2	CO	H_2O
DMR(dry methane reforming	Ref. [16]T=900°C P=4 bars tubes: 2127					

	Feed flow (kmol/h)	0.0	2725	2725	0.0	0.0	
	Outlet flow(kmol/h)	5202	92.5	30.0	5327	62.5	
	Aspen Outlet flow (kmol/h)	5205.5	91.5	30.5	5329	61.5	
	Error (%)	0.07	-1.1	1.7	0.04	-1.6	
	Experiment [17]	H_2	CO	CO_2	CH_3OH	H_2O	Ar
	Feed flow [mole fraction (%)]	59.51	32.4	5.07	0.0	0.0	3.02
Methanol synthesis	Feed flow rate = 20 ml/min,T=220°C Catalyst: $Cu/ZnO/Al_2O_3$ [Cu 5%, Zn/Cu = 1/1 (mol)]						
	Productivity (mmol $kg^{-1}h^{-1}$) = 159.4						
	Aspen Productivity (mmol $kg^{-1}h^{-1}$) = 160.5						
Error (%)	0.69						

3 Results and discussion

3.1 Energy Efficiency Analysis

We use the lower heating value or combustion heat of fuel and material in this paper.According to the above Eq (1), the overall energy efficiency of the FCC process can be calculated.The total energy input of FCC is 2.2371 x 10^{11} MJ. The FCC products include catalytic gasoline and catalytic diesel. Given that catalytic slurry and dry gas involved in the internal energy cycle of the process, as FCC products they are not included in the output, and the output energy is 1.381 x 10^{11} MJ. As a result, the total energy efficiency of FCC is 61.7%. At present, there is no practical case of industrialized methanol production from CO_2-dry gas. However, there are many studies on catalytic reaction of methane dry reforming and process simulation. In addition, there are many industrial production processes for methanol production from coke oven gas for reference. In this study, the energy efficiency calculation of CO_2-dry gas to methanol production process will be based on Aspen simulation data and theoretical calculation. The energy input of CO_2-dry gas to methanol process is mainly brought into the system through fuel methane, fuel gas and net power consumption. The total annual energy input of CO_2-dry gas to Methanol system(CTM) is 3.69×10^{13} kJ. Methanol is the main product of the system, and high-pressure steam and electricity are by-products. The annual output energy of the system can be converted to 2.89×10^{13} kJ. Thus, the overall energy efficiency of the CTM process is 78.32%.

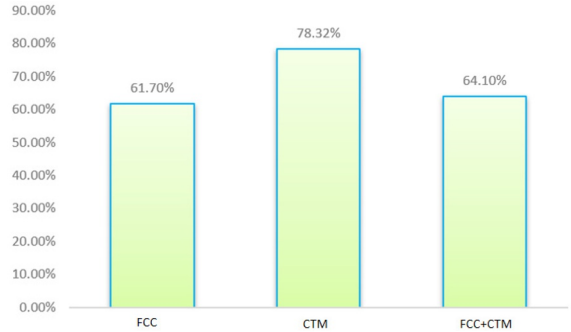

Figure 2. Energy efficiency comparison of FCC and CTM processes

As shown in Fig. 2, it shows that the energy efficiency of FCC is relatively low. The energy efficiency of the original FCC process is increased from 61.7% to 64.1% by coupling with the CTM process, in other words, the energy efficiency of the original FCC is increased by 2.4%. It can be seen that the FCC process integrated with CO_2-dry gas to methanol can effectively improve the energy efficiency of the refinery.

3.2 CO_2 abatement

Based on the previous calculation method(Eq 2), the carbon emissions of CTM system could be estimated. The results are shown as follows:

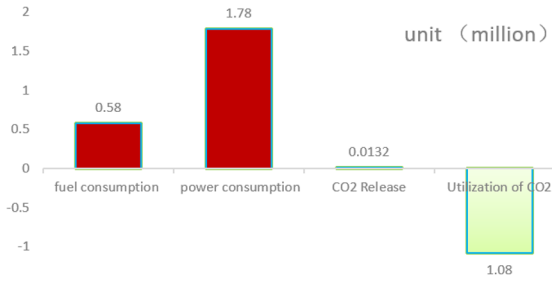

Figure 3. Distribution of CO_2 emissions for the CTM process

In Fig.3, the power and fuel consumption in the CTM process contribute greatly to methanol carbon emissions per unit of the process. The annual indirect CO_2 emission caused by fuel consumption is 0.58 $\times10^6$ t, and that caused by power consumption is 1.78 $\times10^6$ t. The contribution value of CO_2 exhaust gas to methanol production in this process is 1.318 $\times10^4$ t, which is converted into 0.4 t CO_2/t methanol, 1.228 t CO_2/t methanol and 0.0091 t CO_2/t methanol, respectively. CO_2 utilization can reduce the carbon emission value of the process. The consumption of CO_2 in the process is 1.08 million t, converted to -0.745 t CO_2/t methanol per ton of methanol. In summary, the carbon emission per unit of methanol in the CTM process is 0.892 t CO_2/t methanol, and the product replacement emission reduction is 0.891 t CO_2/t methanol. According to the annual methanol production, the total emission reduction of this process route is 1.292 million t CO_2.

4 Conclusion

In this study, we proposed a closed-loop design for CO_2 re-utilization, which enables high value-added application of dry gas simultaneously and promotes carbon cycle in the refinery . Specifically, the system uses CO_2 recovered from FCC unit's flue gas and the CH_4 separated from dry gas as feed stock for producing

methanol. It aimed at finding a practical and feasible solution for petrochemical industry realizing green and low-carbon development with an excellent techno-environmental performance.The results show that the CO_2-dry gas to methanol production process increases the energy efficiency of the FCC by 2.4% and the annual CO_2 mitigation is 1.29t CO_2/ methanol.

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