ISSN 2004-2965 Energy Proceedings, Vol. 22, 2021

International Conference on Applied Energy 2021
Nov. 29 - Dec. 5, 2021,Thailand/Virtual
Paper ID: 013

Reducing Carbon Dioxide Emission in the Process of Oxygen-thermal Coal to Calcium Carbide Polygeneration System

Wanyi Xu, Hongxia Wang, Xiaomei Wu, Zaoxiao Zhang *

State Key Laboratory of Multiphase Flow in Engineering, School of Chemical Engineering and Technology, Xi'an Jiaotong University, No.28 Xianning West Road, Xi'an 710049, P.R.China

ABSTRACT

With the development of economy, the chemical production from coal is becoming more and more important. Calcium carbide is a typical product from coal in China. There are two ways to produce calcium carbide product. Oxygen-thermal method (OTM) is a potential means of preparing calcium carbide from coal. The reuse of the furnace off-gas is one of the reasons restricting its industrial application. Besides, the CO_2 generated during the off-gas reuse process also needs to be captured and utilized. Therefore, this paper proposes two furnace off-gas reuse ways to polygenerate DME and adds Carbon Capture Utilization and Storage (CCUS) system which can be divided into two technologies as Carbon Capture Storage (CCS) and Carbon Capture Utilization (CCU) to reduce carbon emission. First, the Aspen Plus software was used to simulate the whole process of the two production chains, and then the carbon footprint of the production chain was analyzed. Then the CCUS unit was carried out in the system. Finally, the carbon footprint of the production chain before and after the retrofit are compared. CCS system can reduce the total carbon emissions of indirect and direct methods by 41.55% and 60.52%, respectively. As the output of the system increased with the addition of CCU module, the effect of CCU process was evaluated by comparing the different products yield under the same CO_2 emission. The result shows that in the direct polygeneration process, the addition of CCS part can increase the product yield by 2.53 times under the same CO_2 emission. In the indirect process, the addition of CCS part has the best carbon emission reduction effect, and the output of calcium carbide and dimethyl ether can be increased by 1.71 times under the same CO_2 emission. When using CCU technology to transform the polygeneration system, under the same carbon emission, the production of methanol in the direct method is increased to 15.8 times, and the production of dimethyl ether in the indirect method is increased to 2.33 times, which are promising ways to realize carbon reduction in the chemical production.

Keywords: CO_2 emission, CCUS, polygeneration, calcium carbide, oxygen-thermal method

NONMENCLATURE

Abbreviations	
OTM	Oxygen-thermal method
ETM	Electro-thermal method
DME	Dimethyl ether
CCUS	Carbon Capture Utilization and Storage
CCS	Carbon Capture Storage
CCU	Carbon Capture Utilization
LCA	Life Cycle Assessment
P2G	Power to Gas

1. INTRODUCTION

Calcium carbide is a very important chemical product, which plays a very important role in a lot of chemical productions. The production of calcium carbide from coal is very popular for the utilization of coal resources [1], in which the off-gas from the calcium carbide furnace should be treated carefully to avoid the pollution and waste of resources [2]. Therefore, polygeneration can be considered in the calcium carbide production to realize the high efficient utilization of the coal resources. Electro-thermal method (ETM) and oxygen-thermal method (OTM) are two main ways of calcium carbide production [3]. The difference between the two processes is the form of energy supply. The ETM uses the electricity to generate heat for the reaction, while the OTM uses the heat of coal combustion to supply heat. Studies have shown that compared with ETM, OTM can reduce energy consumption by about 30% [4]. In addition, if the off-gas from the calcium carbide furnace can be used to produce other chemicals, the multi-product comprehensive carbon emission of the polygeneration system is much lower than that of the ETM [5]. The main component of OTM off-gas are CO and H_2, which can be used as the ideal feedstock for the DME production after reforming. The DME production is divided into two methods, namely direct and indirect processes. At present, the indirect method is widely used in the industrial production of DME, while the direct process is still in the pilot stage of the experiment, but due to its short process chain and high atomic yield, the direct method has a great potential for development. The IEA reported the global energy-related carbon dioxide emissions in 2020 fell by 5.8%, the total emission of about 31.8 Gt [6]. But the world still faces the challenge of curbing carbon dioxide emissions while ensuring economic growth and energy security. "Low carbon production, green chemical industry" is the trend of the development of the chemical industry and the CCUS technology is the effective way to reduce emissions.

Here, Aspen Plus are used to simulate two OTM-DME polygenration routes, and Life Cycle Assessment (LCA) are used to analyze the carbon footprint of the two polygeneration processes. Then the CCUS emission reduction transformation was carried out. Power to Gas (P2G) and CCU technology are combined to achieve the system emission reduction transformation. Finally, the carbon footprint analysis and cost accounting of the system before and after the transformation are compared, so as to select the optimal process route.

2. METHODOLOGY

2.1 System boundary definition

The system only considers the carbon emissions generated during the whole production process from the raw material to the product. LCA is used to analyzed the carbon footprint of the polygeneration system and the boundary of the whole process is shown in Fig 1.

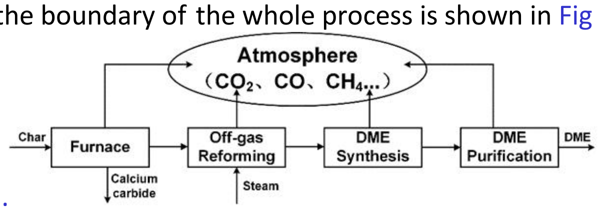

Fig. 1. System boundary of OTM-DME polygeneration process

In Aspen Plus simulation process, the whole process includes four units such as calcium carbide production, off-gas reforming, DME synthesis and DME purification. Besides, boilers and coolers are required to maintain appropriate operating temperatures.

2.2 CCUS with P2G system

CCUS can be divided into two technologies as CCS and CCU. CCS will only capture and compress CO_2 for storage, while CCUS will use the collected CO_2 to produce other chemicals. In this paper, methanol was selected as the target product of CCU unit. Because in the indirect synthesis method, methanol can be used as feedstock to directly participate in the production of DME, while in the direct synthesis method, it can also be coupled with the DME purification unit to produce by-product methanol.P2G is a process that converting electricity from fossil fuel combustion or clean energy sources such assolar or wind power to hydrogen or methane with water electrolysis[7]. The process of CCUS with P2G system coupled with two polygeneration routes are shown in Fig 2.

2.3 Simulation and calculation assumption

(1) The whole process is operated under a stable state condition;

(2) The ash, which includes metals such as SiO_2, MgO, and Fe_2O_3, is assumed inert;

(3) When the stream temperature needs to be below 25℃, additional cooling is provided;

(4) All the gas-phase reactions are very fast and quickly reach equilibrium;

(5) Both CCS and CCU unit are powered by solar photovoltaic power generation.

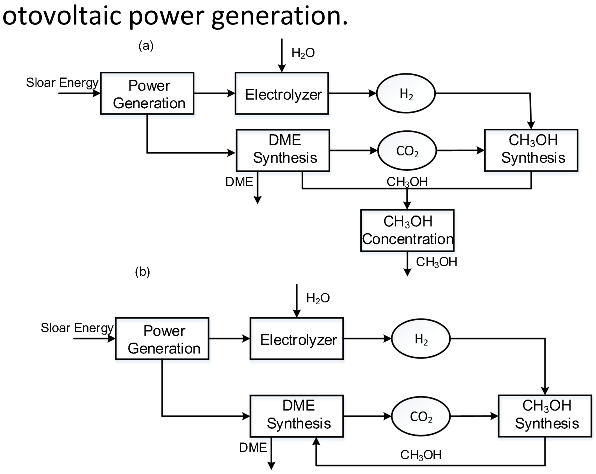

Fig. 2. CCUS with P2G system coupled with (a)direct OTM-DME polygeneration process. (b) indirect OTM-DME polygeneration process.

3. MODELING AND CACULATION

3.1 Indirect/Direct OTM-DME polygeneration route

The calcium carbide production capacity of OTM in this paper is 50kt/y, and the output of the off-gas is 177.17 kt/y. The char mass flow rate is 27.87t/h. The schematic diagram of the two polygeneration routes is shown in Fig. 3 and the product output under different process routes are summarized in Table 1.

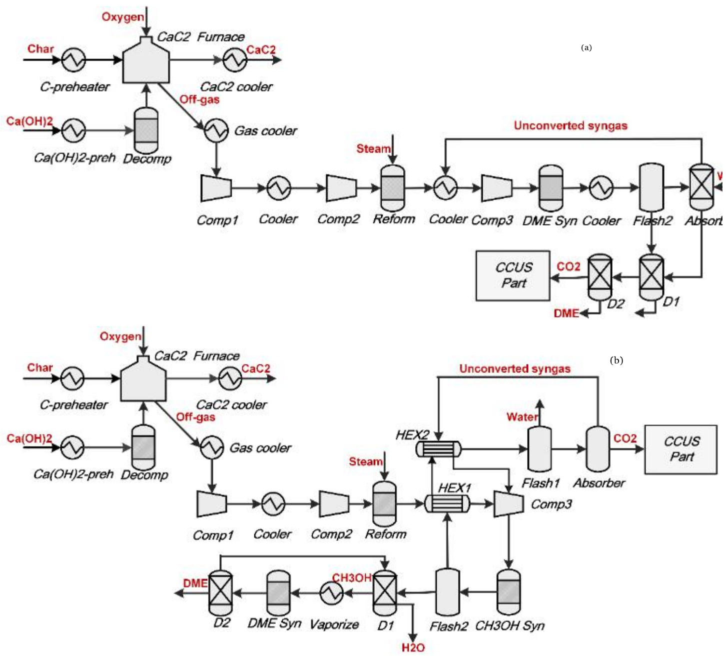

Fig. 3. Flowsheet of production line with (a)direct OTM-DME polygeneration process. (b) indirect OTM-DME polygeneration process.

Table 1 Product outputs under different process routes

Route	CaC_2(kt/y)	DME(kt/y)	CH_3OH(kt/y)
Direct(+CCS)	50	49.23	6.30
Direct+CCU	50	49.23	113.06
Indirect(+CCS)	50	52.69	0
Indirect+CCU	50	129.36	0

The two routes share the same calcium carbide production unit. In this part, the solid reactants are preheated first, and then the OTM process and the decomposition of hydrated lime are simulated by using Gibbs Reactor. After the reaction, the calcium carbide flows from the bottom of the furnace, and the off-gas escapes from the top.

Then in the direct DME polygeneration system, the purified off-gas enters the reforming reactor and the H_2/CO ratio is adjusted to 1.5. After cooling and pressure boosting, it is sent into the reactor of a bifunctional catalyst mixed with solid acid and copper-based catalyst to synthesize DME. Then the unreacted syngas is separated by the flash and absorption column and it is sent back to the DME reactor to react again, the separated liquid successively flows through two distillation column to purify DME, finally the purity of 98.8% DME products are obtained in the bottom of the distillation column.

While in the indirect DME polygeneration system, the purified off-gas enters the reforming reactor and the H_2/CO ratio is adjusted to 2, the waste heat is recovered by the two heat exchangers. Then the syngas passes the flash and PSA unit to separate CO_2. After seperating, syngas goes into methanol synthesis reactor, then the unreacted syngas back to recycle in the high temperature heat exchanger, and crude methanol mixed solution enters into the first distillation column to obtain high purity methanol, pure methanol are sent into DME synthesis reactor after vaporizing. After reacting, rough DME mixture are sent to the second column to continue purification, the methanol mixture obtained at the bottom of the column was returned to the first column for purification, and the DME product with the purity of 98.3% are obtained at the top of the column.

3.2 *Carbon footprint calculation method*

In the production process, the carbon emission equivalent can be divided into direct carbon emission and indirect carbon emission. The indirect CO_2 emissions are caused by power and heat consumption and the calculation formula is presented below:

$$E_{indirect} = AD_{power} \times EF_{power} + AD_{heat} \times EF_{heat} \quad (1)$$

where $E_{indirect}$ is the indirect CO_2 emission, the unit is *ton*. AD_{power} and AD_{heat} are electricity consumption and heat consumption, and the unit is kWh and kJ respectively. EF_{power} is CO_2 power emission factor and value is 0.081 $kgCO_2$/kWh[5]. EF_{heat} is CO_2 heat emission factor, and the value is 0.8112 $kgCO_2$/MWh[9].

CO_2 concentration in the exhaust gas of the process is more than 90%, so only compression, storage and utilization need to be considered during the CCUS. In

CCU part, the CO_2 storage efficiency is 95%. In CCS part CO_2 conversion efficiency is 90% and the compression power consumption is 94kWh per ton CO_2[8].

The carbon footprint of the whole process is calculated based on the equations below. The total carbon emission of the system is the sum of direct emission, indirect emission and CCUS part emission.

$$E = E_{direct} + E_{indirect} + E_{P2G} + E_{CCUS} \tag{2}$$

4. RESULTS AND DISCUSSION

When CCUS is not applied to the polygeneration system, the various CO_2 emissions from the production of one ton of DME are shown in Table 2. In the case of solar photovoltaic power supply, for each ton of DME produced by the two processes, 6.25t and 9.45t of CO_2 will be emitted into the atmosphere, respectively. In the direct method, the proportion of exhaust emissions, indirect thermal emissions and indirect electricity emissions in the total carbon emissions gradually decreases, and the proportion of the above three in the total carbon emissions is 59.86%, 24.23% and 15.90% respectively. While in the indirect method, the indirect thermal carbon emissions are slightly greater than the exhaust emissions. The proportions of these three are respectively 45.66%, 43.90% and 10.43%.

Table 2 CO_2 emmission intensity / *kt* DME before CCUS

	E_{di} *kt*	E_{power} *kt*	E_{heat} *kt*	E_{total} *kt*
Direct method	3.74	1.52	0.99	6.25
Indirect method	4.15	4.31	0.99	9.45

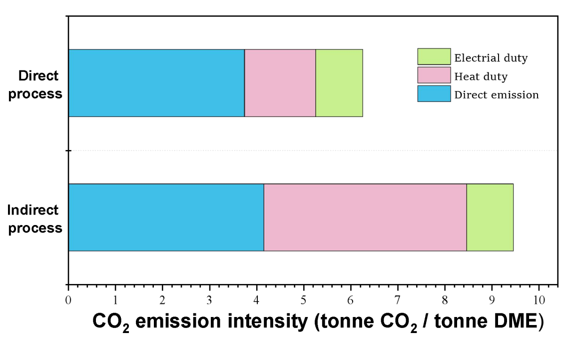

Fig. 4. CO_2 emission intensity of two polygeneration processes

4.1 *Carbon footprint results of polygeneration system after CCS*

In CCS unit, CO_2 is compressed and stored, and these steps also contribute to carbon emissions. In the process of CCS modification of the direct method and the indirect method, the carbon emission is 10.59kt/y and 10.97 kt/y respectively. The CCS system can capture most of the direct carbon emissions produced in the process. After CCS improvement of the system, the CO_2 emission reduction effect of the system is obvious. The specific carbon emission data is shown in Table 3. After CCS treatment, the carbon emission of the system can be reduced by 40%~60%.

Table 3 CO_2 emmission of the whole process after CCS

	CO_2 output before CCS(kt/y)	CO_2 output after CCS(kt/y)	Reduct-ion rate
Indirect method	465.26	271.94	41.55%
Direct method	309.47	122.18	60.52%

4.2 *Carbon footprint results of polygeneration system after CCU*

After the CCU system transformation, most of the direct CO_2 emissions are reused, but the indirect CO_2 emissions generated during the utilization process make the total CO_2 emissions of the system increase intuitively. Specific data are shown in Table 4 and the CO_2 emissions of direct and indirect methods are increased by 5.03% and 6.27% respectively.

Table 4 CO_2 emmission of the whole process after CCU

	CO_2 output before CCU(kt/y)	CO_2 output after CCU(kt/y)	Reduct-ion rate
Indirect method	465.26	488.66	-5.03%
Direct method	309.47	328.87	-6.27%

But actually, the output of process products after CCU retorfit is significantly increased compared with that before the retrofit. In the direct method polygeneration route, CCU system has more than doubled DME production yield, while in the direct method polygeneration route, CCU system has increased the annual methanol production yield by 113.06 t. So it is not reasonable to only focus on the total CO_2 output. Therefore , this paper compares the product outputs of 1*kt* CO2 emission under different processes, and the comparison results are shown in Fig. 4. In the direct method, with the addition of CCS part the output of the three products was increased by 2.53 times, while with the addition of CCU part the output of calcium carbide and DME was basically unchanged, but the output of by-product methanol was increased by 15.8 times from 20.42*t/kt* CO_2 to 344.87*t/kt* CO_2. In the indirect method, methanol is not output as a by-product. The addition of CCS part increases the output of calcium carbide and DME by 1.71 times, while the addition of CCU part does not change the output of calcium carbide basically, but the output of DME was increased by 2.32 times from 113.25 *t/kt* CO_2 to 264.06 *t/kt* CO_2.

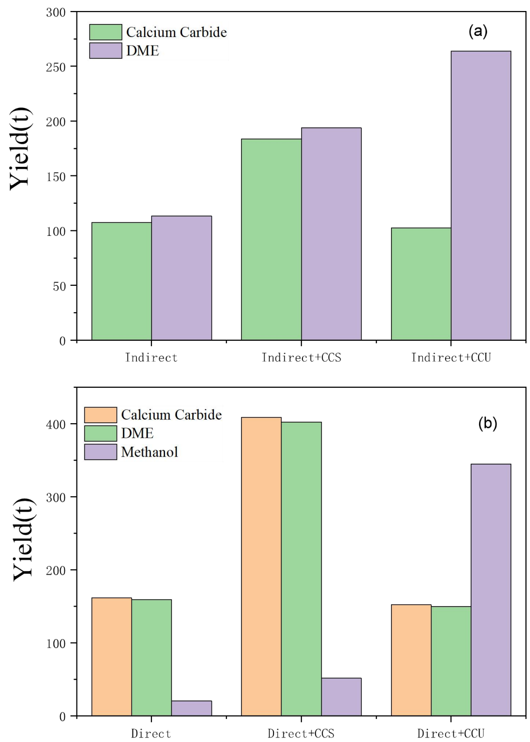

Fig. 5. Comparison of product output of different processes under $ktCO_2$ emission (a) indirect polygeneration process. (b) direct polygeneration process.

5. CONCLUSIONS

In this paper, Aspen Plus is used to simulate the process of polygenerate DME with an annual output of 50kt calcium carbide. When the indirect synthesis method and the direct synthesis method were used to prepare DME, the carbon emissions are 465.26kt/y and 309.47kt/y, respectively. In order to reduce carbon emission, CCS and CCU with P2G system are used to transform the process. The results show that the two methods are beneficial to reduce CO_2 emissions, and CCU system greatly increased the process yield. Besides, this paper compares the product outputs of 1*kt* CO2 emission under different processes to evaluate the emission reduction effect. In the direct method, the addition of CCS part can increase the product yield by 2.53 times under the same CO_2 emission, while the addition of CCU

module can increase the by-product methanol yield sharply. Therefore, the effectiveness of the two carbon reduction processes in the direct method depends on the price of the three products. In the indirect process, the addition of CCS module has the best carbon emission reduction effect, and the output of calcium carbide and DME can be increased by 1.71 times under the same CO_2 emission. The results show that CCUS system is an effective way to reduce carbon emissions and mitigate global warming.

ACKNOWLEDGEMENT

The authors would like to acknowledge the support from the National Natural Science Foundation of China (Nos. 51876150 and 21736008).

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