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REDUCING CARBON DIOXIDE EMISSION OF COAL-TO-METHANOL CHAIN USING CCS AND CCU WITH P2G SYSTEM

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ABSTRACT

Coal plays an indispensable role in the chemical industry, in which methanol from coal is a largely crucial part. In the process of coal-to-methanol chain, a large amount of CO_2 is emitted into the atmosphere, which should be captured and utilized. In this paper, firstly Aspen Plus software is used to simulate the whole process of coal-to-methanol production chain. The simulation results indicate that the carbon footprint of a certain amount of coal-to-methanol process is 3.01t CO_2/t methanol, and then we compare the carbon footprint of methanol production processes with two cases which are CCS (Carbon Capture and Storage) and CCU (Carbon Capture and Utilization) with P2G (Power-to-Gas) to reduce carbon emissions. It shows that CO_2 emission of methanol production after CCS is 0.64 t CO_2/t methanol with reducing by 78.7% and that after CCU with P2G is 1.42 t CO_2/t methanol, with reducing by 52.82%, and simultaneously increases methanol production doubly to 1378.31kt/y. The results show that CCS and CCU are effective ways to alleviate global warming.

Keywords: CO_2 emission, CCS, coal-to-methanol chain, P2G, CCU

NONMENCLATURE

Abbreviations	
CCS	Carbon Capture and Storage
CCU	Carbon Capture and Utilization
P2G	Power to Gas
LCA	Life Cycle Assessment
GHG	Greenhouse Gas

1. INTRODUCTION

Global energy-related CO_2 emissions grew 1.7% in 2018 to reach a historic high of 33.1Gt[1]. Nowadays, coal remains a major component of global fuel supplies, due to the growing demand for energy and the oil shortage in some countries, there has been increasing interest in advanced coal chemical industry[2], among which coal based methanol is one of the most benchmark chemical material. It is obvious that coal route to methanol production leads to serious CO_2 emissions, and the current international and global warming situations require low-carbon production of this process.

Among the most of solutions to reduce carbon emission, CCS and CCU are hot topics in recent years. One of the key points is whether these two technologies are effective in reducing emissions from a life cycle perspective. The LCA evaluation in methanol production process can reveal the distribution of carbon footprint and provide the guidance for CO_2 emission reduction. In this paper, Aspen Plus software is used to simulate the methanol production process, and the carbon footprint of this process is calculated, after then a comprehensive calculation of coal-to-methanol chain was carried out with CCS and CCU with P2G by using LCA.

2. METHODOLOGY

2.1 System boundary definition

LCA mainly includes cradle-to-gate and cradle-to-grave system boundary demarcation methods, and cradle-to-gate method is adopted in this paper. The boundary of methanol production system is shown in Fig 1.

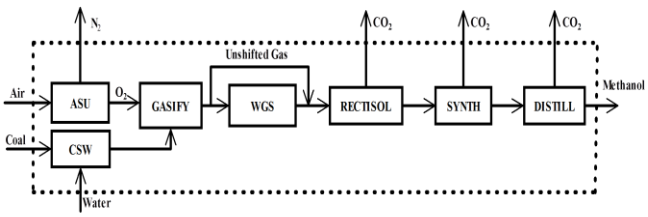

Fig 1 System boundary of methanol production process

In Aspen Plus simulation process, the technical route of methanol production includes the sections of GASIFY, WGS, RECTISOL, SYNTH and DISTILL, which respectively represent different operation units of coal gasification, water gas shift, acid gas removal, methanol synthesis and distillation. An additional section of BOILER is involved to provide extra steam for boiler combustion in the production process.

2.2 CCU with P2G system

P2G is a process that converting electricity from fossil fuel combustion or clean energy sources such as solar or wind power to hydrogen or methane with water electrolysis[3]. Hydrogen produced by the electrolysis of P2G can further react with carbon dioxide to form methanol. Water electrolysis powered by renewable energy sources, is expected to enable scale-up of hydrogen production, and zero direct CO_2 emissions are produced during water electrolysis process, hence this paper adopts renewable energy solar photovoltaic power generation. The process of combing CCU with P2G is shown in Fig 2.

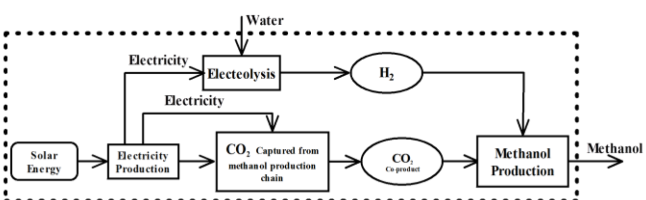

Fig 2 CCU with P2G system

2.3 Simulation and calculation assumptions

In the calculation, the following assumptions are made to formulate models.

①The coal-to-methanol process is operated in a stable state;

② Ash is assumed as inert substances in the gasification reaction;

③The coal used in the boiler is the same as that used in methanol production;

④ The coal used in the boiler is combusted completely, and all the carbon element is converted into CO_2;

⑤All the gas-phase reactions are very fast and quickly reach equilibrium;

⑥The electricity used by CCS with photovoltaic power generation and CCU with P2G system is all obtained from solar photovoltaic power generation.

3. MODELING AND CALCULATION

The production capacity of coal to methanol in this paper is 600kt/y, and the feeding coal used to produce methanol is conventional bituminous coal. The main parameters in Aspen Plus simulation of methanol production and flow rate of raw coal are listed in Table 1.

Table 1 Parameters of coal feed and Aspen Plus simulation

Parameters	Value
Coal mass flow rate	120.4kt/h
Low heating value(LHV)	25.85MJ/kg
Compositions (wt.%)	-
C	74.46
H	4.96
O	6.84
N	1.59
S	2.44
Cl	0.07
Fixed carbon	50.91
Volatile	34.54
Moisture	4.91
ASH	9.64

Verification of coal gasification model is shown in Table 2. After gasification, coal-based syngas is generally rich in CO, however, it requires a higher hydrogen ratio for methanol production. Therefore, water gas shift is of great necessity to achieve an ideal hydrocarbon ratio and finally increase methanol conversion rate and yield. Syngas after WGS unit contains certain acid gas products such as CO_2 and H_2S. The acid gases can poison the catalysts, which is detrimental to methanol synthesis reaction. Consequently, such acid gases are needed to be removed before synthesis reaction[4]. In this paper, gas purification unit adopts RECTISOL to eliminate CO_2, H_2S

and other acid gases. Crude methanol is synthesized in the reactor loaded with copper-based catalyst. Three-column distillation is used for methanol rectification. Finally refined methanol with 99.9% concentration (wt) is extracted from the top of the pressurized and atmospheric distillation columns.

Table 2 Verification of coal gasification model

Main components	H_2	CO	CO_2	H_2O
Mole fraction (mol%)	24.90	37.80	11.06	18.85
Reference data[5]	26.53	40.51	11.2	19

3.1 Carbon footprint calculation method of CCS

Capture rate of CO_2 is 90%, and the concentration of MEA solvent used for capture is 30%[6]. After CO_2 is partly captured and stored, the carbon footprint of the whole methanol production is calculated according to equation (1).

$$CF_{CCS} = CF_{CC} + CF_{boil} + CF_{meth} + CF_{cs} \quad (1)$$

$$CF_{CC} = ER_{cc} \times Y_{CO_2} \times EF_{elec} \quad (2)$$

$$CF_{CS} = ER_{cs} \times Y_{CO_2} \times EF_{elec} \quad (3)$$

where CF_{cc} is the indirect carbon emission from CO_2 capture electricity consumption; CF_{boil} is direct carbon emission caused by the energy used to capture CO_2; CF_{cs} is the indirect carbon emission released by compressing CO_2 with electricity. CF_{cc} can be calculated according to equation (2), in which ER_{cc} is the required electricity consumption for CO_2 capture (kWh/t CO_2). Y_{CO2} is the amount of captured CO_2; EF_{elec} is electricity emission factor. CF_{cs} is calculated by equation (3), where ER_{cs} is the electricity needed to compress CO_2.

3.2 Carbon footprint calculation method of CCU with P2G

CCU process combines hydrogen generated by P2G system with CO_2 to synthesis methanol, and the conversion rate of CO_2 is assumed to be 80%[7]. Energy consumption of methanol distillation is mainly derived from the steam generated by coal combustion, which will definitely increase the extra CO_2 emissions. Therefore, equation (4) is used to calculate the carbon footprint of methanol production with CO_2 partly utilized.

$$CF_{ccu} = CF_{cc}^{'} + CF_{P2G} + CF_{boil}^{'} + CF_{meth}^{'} \quad (4)$$

where CF_{P2G} is the carbon emission generated by electricity consumption in the P2G system. It should be noted that the electricity consumption for CO_2 compression and the P2G process are all produced by solar photovoltaic power generation.

4. RESULTS AND DISCUSSION

4.1 Carbon footprint results of methanol production after CCS

By using Aspen Plus, carbon footprint of each part of methanol production process is calculated, as shown in Table 3, the total carbon footprint is 1832.74ktCO_2/y, in which carbon footprint of WGS is 874.71ktCO_2/y, accounting for 45.88% of the total carbon footprint.

Table 3 CO_2 flow rate results based on Aspen Plus simulation

Production unit	Inlet CO_2 flow(kt/y)	Outlet CO_2 flow(kt/y)	Net CO_2 flow(kt/y)
GASIFY	0	512.34	512.34
WGS	317.4	1192.11	874.71
RECTISOL	1385.28	1385.28	0
SYNTH	38.77	1.91	-36.86
DISTILL	0.8	0.8	0
BOILER	0	482.55	482.55
TOTAL	1742.25	3505.58	1832.74

CO_2 produced by RECTISOL and BOILER units is captured, compressed, stored or utilized. The amount of CO_2 for each unit after CCS is calculated as shown in Table 4, and carbon emissions of CCS process are listed in Table 5.

Table 4 Carbon footprint of methanol production chain after CCS

Production unit	Inlet CO_2 flow(kt/y)	Outlet CO_2 flow(kt/y)	Net CO_2 generation(kt/y)
GASIFY	0	512.34	512.34
WGS	317.4	1192.11	874.71
RECTISOL	1385.28	38.77	-1346.51
SYNTH	38.77	1.91	-36.86
DISTILL	0.8	0.8	0
BOILER	0	48.26	48.26
Total	1742.25	1794.19	51.94

Table 5 CO_2 emission of CCS

CCS	CO_2 emission(kt CO_2/y)
Indirect emission by capture	10.16
Indirect emission by compression	163.14
Direct emission of coal combustion	165.61
Total	338.91

The total carbon emission of methanol production chain with CCS is 390.85 ktCO_2/y. Compared with the direct carbon emission of methanol production 1832.74

$ktCO_2$/y, CCS can greatly reduce carbon emission. However, CCS process will generate additional CO_2, and indirect carbon emissions from CO_2 capture and compression account for 51.14% of the total carbon emission of CCS process.

4.2 *Carbon footprint results of methanol production after CCU*

In this paper, CO_2 is converted into methanol by the hydrogenation and the hydrogen comes from the P2G system. According to section 3.2, the results of CCU process and methanol production emissions are shown in Table 6.

Table 6 CO_2 emissions results of CCU with P2G

Methanol Production Capacity	1378.3kt/y
CCU CO_2 emission	Kt/y
Indirect CO_2 emission in P2G	863.58
Indirect CO_2 emission by capture	0.83
Direct CO_2 emission by extra combustion	683
Direct CO_2 emission in methanol production	408.1
Total	1955.51

The results show that when the captured CO_2 is used to synthesize methanol product, methanol production is doubled larger than that of the referenced scenario. Compared with the traditional technical route of producing methanol from raw coal with the same output, 963.2kt/y of coal can be saved, thus reducing the dependence on fossil energy. As can be seen from Table 5, carbon emission of P2G system is 863.58kt/y, accounting for 44.16% of the total emission. Although the carbon emission of photovoltaic power generation process is very small, only 81g/kWh[7], the overall electrolysis efficiency of hydrogen production is very low at about 22%, which requires 4.9kWh per Nm3 hydrogen production. In order to obtain high purity methanol, energy consumption of methanol distillation unit will increase by 5.56 × 109MJ/y. Therefore, additional CO_2 emission from coal combustion is 683kt/y, accounting for 34.93% of the total carbon emission. Conversion rate of CO_2 to methanol is only 80%, and the unreacted CO_2 gas is directly discharged into the atmosphere in methanol production unit. Therefore, the direct carbon emission of methanol production process is 408.1kt/y, accounting for 28.87% of the total carbon emission. Carbon emissions of coal-to-methanol chain with a unified unit (t CO_2/t methanol) are shown in Table 7. It is seen that when CCS and CCU are applied to methanol production chain, carbon emissions will be reduced. CCU process can increase methanol production doubly, however, due to the low efficiency of hydrogen production by electrolysis, indirect carbon emission reaches to 1.42 t CO_2/t methanol, accounting for a large part of total emissions. It is worth mentioning that P2G system produces not only hydrogen, but also the high-purity oxygen. So some of the oxygen for the gasifier can be saved and the energy consumption in the air separation unit can be reduced.

Table 7 CO_2 emission results of CCS and CCU with the same unit (t CO_2/t methanol)

Methods	CO_2 generation(kt/y)	Methanol Production(kt/y)	Carbon footprint(tCO_2/t methanol)
Direct emission	1832.74	608.41	3.01
CCS	390.85	608.41	0.64
CCU with P2G	1955.51	1378.31	1.42

5. CONCLUSIONS

In this paper, Aspen Plus software is used to simulate the coal-to-methanol process with a capacity of 600kt/y. Carbon emission of coal-to-methanol production chain is calculated as 3.01t CO_2/t methanol. In order to reduce carbon emission, two different technical cases are used, namely CCS and CCU with P2G system. The results show that these two methods are beneficial to reduce CO_2 emission, among which CCS performs better, with carbon emission reduced by 78.7%. Due to the synthesis of CO_2 into methanol by CCU with P2G, methanol production increases to 1378.31kt/y. The final carbon emission of CCU with P2G system is 1.42 t CO_2/t methanol, reducing by 52.82%. The results show that CCS and CCU with P2G are effective ways to alleviate global warming.

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