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Coal based hydrogen production process with CO_2 recovery

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***Abstract*—**Hydrogen is recognized as an environmentally clean energy source for electricity generation, alternative fuel and other applications since it is zero emission. Coal is one important source for hydrogen production, which has special value for China because it's rich in coal but limited in natural gas and oil. More important, coal can be utilized in low carbon way through integrating CO_2 capture into hydrogenation production process. However, with the current technology, the energy efficiency of producing hydrogen from coal is around 60%, which limits the full chain efficiency of coal utilization. It is therefore extremely important to develop more efficient methods of H_2 production from coal. In this paper, a new type of hydrogen production process with a three-step coal gasification is introduced. The Aspen Plus Software is selected to simulate the system. Then the Exergy-Utilization Diagram (EUD) analyses are applied to disclose the mechanism of key processes. The result reveals that the efficiency of hydrogen production can be upgraded to 67% due to removing air separation unit and CO_2 separation process. Thereby the hydrogen production process introduced in this paper has a good thermodynamic performance and may provide a quite promising way for high efficient and clean coal utilization.

Keywords—Hydrogen production, CO_2 capture, three-step coal gasification

I. INTRODUCTION

Hydrogen is a flexible energy carrier with potential applications across all energy sectors including electricity generation, alternative fuel and so on. It is one of environmentally clean energy carrier since it is zero CO_2 emission[1]. Hydrogen can be produced from fossil fuels or renewable sources. However, on a shorter term, with increasing but still insufficient supply of renewable energy, hydrogen production from fossil fuels with CO_2 capture and storage (CCS) may prove to be an enabler for low CO_2-emission hydrogen production [2]. Therefore, hydrogen production from coal is one of the most important technologies for China, which is rich in coal but limited in natural gas and oil.

In the traditional process of hydrogen production from coal, coal is gasified to syngas in an entrained gasifier. After heat recovery, the syngas is cooled and then shifted to mainly CO_2 and H_2. Following a separation step, in which H_2S and CO_2 is removed by Selexol process, high purity H_2 (99.999%) is produced via pressure swing adsorption (PSA). The purge gas of PSA is compressed and burned in a gas turbine combined cycle to produce electricity. Kreutz, Consonmi et al [3]-[5] studied performances, costs and prospects of using commercially ready technology to convert coal to H_2 and electricity with CO_2 capture and storage. Results show that the process of hydrogen production from coal with commercial technology has an efficiency of 57-58% (LHV), while exporting to the grid decarbonized electricity amounting to 2-6% of coal LHV. Jin [6][7] proposed two novel multifunctional energy systems for the production of hydrogen and power, in which a new type of coke oven, firing coal as heating resource for coking is adopted.

Coal gasification technology is an effective method for hydrogen production and is considered a key technology in the transition to a hydrogen economy [8]. In the coal gasification process, coal is partially oxidized by oxygen agent (steam and pure oxygen) at high temperature, in which around 15%-28% of the fuel chemical energy is converted into sensible heat of syngas instead of chemical energy [9]. Meanwhile, the exergy destruction of coal gasification is still the main contributor for the exergy destruction in the energy system [10]. Therefore, a novel three-step gasification technology is introduced and integrated with hydrogen production. In this gasification process (Fig.1), coal is

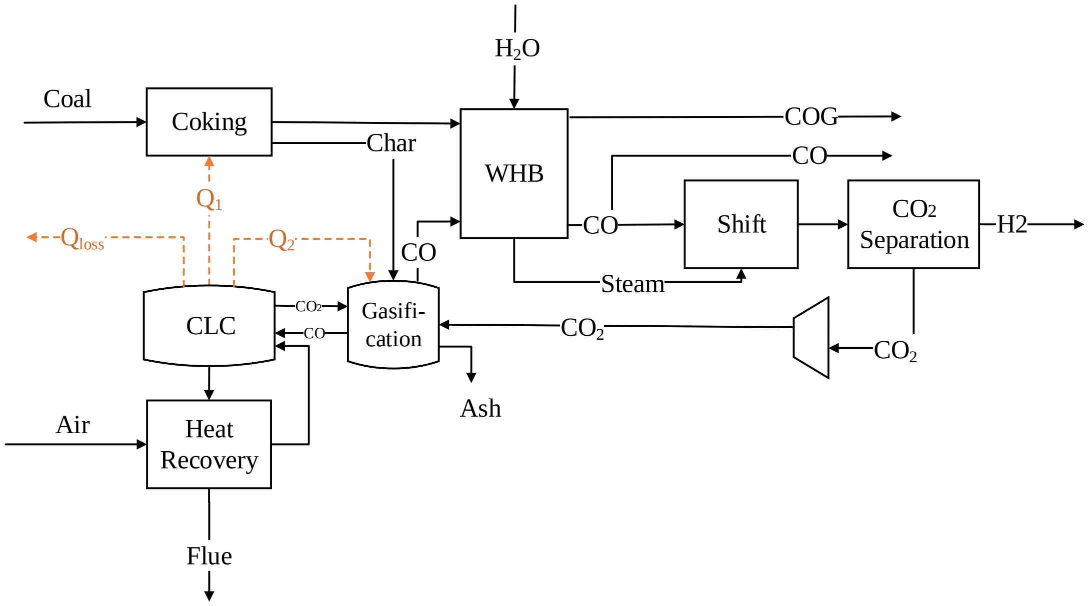


Fig. 1 Flowsheet of three-step gasification

gasified through three separated units including coking, char-CO_2 gasification and water gas shift reaction. Coal is first fed into the coking room and decomposed into coke oven gas (COG) and char; then char is gasified with CO_2 in gasifier and converted to syngas mainly with CO. Part of syngas from CO_2-char gasifier is sent to chemical looping combustion (CLC) process as fuel to provide heat for coking and char-CO_2 reaction, meanwhile, CO_2 produced in the CLC process is recycled to char-CO_2 reaction gasifier as gasifying agent. To satisfy the CO_2 demand of char-CO_2 reaction, part of CO_2 is separated from shifted syngas and recycled to gasifier. As a result, three gases including H_2-riched COG, syngas composed of mainly CO and H_2-riched syngas are produced. With this method, an additional work for air separation and CO_2 emission of firing coal are avoided.

Considering the higher CO_2 fraction in the shifted syngas, which is beneficial for reducing energy consumption for CO_2 capture. Therefore, coal can be utilized in low carbon way through integrating CO_2 capture into hydrogen production process. In this paper, a new type of hydrogen production system with a three-step coal gasification is introduced and the thermodynamic performances of the whole system will be simulated by Aspen Plus software. Energetic and exergetic analysis of the whole system will be presented to investigate the energy utilization level of each process. Finally, the internal irreversible mechanisms of key process will be revealed by the aid of exergy-utilization diagram (EUD) analysis.

II. SYSTEM DESCRIPTION AND SIMULATION

The simplified flowsheet of traditional coal-based hydrogen production system is shown as Figure 2. It employs the coal-water slurry gasification technology, where pure oxygen from air separation unit is required as gasifying agent. Following a waste heat boiler (WHB), the syngas is shifted and converted to mainly H_2 and CO_2. CO_2 is captured in the syngas Clean up unit with Selexol technology, then the high purity H_2 (99.999%) is extracted from the H_2-rich gas via PSA. Afterwards, the purge gas from PSA is sent to a gas turbine combined cycle for electricity co-production.

In the novel hydrogen production system (Fig.3), a three-step coal gasification technology is employed. In the three-step gasification, coal is first coked in the coking room and decomposed into char and coke oven gas (COG) thermally. Char from the coking room is sent to the gasifier to react with CO_2, where syngas mainly with CO is produced. After CO_2-char reaction, the syngas mainly with CO is partially sent to chemical looping combustion process to supply heat for coking process and CO_2-char reaction. Afterwards, the CO_2 produced in the chemical looping combustion process is recycled back to the CO_2-char gasifier as gasifier agent. The rest of syngas is shifted to CO_2 and H_2 with steam after heat recovery. To satisfy the CO_2 demand of the gasifier, CO_2 captured in the syngas clean up process is partially compressed and recycled to gasifier, which means the CO_2 required in the gasifier are supplied from chemical looping combustion process and syngas clean up process. Considering the high H_2 content in COG, H_2 can be extracted from COG and gasifier syngas after heat recovery and clean up, then the tail gas of PSA is compressed and burned in gas turbine combined cycle to produce electricity. Compared with traditional gasification technology, in the three-step coal gasification, char is gasified with CO_2 not pure oxygen, which avoid power for air separation. Furthermore, decomposing the traditionally gasification into moderate coking process, char-CO_2 gasification process and CO chemical looping combustion process, the three-step gasification turns out to have a smaller exergy destruction and higher cold gas efficiency.

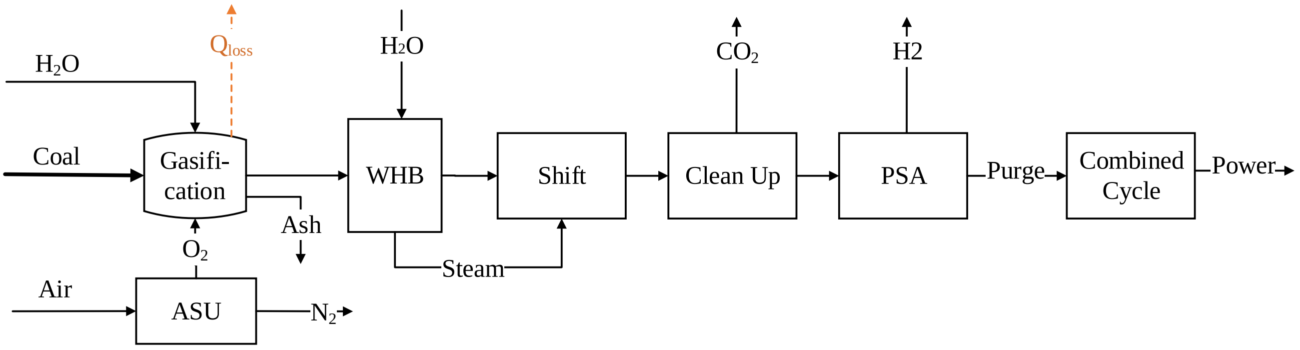


Fig. 2 Simplified flowsheet of traditional coal-based hydrogen production system

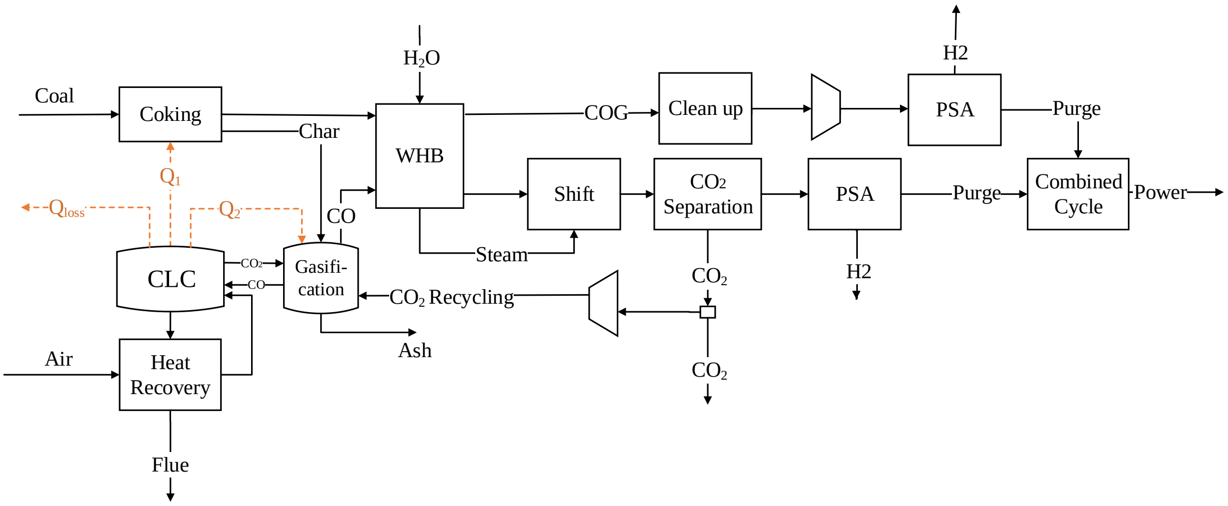


Fig. 3 Simplified flowsheet of novel coal-based hydrogen production system

III. RESULTS AND DISCUSSIONS

This paper presents an evaluation of systems using the Aspen Plus software. The feedstock coal and important process design parameters used in this model are shown in Table1 and Table2, respectively.

The traditional gasification process employs a Texaco slurry-feed gasifier with a heat loss about 5%. in the three-step gasification, the coking and char-CO2 reaction are conducted at 900 ˚C and 1100 ˚C, respectively. the chemical looping combustion process are composed of air reactor (AR) and fuel reactor (FR), in the fuel reactor, CO is oxidized to CO_2 by oxygen carrier. In the air reactor, oxygen carrier is oxidized at atmosphere pressure and recycled to fuel reactor. In this model, Fe_2O_3/Fe_3O_4 oxygen carrier is selected and the reaction temperature of FR and AR are 1200 ˚C. the water gas shift process consists of two staged reactors (adiabatic and isothermal reactor) with an inter-bed cooling, and the Selexol technology with 95% CO_2 recovery ratio is used in the clean up process. In the PSA process, H_2 recovery ratio is 0.88 and the tail gas is compressed and sent to a combined cycle unit [7]. The combined cycle unit has a gas turbine with an initial temperature 1327 ˚C, and a pressure ratio of 16.5, besides, the highest initial pressure and initial temperature of steam produced in the heat recovery unit are 126 bar and 566 ˚C, respectively.

TABLE I. COAL COMPOSITION ANALYSIS

Item	Value
Mass fraction, %	
C	71.63
H	4.53
O	10.28
N	0.84
S	0.33
Ash	8.79
W	3.60
LHV, kJ/kg	28670

The energy balance of the traditional hydrogen production process and novel hydrogen production process are listed in Table3, where we could see that the overall efficiency of novel hydrogen production process reaches 67.8%, while the thermal efficiency of traditional hydrogen production process is 57.5%. The performance improvements mainly come from the employment of three-step gasification, which has a higher cold gas efficiency and eliminate air separation unit. Compared with Texaco coal gasification, the three-step coal gasification has a cold gas efficiency of 88.2%， which is about 15.7 percentage points higher. The avoidance of ASU contributes a 45124.4 kW reduction of work for air separation and oxygen compression.

Exergy analysis is presented in this section. Table 4 presents the exergy balance of the two systems. Compared with the traditional hydrogen production process, the exergy efficiency of hydrogen production process with three-step gasification increases from 54.8% to 64.5%. Among these processes, gasification is the largest exergy destruction process. The exergy destruction of the new gasification is 5.6% smaller than that of traditional coal-slurry gasification. Besides, the elimination of ASU further brings 3.0% reduction of exergy destruction. Since more electricity generated in combined cycle unit of the novel system, the exergy destruction is 3.6% higher than that in traditional system. Similarly, the exergy destruction of WHB in traditional is 2.3% higher.

TABLE II. DESIGN PARAMETERS

Item	Description
Coking	P=1.013 bar, T=900 ° C.
Char-CO_2 gasification	T=1100 ° C, P=20 bar，CO_2/C mole ratio: 1.15.
CLC	AR: T=1200 ° C, P=1.013 bar; FR: T=1200 ° C P=20 bar.
Texaco gasification	T=1346 ° C, P=20bar, Heat loss: 5.0%，Slurry concentration:66.5%.
WGS	Two stages with inter-bed cooling; first stage adiabatic and second stage isothermal with 225 ° C.
Clean Up	Selexol Technology，CO_2 recovery ratio: 95%.
Gas Turbine	Pressure Ratio:16.5bar, Gas turbine initial temperature:1327 ° C, Isentropic efficiency of GT: 0.9.
WHB & Steam Turbine	Triple-pressure reheat steam: 126/26/5.5, Steam temperature: 566 ° C, Isentropic efficiency of ST: 0.88/0.89/0.87.
PSA	H_2 recovery ratio: 0.88.

TABLE III. ENERGY BALANCE OF THE TRADITIONAL SYSTEM AND NOVEL SYSTEM

Item		Traditional system	Novel system
Energy Input			
	Coal (kW)	821069	821069
Utility consumption			
	ASU (kW)	35435.4	0
	O_2 compression (kW)	9689	0
	Mill and fan (kW)	3203.8	3203.8
	Syngas clean up (kW)	23951.8	22161.8
	COG compression (kW)	0	13460
	Pumps (kW)	652.4	552
	Subtotal (kW)	72932.4	39377.6
Power Output			
	WHB (kW)	37554	11426
	Gas turbine (kW)	27814	65875
	Steam turbine (kW)	16294	38346
	Subtotal (kW)	81662	115647
H_2 output	(kW)	463064.5	480352.2
Electricity Output	(kW)	8729.6	76269.4
Efficiency, LHV		57.5%	67.8%

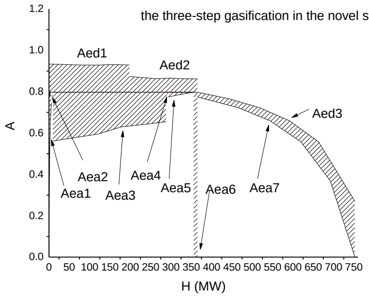
TABLE IV. EXERGY DESTRUCTION IN THE SYSTEMS

Item		Traditional System		Novel system	
Exergy Input		Exergy(kW)	Proportion (%)	Exergy(kW)	Proportion (%)
	Coal	874224.7	100	874224.7	100
Exergy destruction					
	ASU	26355.4	3.0	0	0
	Gasification	183064.1	20.9	133708.4	15.3
	WHB	38437	4.4	18763.7	2.1
	Heat Recovery	0	0	2394	0.3
	WGS	41129	4.7	43037.3	4.9
	Clean up	29798.2	3.4	38049.6	3.2
	PSA	1918.4	0.2	3062.0	0.3
	COG Compression	0	0	790.9	0.1
	Combined Cycle	28818.5	3.2	59188.7	6.8
	Subtotal				
Exergy Output					
	Electricity	8729.6	1.0	76269.4	8.7
	Hydrogen	470538.7	53.8	488105.4	55.8
	Subtotal	487678.1	54.8	564374.8	64.5
Exergy Efficiency			54.8		64.5

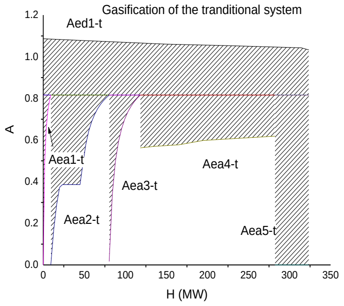
IV. EXERGY-UTILIZATION DIAGRAM (EUD) ANALYSIS

To reveal the inner phenomena of the key chemical energy transformation process, the exergy-utilization diagram (EUD) methodology proposed by Ishida is adopted. Combined with energy and exergy analysis, the internal irreversibility mechanism is graphically illustrated by the energy level difference between an energy donor and energy acceptor pair. The energy level (A) is equal to the exergy change ($\Delta\acute{\varepsilon}$), divided by the energy transformation quantity (enthalpy change ΔH), i.e. $A=\Delta\acute{\varepsilon}/\Delta H$. in the EUD method, the exergy destruction is illustrated by the area between the curves of the energy donor and energy acceptor.

The EUD for gasification process is presented in Fig 4. For the three-step gasification technology (a), the energy transformation takes place between the chemical looping combustion of CO (including oxidation reaction Aed1 and reduction reaction Aed2) and the endothermic process (including heating of coal Aea1, heating of CO_2 in char gasification, coking and CO_2-char reaction Aea3; heating of CO Aea4 and Air heating Aea5 in chemical looping combustion process). And the heat exchange process of external combustion between flue and air is represented by Aed3 and Aea7, the heat exchange process between COG and CO_2 is represented by Aed5 and Aea5. For the traditional gasification process (b), the energy donor denoted by Aed1 is the exothermic reaction occurred during coal gasification, while the energy acceptors include the process of coal heating Aea1-t, water heating Aea2-t, oxygen heating Aea3-t, endothermic reactions Aea4-t, and heat dissipation Aea5-t in gasification process. Comparing the EUD charts of the gasification process, it shows that the energy donor of three-step gasification is less than that of coal-water slurry gasification. Furthermore, the exergy destruction of heating reactants diminishes significantly because of the high temperature of gasify agent and fuel. Hence, the overall exergy destruction of three-step gasification technology is 133708.4 kW, which is 5.6% lower than the traditional gasification.



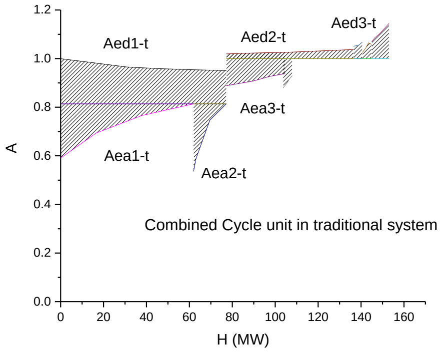
(a) the three-step gasification



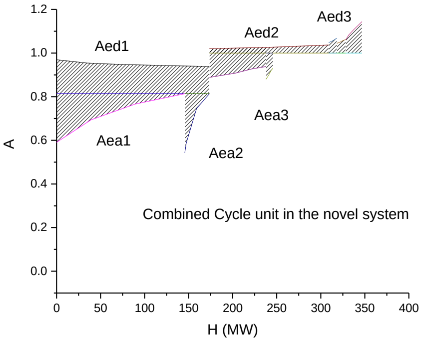
(b) traditional gasification

Fig. 4 EUD comparison of the three-step gasification and traditional gasification

The power generation process comprises of adiabatic combustion of syngas, gas turbines, steam turbines, and compressors. Fig 5 shows the EUD of the power generation process in the novel (a) and traditional (b) system. In the syngas adiabatic combustion process, the energy donor is oxidized reaction of syngas Aed1 while the heating of reactants acts (including Aea1 and Aea2) as energy acceptor. Meanwhile, the gas turbine process Aed2 and steam turbine process Aed3 act as energy donors, while the corresponding energy acceptor is the compress process Aea3. Compared with power process in the traditional system, the energy transformation of adiabatic combustion and power generation in novel system are larger, while the energy quality difference between donor and accepter is similar, so the exergy destruction of power process in novel system is larger.



(a) Combined cycle unit in traditional system



(b) Combined cycle unit in the novel system

Fig. 5 EUD comparison of combined cycle unit

V. CONCLUSION

A novel coal-based hydrogen production process with CO_2 recovery system is introduced, in which a three-step coal gasification is employed. Compared with traditional hydrogen production system, the thermal efficiency of the novel system reaches 67.8%, 10.2% higher than traditional system. In addition, the inner phenomena of the integration of the system are demonstrated by the use of exergy-utilization diagram method. The exergy destruction of gasification is decreased by about 4.3% compared with traditional system. Although the exergy destruction combined cycle unit are larger, the exergy output is still 10.2% higher. For these reasons, the proposed system provides a promising option for future sustainable energy systems.

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