Carbon-Calcium Composite Conversion Calcium Carbide Acetylene System: Material and Energy Transformation, Exergy Evaluations

Hongxia Wang^a, Wanyi Xu^a, Maimoona Sharif^a, Guangxu Cheng^a, Xiaomi Cui^b, Zaoxiao Zhang^{a,*}

a. 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;

b. Yang Quan Coal Industry Co., Ltd, Taiyuan 030000, Shanxi, P. R. China

*Corresponding author. E-mail address: zhangzx@xjtu.edu.cn (Z. Zhang)

ABSTRACT

Calcium carbide is one of the important basic coal chemical products in China. Oxy-thermal method is a potential alternative to electro-thermal method to overcome the disadvantages of high energy consumption, high material consumption, and high pollution. However, the traditional oxy-thermal method is in the laboratory research stage due to the constraints of high carbon consumption, low utilization rate of solid waste and immature technology. Therefore, a novel system of carbon-calcium compound conversion for calcium carbide-acetylene production, which couples carbon capture and calcium carbide waste slag reuse process to achieve CO₂ enrichment and calcium cycle, is proposed in this paper. Based on the simulation data, the system is comprehensively evaluated by material conversion, energy utilization, exergy analyses. It is found that the proposed coupling process has the largest effective atom yield of carbon, hydrogen, and calcium, which is 85.41%. In addition, the coupling module of this process can recycle the solid waste carbide slag and the carbon capture rate is more than 90%. It is worth noting that the unit product carbon consumption of proposed system is 2.02 t Coal· t^{-1} C₂H₂, which is only 0.37 times that of the traditional process. Moreover, although the 43.21% exergy efficiency of the proposed system with steam gasification agent is slightly lower than the 49.37% of traditional system, it was considered that the former is a relatively superior process because of its comprehensive better performance than the latter. From above, the proposed system is high-efficiency, lowcarbon and clean for calcium carbide-acetylene production, which could be a promising process as innovative technology for carbon emission reduction in practical applications.

Keywords: carbon-calcium compound conversion, module coupling, material conversion, energy utilization, exergy analysis

1. INTRODUCTION

China is currently the largest producer and consumer of calcium carbide in the world, and the coal reserves are adequate for coal based calcium carbide industry[1]. At present, the electro-thermal method is mainly used in industry to produce calcium carbide at 2000 °C, and the power consumption for each ton of calcium carbide is about 3500 kWh[2,3]. However, the production of calcium carbide basically relies on coal electricity[3,4]. Considering that the thermal efficiency from coal to electricity is less than 40%, the energy consumption of calcium carbide production is more than 2.5 times of that of electricity^[5]. Moreover, only 40% of the large amount of carbide slag produced in the calcium carbide industry is effectively used, which seriously pollutes the environment. From the above, the disadvantages such as high energy consumption and pollution of calcium carbide production by electro-thermal method slowed its development, therefore, some scholars turn to oxythermal method as an alternative, which directly uses the combustion heat of coal for calcium carbide production, avoiding the energy loss of electric arc discharge [6,7,8]. Moreover the purity of CO in the tail gas produced by oxy-thermal method is as high as 90%[4]. However, the oxy-thermal method is still in the laboratory research stage due to the immature technology, high carbon consumption and emissions, and insufficient exhaust gas utilization. Therefore, establishing a low-carbon circular economy calcium carbide production model with carbon emission reduction and solid waste resource utilization is the key to promoting the development of oxy-thermal method.

Selection and peer-review under responsibility of the scientific committee of the 13th Int. Conf. on Applied Energy (ICAE2021). Copyright © 2021 ICAE

In view of the above problems, in this paper, the process flow of calcium carbide-acetylene by coal based oxy-thermal method was established, coupled with the calcium recycling process of carbon capture and resource utilization of solid waste carbide slag. The coupled process enriches CO₂ for subsequent use, and at the same time reuses carbide slag for the production of calcium carbide. Furthermore, in order to establish a better process route, the material conversion, energy and exergy analysis were carried out to calculate and evaluate the material consumption, energy consumption and economy of the whole process.

2. SYSTEM DESCRIPTION AND ASSUMPTION

Fig. 1 illustrates the schematic diagram of the proposed coal to calcium carbide-acetylene system for partial coal steam gasification, which consists of the four main submodules including gasifier, coupling module of recarbonization furnace and calciner, carbide furnace and acetylene furnace. The entire system focuses on the efficient, clean, and high-value conversion of coal. The detailed working principle of this system can be summarized as follows. Part of the coal (point 1) enters the gasifier through the preheater and water (point 26) through heat exchange as a steam gasification agent (point 27) to cause coal gasification reaction. The gasification gas (point 28) and a small amount of preheated quicklime CaO (point 3) enter the recarbonization furnace. The CO₂ in the gasification gas is absorbed by calcium and converted into CaCO₃, and then the gasification gas with high heating value (mainly CO, H₂, point 6) is separated and sent to the calcium carbide furnace. The CaCO₃ (point 7) is decomposed into CaO and CO₂ in the calciner, and CaO (point 9) is separated from the gas (point 10) by a separator. A part of CaO (point 11) is then fed into the calcium carbide furnace for standby through the separator, and the rest (point 29) is returned to the recarbonization furnace for recycling. The gas (point 10) is separated by the separator to CO₂ (point 23) and high-temperature steam (point 22). The steam is used as the raw material (point 24) of the acetylene reactor after heat exchange. Coal (point 12) and quicklime CaO (point 11) undergo calcium carbide formation reaction under the action of highcalorific value gas (point 6), and the generated calcium carbide (point 18) is sent to the acetylene reactor, and the remaining products (point 15) are separated by the separator to separate the tail gas (point 16) and byproducts (point 17) such as CaCO₃ and Ca(OH)₂. The product in the acetylene generator is separated from the acetylene (point 20) and carbide slag (point 21) through

a separator, and the carbide slag (point 21) and the byproducts (CaCO₃ and Ca(OH)₂, point 17) of the calcium carbide furnace are sent to the calciner to continue hightemperature calcination, then the generated CaO is used for calcium recycling.





3. MODEL DESIGN

3.1 Model comparison

Here the traditional oxy-thermal calcium carbide process adopted by the team of Beijing University of chemical technology and the process proposed in this paper were compared. We have established three process cases, and the process diagram is shown in Fig. 2. Case 1 is the oxy-thermal process adopted by the team of Beijing University of chemical technology[9], Case 3 is the process proposed in this paper (Fig. 1), and the process flow of Case 2 is exactly the same as that of Case 3, except that the gasification agent of the two coal pyrolysis modules is different (Case 2 is oxygen and water vapor, and Case 3 is water vapor).



Fig. 2. Schematic diagram of three cases of coal-based calcium carbide acetylene process

3.2 Material conversion and energy utilization

Some basic evaluation indicators to preliminarily reveals the material conversion and energy consumption characteristics of the system are established. The carbide furnace effective atomic yields, the CO_2 capture rate of the recarbonization module, the CO_2 emissions, carbon consumption and energy consumption per unit of C_2H_2 product are respectively expressed as Eqs. (1) to (5).

$$Y = \sum_{i} \left(m_{p,i}^{c} + m_{p,i}^{H} + m_{p,i}^{Ca} \right) / \sum_{j} \left(m_{m,j}^{c} + m_{m,j}^{H} + m_{m,j}^{Ca} \right)$$
(1)

$$Y_{CO_2 \text{ capture}} = \frac{m_{frac,in} - m_{frac,out}}{m_{frac,in}}$$
(2)

$$Y_{\underline{CO_2emission}\atop C_2H_2} = \frac{m_{CO_2,tot}}{m_{C_2H_2,tot}}$$
(3)

$$Y_{\underline{C\ consumption}}_{\underline{C_2H_2}} = \frac{m_{Coal,tot}}{m_{C_2H_2,tot}}$$
(4)

$$Y_{\underline{energy}}_{\underline{C_2H_2}} = \frac{\sum m_{in}h_{in} - \sum m_{out}h_{out}}{m_{C_2H_2,tot}}$$
(5)

where $m_{m,j}^{C}$, $m_{m,j}^{H}$, $m_{m,j}^{Ca}$ are the masses of C, H, Ca elements in raw material *j*, and $m_{p,i}^{C}$, $m_{p,i}^{H}$, $m_{p,i}^{Ca}$ are the masses of C, H, Ca elements in the target product *i*, respectively. $m_{frac,in}$ is the mass of CO₂ entering the recarbonization module, $m_{frac,out}$ is the mass of CO₂ flowing out of the recarbonization module. $m_{CO_2,tot}$ is the mass of CO₂ emitted by the entire system, $m_{Coal,tot}$ is the mass of coal consumed by the entire system, $m_{C_2H_2,tot}$ is the mass of the final target product C₂H₂ of the system, m_{in} , m_{out} , h_{in} , h_{out} is the mass and mass enthalpy of the system input and output logistics respectively.

3.3 Exergy modeling

The usefulness of energy depends entirely on the convertibility of this energy form. In order to evaluate the energy utilization efficiency, the exergy or effective energy is used in this paper. That is, exergy can be used to characterize the quality or grade of energy[10,11]. Relative to the complete equilibrium state, the exergy possessed by the system is the sum of physical exergy ($\dot{E}_{x,ph}$) and chemical exergy ($\dot{E}_{x,ch}$), which are the expressions (6-8):

$$\dot{E}_x = \dot{E}_{x,ph} + \dot{E}_{x,ch}_k \tag{6}$$

$$\dot{E}_{x,ch} = \sum_{i=1} \phi_i x_i e_{x_i}^{ch} + RT_0 \sum_{i=1} \phi_i x_i ln x_i$$
(7)

$$\dot{E}_{x,ph} = \sum_{i=1}^{\kappa} [\phi_i (h_i - h_0) - \phi_i T_0 (s_i - s_0)]$$
(8)

where $e_{x_i}^{ch}$ is the standard chemical exergy of composition *i*, h_i and s_i are the specific enthalpy and specific entropy of composition *i*, h_0 and s_0 are the specific enthalpy and specific entropy of composition *i* in the environmental state, respectively. ϕ_i is mole flux and x_i is mole fraction.

The exergy destruction $(\dot{E}_{x_{D,k}})$ within the component during the operation is calculated at the component level, which is the difference between exergy of fuel $(\dot{E}_{x_{F,k}})$ and exergy of product $(\dot{E}_{x_{P,k}})$, as described by Eq. (10).

$$\dot{E}_{x_{D,k}} = \dot{E}_{x_{F,k}} - \dot{E}_{x_{P,k}} \tag{10}$$

The exergy destruction ratio y_k and relative exergy destruction ratio y_k^* of each component are defined by Eqs. (11) and (12)[12].

$$y_k = \frac{E_{x_{D,k}}}{\dot{E}_{x_{F,k}}} \tag{11}$$

$$y_{k}^{*} = \frac{E_{x_{D,k}}}{\sum \dot{E}_{x_{D,k}}}$$
(12)

The exergy efficiency for k-th component can be expressed by Eq. (13).

$$\eta_{ex,k} = \frac{\dot{E}_{x_{P,k}}}{\dot{E}_{x_{F,k}}} = 1 - \frac{\dot{E}_{x_{D,k}}}{\dot{E}_{x_{F,k}}}$$
(13)

4. RESULTS AND DISCUSSION

4.1 Material conversion and energy utilization

Table 1 shows that Case 3 has the highest effective atom conversion rate of C, H, and Ca for the calcium carbide furnace module, which is 85.41%. Because there are combined recarbonization and calcination coupled calcium recycling processes in Case 2 and Case 3 systems, these two systems can capture part of the CO₂ generated upstream in this module, and the capture rate is above 90%. Secondly, the CO₂ emission per unit acetylene product of Case 3 is 2.81t, which is 1.25 times that of Case 1 and 1.36 times that of Case 2. However, due to the characteristics of the coupled calcium cycle process of Case 2 and Case 3, the CO₂-enriched gas stream is generated, which we will store for further use to create economic benefits rather than as emission gas, and this is also our next research work. In particular, one of the key problems that the current oxy-thermal calcium carbide process fails to be industrialized is that the C consumption is too high. Table 1 indicates that the C consumption per unit product of Case 3 is the lowest at 2.02 t, while the C consumption of Case 1 is much greater than that of Case 2 and Case 3, and the C consumption of Case 1 is 2.69 times that of Case 3.

Table 1 Comparison of material conversion and energy	1
utilization index values in three cases.	

Index	Case 1	Case 2	Case 3
$Y_{C H Ca}$	64.51%	81.75%	85.41%
Y _{CO2} capture	—	92.62%	90.35%
YCOpemission		2.06	2.81
$\frac{C_2 C_2 H_2}{C_2 H_2}$	2.25	(CO ₂ -enriched	(CO ₂ -enriched
/tCO ₂ ·t ⁻¹ C ₂ H ₂		gas)	gas)
$\frac{Y_{\underline{C} \ consumption}}{C_2 H_2}$ / t Coal·t ⁻¹ C ₂ H ₂	5.43	2.55	2.02
$\frac{Y_{energy}}{C_2H_2}$ / MJ·t ⁻¹ C ₂ H ₂	22060.83	32529.91	29672.93

4.2 Exergy analysis

For the aforementioned process system 3, the thermodynamic properties and composition of each stream calculated by ASPEN can calculate the exergy performance of each component of the system, including exergy efficiency, exergy loss and relative exergy loss rate. The results of several important components of the system are summarized in Table 2.

It can be seen that the overall exergy flow destruction of the proposed system is 129268.72 kW. The exergy efficiency is calculated to be 43.21%. The exergy destructions of the gasifier, recarbonization furnace, carbide furnace, and acetylene reactor are 12605.95 kW, 9650 kW, 63216.01 kW, and 20131.93 kW, which account for 9.75%, 7.47%, 48.90%, and 15.57% of the total exergy destruction, respectively. Because these components are the key energy-consuming modules in the system, their exergy destructions account for the main part of the total exergy loss, accounting for 81.69%.

Та

As shown in Table 2, the exergy destruction of the carbide furnace is 12605.95 kW, which is 5.01 times and 3.14 times that of the gasifier and acetylene reactor, respectively. This is mainly because the operating temperature of the carbide furnace (2000 °C) is far outweigh the gasifier (700 °C) and acetylene reactor (40 °C), from which the large heat loss occurs in the carbide furnace. Therefore, it could be concluded that the carbide furnace has a small contribution to the efficient energy utilization but exhibits a large exergy destruction in the system.

For the heat exchange device, the relative exergy destructions of Heater 3 and Cooler are relatively large, which are 2.49% and 3.05%. That is mainly because of the extremely large temperature difference between the inlet and the outlet fluids. For example, the inlet and outlet temperatures of Heater 3 are 25 $^{\circ}$ C and 2000 $^{\circ}$ C, respectively, with a temperature difference up to 1975 $^{\circ}$ C. Similarly, the temperature difference of Cooler reaches 1887 $^{\circ}$ C.



Fig. 3. Sankey diagram to show the exergy flow through the proposed system (Case 3).

In addition, Fig. 3 is the exergy flow diagram of the aforementioned proposed system (Case 3). Through this Sankey diagram, the fuel and product exergy of each component and the corresponding exergy loss can be

Tuble 2 The exergy results of the proposed coupling system (ease 5).						
Component	$\dot{E}_{x_{F,k}}$	$\dot{E}_{x_{P,k}}$	$\dot{E}_{x_{D,k}}$	η_k (%)	y _k (%)	<i>y</i> [*] _k (%)
	(kW)	(kW)	(kW)			
Component level results						
Gasifier	31321.22	18715.27	12605.95	59.75	40.25	9.75
Recarbonization furnace	26693.66	17043.66	9650	63.85	36.15	7.47
Calciner	20954.58	19291.84	1662.74	92.07	7.93	1.29
Carbide furnace	116740.55	53524.54	63216.01	45.85	54.15	48.90
Acetylene reactor	56494.3	36362.37	20131.93	64.36	35.64	15.57
Heater 3	13603.3	10388.52	3214.78	76.37	23.63	2.49
Cooler	11515.9	7569.36	3946.54	65.73	34.27	3.05
System level results						
	227624.72	98356	129268.72	43.21		

ble 2	The exergy	results of the	proposed	coupling system	(Case 3).
				1 0 /	· /

obtained intuitively. For example, the exergy of fuel flows into gasifier is No. 2 and 27 streams, which is 31321 kW in total. The corresponding exergy of product is No. 28 stream, which is 18715 kW. As a result, the exergy destruction of the gasifier is calculated to be 12606 kW. In the same way, the exergy flow diagrams of Case 1 and Case 2 processes were calculated and plotted, and the exergy efficiencies were 49.37% and 37.43%, respectively. Thus the Case 3 was considered to be a relatively superior process with higher atomic yield and CO_2 capture rate, as well as lower C consumption and CO_2 emissions as described earlier. Therefore, the Case 3 process was finally chosen as the follow-up research system.

5. CONCLUSIONS

In this paper, a novel carbon-calcium compound conversion system of calcium carbide-acetylene production coupled with the carbon capture and calcium carbide waste slag reuse process was proposed. Then, the material conversion, energy utilization, exergy analyses are conducted to comprehensively compare the proposed system with the traditional process. The results show that, compared with the traditional calcium carbide-acetylene production system (Case 1), the proposed novel carbon-calcium compound conversion processes (Case 2 and Case 3) can capture the upstream CO₂ and utilize the downstream carbide waste slag, and the CO_2 capture efficiency reach up to 92.62% and 90.35%, respectively. The proposed process Case 3 has the largest effective atom yield of carbon, hydrogen, and calcium, which is 85.41%. It is worth noting that the unit product carbon consumption of Case 3 is 2.02 t Coal· t⁻¹ C_2H_2 , which is only 0.37 times that of the traditional process Case 1. The exergy efficiencies of three cases are 49.37%, 37.43% and 43.21%, respectively. Although the exergy efficiency of Case 3 is slightly lower than Case 1, Case 3 is considered to be a feasible process because of its novel coupling module of carbon capture and waste slag reuse and its comprehensive better performance with its higher atomic yield and CO₂ capture rate, as well as lower C consumption and CO₂ emissions. Therefore, the Case 3 proposed in this paper is a more feasible, efficient, and conducive to carbon emission reduction calcium carbide-acetylene production system.

ACKNOWLEDGEMENT

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

REFERENCE

[1] R. Diercks, J.-D. Arndt, S. Freyer, R. Geier, O. Machhammer, J. Schwartze, M. Volland, Raw Material Changes in the Chemical Industry, Chemical Engineering & Technology 2008;31:631-637.

[2] D. Shi, K. Qiao, Z. Yan, Effect of potassium carbonate on catalytic synthesis of calcium carbide at moderate temperature, Frontiers of Chemical Science Engineering 2011;5:372-375.

[3] H.L. Huo, X.L. Liu, Z. Wen et al. Case study of a novel low rank coal to calcium carbide process based on techno-economic assessment, Energy 2021;228:120566.
[4] Y. Mi, D. Zheng, J. Guo, X. Chen, P. Jin, Assessment of energy use and carbon footprint for low-rank coal-based oxygen-thermal and electro-thermal calcium carbide manufacturing processes, Fuel Processing Technology 2014;119:305-315.

[5] R.X. Wang, L.M. Ji, Q.Y. Liu, D.X. Zheng, H. Liu, Z.Y. Liu, Development of auto-thermal production of calcium carbide, CIESC Journal 2014;2417-2425.

[6] X.Z. Gong, J.Q. Zhang, Z. Wang, D. Wang, J.H. Liu, X.D. Jing, G.Y. Qian, C. Wang, Development of calcium coke for CaC₂ production using calcium carbide slag and coking coal, International Journal of Minerals, Metallurgy and Materials 2021;28:76-87.

[7] Y. Mi, D. Zheng, X. Jiang, Multi-product carbon footprint assessment for low-rank coal-based acetylene manufacturing process, Journal of Cleaner Production 2016;112:1676-1682.

[8] A. Perejon, L.M. Romeo, Y. Lara, P. Lisbona, A. Martinez, J.M. Valverde, The Calcium-Looping technology for CO_2 capture: On the important roles of energy integration and sorbent behavior, Applied Energy 2016;162: 787-807.

[9] C. Ge. Investigation and engineering design of oxythermal calcium carbide poly-generation system. Beijing University of Chemical Technology, 2017.

[10] X. Feng, Principle and technology of chemical energy saving [In Chinese]. Chemical Industry Press; 2015, p. 29-62.

[11] Z. Wu, P. Zhu, J. Yao, S. Zhang, Z. Zhang, Combined biomass gasification, SOFC, IC engine, and waste heat recovery system for power and heat generation: Energy, exergy, exergoeconomic, environmental (4E) evaluations, Applied Energy 2020;279,115794.

[12] Y.D. Lee, K.Y. Ahn, T. Morosuk, G. Tsatsaronis, Exergetic and exergoeconomic evaluation of an SOFC-Engine hybrid power generation system. Energy 2018; 145:810-822.