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RESEARCH ARTICLE

Life cycle assessment and economic analysis of HFC-134a production from natural gas compared with oil-based and coal-based production

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Abstract China is the largest producer and consumer of HFC-134a (1,1,1,2-tetrafluoroethane) in the world. Coal-based route is mainly adopted to produce HFC-134a, which suffers from large waste and CO_2 emissions. Natural gas is a low-carbon and clean energy resource, and no research has been found on the environment and economy of producing HFC-134a from natural gas. In this study, CML 2001 method was used to carry out the life cycle assessment of natural gas (partial oxidation)-based and natural gas (plasma cracking)-based routes (abbreviated as gas(O)-based and gas(P)-based routes, respectively), and their environmental performances were compared with coal-based and oil-based routes. Meanwhile, considering that China is vigorously promoting the transformation of energy structure, and the application of electric heating equipment to replace fossil-based heating equipment in industrial field, which has a great impact on the environmental performance of the production processes, the authors conducted a scenario analysis. The results showed that the gas(O)-based route had the most favourable environmental benefits. However, the gas(P)-based route had the highest potential for reducing environmental burdens, and its environmental benefit was the most favourable in scenario 2050. Additionally, the economic performance of the gas(P)-based route was significantly better than that of gas(O)-based and coal-based routes.

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1 Introduction

HFC-134a (1,1,1,2-tetrafluoroethane), an environment-friendly refrigerant with zero ozone depletion potential and high safety, is widely used in automobile air conditioners [1,2]. At present, China is the largest producer and consumer of HFC-134a in the world. In 2018, HFC-134a’s production capacity was approximately 250 kilotons, and increased to 345 kilotons in 2020. In addition to being applied in automobile air conditioners, the consumption of HFC-134a in other fields (aerosols, industrial refrigeration equipment, and mixed refrigerants) continues to grow in China, and accounts for 55% of the total consumption in 2020 [3].

The main production processes of HFC-134a include natural gas-based route, coal-based route, and oil-based route, as shown in Fig. 1. The oil-based route is mainly used in non-Chinese countries, while the coal-based route is basically adopted in China due to its abundant coal resources. However, coal-based route suffers from various drawbacks, such as the production of large waste and CO_2 emissions. China has clearly proposed to peak CO_2 emissions by 2030 and strives to achieve carbon neutrality by 2060, which makes the environmental constraints more stringent, and the use of coal is limited. Therefore, the research on coal substitution has become

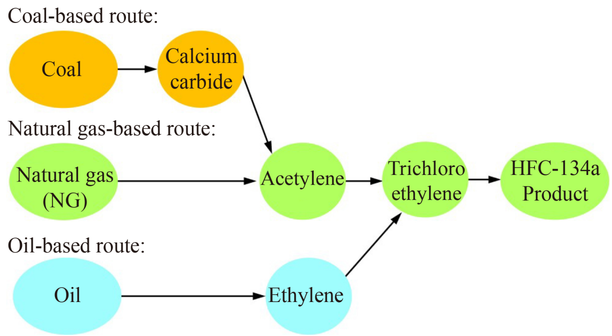

Fig. 1 HFC-134a production routes.

very important. Natural gas is an important low-carbon and clean energy resource. China is rich in unconventional natural gas resources such as shale gas, coalbed methane and tight sandstone gas, and ranks second in the world in total recoverable resources that account for 14% of the global total [4]. While China's acetylene produced from natural gas is mainly used to produce 1,4-butanediol, vinyl chloride, and vinyl acetate, and is not used to produce trichloroethylene. Therefore, it is necessary and important for HFC-134a industry to conduct the environmental and economic research on producing HFC-134a through natural gas-based route.

Natural gas-based route includes natural gas (partial oxidation)-based and natural gas (plasma cracking)-based routes in China, which are abbreviated as gas(O)-based and gas(P)-based routes, respectively. The main difference between these two processes lies in the acetylene production process the partial oxidation of natural gas and the natural gas plasma cracking [5]. The former uses a large amount of heat generated by partial combustion of natural gas to heat another part of natural gas to above 1230 °C and crack it into acetylene, hydrogen, carbon monoxide, etc. It is the main technology for producing acetylene from natural gas in China, and is quite mature. The latter is a novel Chinese technology, and is based on the principle that natural gas is cracked in a plasma reactor to generate high-temperature cracking gas containing acetylene. Although it has not been fully commercialized in China [6], it has obvious advantages, such as the natural gas consumption is only one third that of the partial oxidation method, and the investment is lower than that of the partial oxidation method.

Great research efforts have been placed on the physical characteristics of HFC-134a, as well as the performance and global warming effect of HFC-134a air conditioning systems [7,8]. Regarding the environmental aspects of the HFC-134a production process, our previous work [9] used a life cycle assessment (LCA) method to quantify the environmental burdens of HFC-134a production using coal-based route and identify ways to improve its environmental benefits. Besides, to the best of our knowledge, no other study has systematically evaluated the environmental and economic performance of the production of HFC-134a using natural gas from a life cycle perspective.

In this study, the LCA of HFC-134a production by gas(O)-based and gas(P)-based routes was carried out using CML 2001 method. Moreover, a comparative study was carried out with the oil-based and coal-based routes. At the same time, the impacts of China's energy transition on their environmental performance were considered. Finally, the production cost was used to evaluate their economic performance. The purpose of this study was to comprehensively evaluate the production process of HFC-134a, fill the gaps in the life cycle inventory (LCI) database of HFC-134a production in China, and provide the basis for future development of China's HFC-134a industry.

2 Methodology

2.1 LCA method

The LCA study is carried out based on the ISO 14040 series of standards [10,11], and consists of four main steps, namely goal and scope definition, LCI analysis, life cycle impact assessment (LCIA), and life cycle interpretation.

2.1.1 Goal and scope definition

This study aims to evaluate the environmental impact of HFC-134a production by different routes, systematically analyze their resources and energy consumptions, and waste emissions, and recognize the production route that has the least impact on the environment. One ton HFC-134a was selected as the functional unit. The system boundary was determined using the "cradle to gate" method.

(1) Scope of the gas(O)-based and gas(P)-based routes. Figure 2 shows the system boundaries of the gas(O)-based and gas(P)-based routes, including the stages of acetylene production using the partial oxidation method (or plasma method), trichloroethylene production from acetylene, and HFC-134a production.

In the gas(O)-based route, natural gas reacted with oxygen, and was cracked to high-temperature cracking gas (1400 °C). The high-temperature cracking gas was quenched with water to about 80 °C, and purified with absorbent *N*-methylpyrrolidone (NMP) to obtain acetylene and syngas. Then, acetylene was used as the raw material for producing trichloroethylene, which reacted with chlorine to produce tetrachloroethane. Hydrogen chloride was removed from tetrachloroethane to obtain trichloroethylene, and the by-products of tetrachloroethylene and 30% hydrochloric acid were obtained. Trichloroethylene was the main raw material for producing HFC-134a. It reacted with anhydrous hydrofluoric acid in the first reactor to produce HCFC-

133a (CF_3CH_2Cl). Then, the materials entered the second reactor, where HCFC-133a reacted with anhydrous hydrofluoric acid to produce HFC-134a. Finally, the mixture containing HFC-134a was separated and purified to obtain HFC-134a, as well as the by-products of HFC-143a and 31% hydrochloric acid.

In the gas(P)-based route, natural gas was directly cracked into high-temperature cracking gas in the plasma reactor. After being quenched by water, it was purified with NMP to obtain acetylene and H_2. Acetylene was used as raw material for the production of trichloroethylene, as in the gas(O)-based route.

(2) Scope of the oil-based route. Figure 3 shows the system boundary of the oil-based route, involved in the productions of ethylene, trichloroethylene and HFC-134a. Ethylene and chlorine were catalyzed to form 1,2-dichloroethane, which was further chlorinated at 280–450 °C to produce trichloroethylene, tetrachloroethylene, and hydrogen chloride. After hydrogen chloride was separated from the system, the crude trichloroethylene was subjected to the steps of rectification, alkali washing and dehydration to obtain trichloroethylene. Similarly, trichloroethylene was used for HFC-134a production.

(3) Scope of the coal-based route. Figure 4 shows the system boundary of the coal-based route, including the stages for the productions of calcium carbide, trichloroethylene and HFC-134a. First, calcium carbide was prepared by the reaction of lime and coke in the closed calcium carbide furnace at 2000–2200 °C. Meanwhile, vast quantities of furnace gas were also generated, which were sent to the lime kiln for calcining limestone after dry purification treatment. Then, calcium carbide reacted exothermally with water to produce acetylene, during which the reactor temperature was controlled at about 85 °C. After purification and cooling, acetylene was chlorinated to generate tetrachloroethane. Then, dehydrochloride was used to produce trichloroethylene. Trichloroethylene was used as raw material for HFC-134a production, similar to that in the gas(O)-based route.

2.1.2 LCI analysis

The LCI of the gas(O)-based, gas(P)-based, oil-based and coal-based routes are presented in Tables 1–4 [9,12–17].

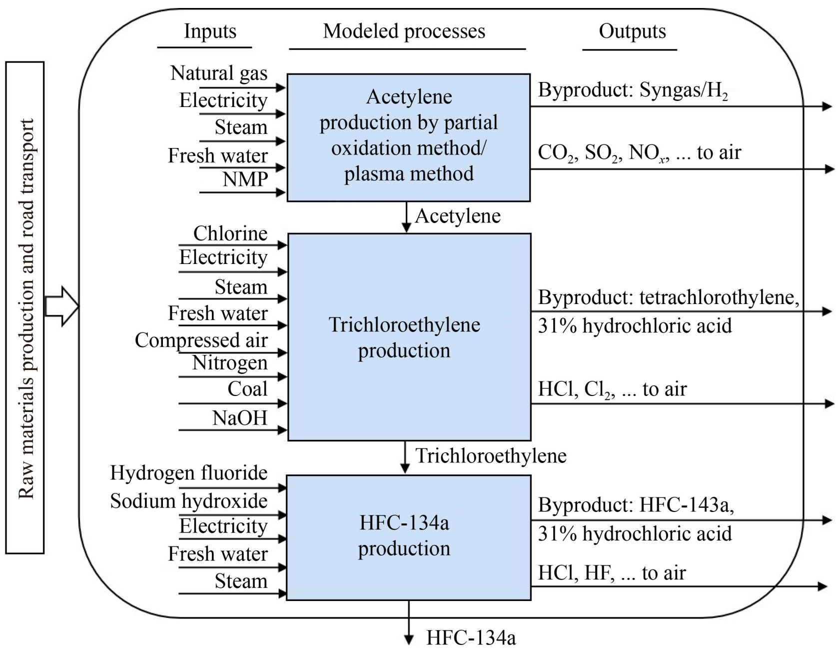

Fig. 2 System boundaries of the gas(O)-based and gas(P)-based routes.

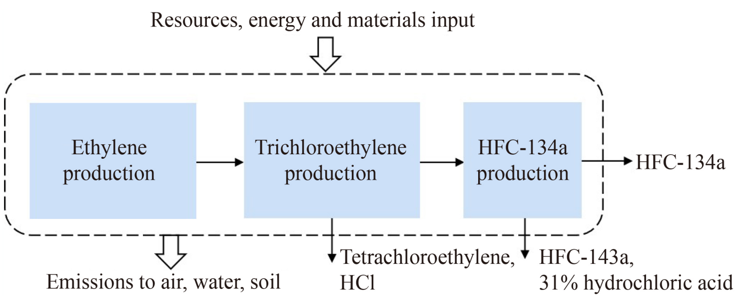

Fig. 3 System boundary of the oil-based route.

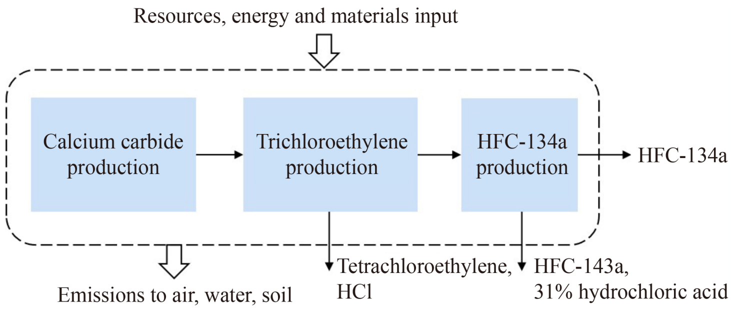

Fig. 4 System boundary of the coal-based route.

Table 1 LCI of the gas(O)-based route based upon 1 t of HFC-134a

Acetylene production stage using partial oxidation method			
Input		Output	
Substance	Value	Substance	Value
Natural gas/Nm^3	2035.91	Acetylene/t	0.35
Electricity/kWh	1169.76	Syngas/Nm^3	3103.52
Steam/t	1.60	CO_2/t	0.28
Fresh water/t	1.10	Particle matters to air/g	88.96
NMP/kg	2.66	SO_2 to air/g	22.88
		NO_x to air/g	169.12
		NMVOC[a)] to air/g	10.64
Trichloroethylene production stage from acetylene			
Input		Output	
Substance	Value	Substance	Value
Acetylene/t	0.35	Trichloroethylene/t	1.32
Chlorine/t	1.72	Tetrachloroethylene/kg	47.91
Electricity/kWh	237.78	31% hydrochloric acid/t	1.45
Steam/t	5.28	Cl_2 to air/g	133.29
Fresh water/t	9.25	HCl to air/g	28.80
Compressed air/Nm^3	29.06	NMVOC to air/g	29.24
Nitrogen/Nm^3	165.13		
Coal/kg	132.11		
NaOH/kg	2.11		
HFC-134a production stage			
Input		Output	
Substance	Value	Substance	Value
Trichloroethylene/t	1.32	HFC-134a/t	1
HF/t	0.84	31% hydrochloric acid/t	3.20
Sodium hydroxide/kg	6.06	HFC-143a/kg	4.90
Electricity/kWh	1875.20	HF to air/g	
Fresh water/t	5.19	HCl to air/g	
Steam/t	7.01	NMVOC to air/g	7.69
		Trichloroethylene to air/g	230.13

a) NMVOC: non-methane volatile organic compound

Table 2 LCI of acetylene production stage by plasma method in the gas(P)-based route based upon 1 t of HFC-134a

Input		Output	
Substance	Value	Substance	Value
Natural gas/Nm^3	709.38	Acetylene/t	0.35
Electricity/kWh	3901.57	H_2/Nm^3	886.72
Steam/t	1.42	CO_2 to air/kg	25.01
Fresh water/t	2.13	Particle matters to air/g	82.15
NMP/kg	2.48	SO_2 to air/g	25.64
		NO_x to air/g	159.72
		NMVOC to air/g	12.59

Table 3 LCI of trichloroethylene production stage from ethylene in the oil-based route based upon 1 t of HFC-134a

Input		Output	
Substance/t	Value	Substance	Value
Ethylene/t	0.4	Trichloroethylene/t	1.3
Chlorine/t	1.4	Tetrachloroethylene/kg	211.4
Steam/t	6.6	HCl/kg	184.9
Water/t	7.9	CO_2 to air/kg	169.1
Oil/kg	54.2	NO_x to air/g	53.5
Electricity/kWh	383.1	VOCs[a)] to air/g	26.8
Nitrogen/Nm^3	99.1		

a) VOCs: volatile organic compounds

Table 4 LCI of calcium carbide and trichloroethylene production stage in the coal-based route based upon 1 t of HFC-134a

Calcium carbide production stage			
Input		Output	
Substance	Value	Substance	Value
Limestone/t	1.87	Calcium carbide/t	1.19
Coke/t	0.77	Particle matters to air/g	191.10
Electrode paste/kg	29.72	SO_2 to air/g	530.96
Iron sheet/kg	2.97	NO_x to air/g	295.01
Electricity/kWh	3894.8	CO_2 to air/t	1.37
Fresh water/t	2.38		
Compressed air/Nm^3	63.60		
Nitrogen/Nm^3	53.50		
Trichloroethylene production stage from calcium carbide			
Input		Output	
Substance	Value	Substance	Value
Calcium carbide/t	1.19	Trichloroethylene/t	1.32
Chlorine/t	1.72	Tetrachloroethylene/kg	39.63
NaClO/kg	64.4	HCl (⩾ 98%)/kg	360.63
NaOH/kg	2.11	Cl_2 to air/g	133.29
Electricity/kWh	356.67	HCl to air/g	28.80
Steam/t	5.28	NMVOC to air/g	130.28
Fresh water/t	18.49	Trichloroethylene to air/g	142.67
Compressed air/Nm^3	67.37		
Nitrogen/Nm^3	126.82		
Coal/kg	132.10		
Ferric chloride/kg	0.22		

The LCI of coke, natural gas, ethylene, and the background data (such as electricity, water, steam, coal, chemicals) were all obtained from the GaBi database. The power model adopted the state grid in 2019, of which hard coal accounted for 64.8%, hydro 17.4%, wind 5.4%, nuclear 4.6%, natural gas 3.2%, photovoltaic 3.0%, biomass and other 1.6% [18]. Steam model considered coal-fired steam since coal is China's dominant energy source [19]. HFC-134a production was considered a multi-product system, and inputs and outputs were needed to be allocated to different products. According to ISO 14044 [11], physical attribute allocation was given priority, followed by economic value allocation. The allocation factors of each production route are detailed in Appendix A1.

2.1.3 LCIA methodology

According to ISO 14040 [10], LCIA can be defined as a three-step model: impact classification, characterization, and quantitative assessment. In this study, LCA models for HFC-134a production were built via GaBi software. CML 2001 [20], a widely used midpoint method, was applied for LCA evaluation. The selected impact categories included abiotic depletion potential (ADP elements), abiotic depletion potential (ADP fossil), acidification potential (AP), eutrophication potential, freshwater aquatic ecotoxicity potential (FAETP), global warming potential (GWP 100 years), human toxicity potential (HTP), ozone layer depletion potential (ODP), photochemical ozone creation potential (POCP), and terrestric ecotoxicity potential. To further understand their respective contributions to overall environmental burdens, the normalization [21] and weighted evaluation [22] were conducted. The normalized factor is the ratio of per unit of emission impact divided by the per capita global impact for the year 2000 [23], and weighted factors adopt the Thinkstep LCIA Survey 2012.

2.2 Economic assessment

The calculation of product cost (*PC*) is an important part of the economic analysis, and includes raw material cost (C_R), utility cost (C_U), operation and maintenance cost (C_{OM}), depreciation cost (C_D), plant overhead (C_O), management expenses (C_M), distribution and selling cost (C_S) and by-product cost (C_B). The PC is calculated using Eq. (1) [24,25].

$$PC = C_R + C_U + C_{OM} + C_D + C_O + C_M + C_S - C_B. \quad (1)$$

The assumptions for calculating *PC*s [26], and the market prices of major materials, utilities and by-products are summarized in Table 5. The by-products are sold at market prices. In this paper, 1 t HFC-134a product was taken as the calculation basis. A certain raw material cost or utility cost is its unit consumption multiplied by the market price. The operating labor cost is 100000 CNY per capita per year, and the number of labors is estimated based on survey data. Depreciation expenses are depreciated according to the straight-line method for 20 years, and the salvage value is set to be 4%. The remaining costs are calculated according to each scale coefficient.

3 Results and discussion

3.1 Comparison of environmental performance

3.1.1 Comparison of LCIA results

Figure 5 shows the relative contribution of each process

Table 5 Assumptions for the estimation of PC

Component	Basis
(1) Raw material	Coke 546 CNY·t^{-1}; natural gas 2.5 CNY·Nm^{-3}; ethylene 7100 CNY·t^{-1}; hydrogen fluoride 8550 CNY·t^{-1}; chlorine 550 CNY·t^{-1}
(2) Utilities	Steam 80 CNY·t^{-1}; water 1 CNY·t^{-1}; electricity 0.6 CNY·kWh^{-1}
(3) Operating & maintenance	
(3.1) Operating labor	Coal-based route 319 labors; gas(O)-based route 288 labors; gas(P)-based route 284 labors; oil-based route 211 labors; 100000 CNY·$labor^{-1}$·$year^{-1}$
(3.2) Direct supervisory & clerical labor	20% of operating labor
(3.3) Maintenance and repairs	2% of fixed capital investment
(3.4) Operating supplies	0.7% of fixed capital investment
(3.5) Laboratory charge	15% of operating labor
(4) Depreciation	Life period 20 years, salvage value 4%
(5) Plant overhead cost	60% ((3.1) + (3.2) + (3.3))
(6) Administrative cost	2% of production cost
(7) Distribution and selling cost	2% of production cost
(8) By-product	Syngas 0.56 CNY·Nm^{-3}; H_2 1.2 CNY·Nm^{-3}; perchloroethylene 3000 CNY·t^{-1}; R143a 20000 CNY·t^{-1}; 31% hydrochloric acid 280 CNY·t^{-1}; HCl 1400 CNY·t^{-1}
(9) PC	(1) + (2) + (3) + (4) + (5) + (6) + (7) – (8)

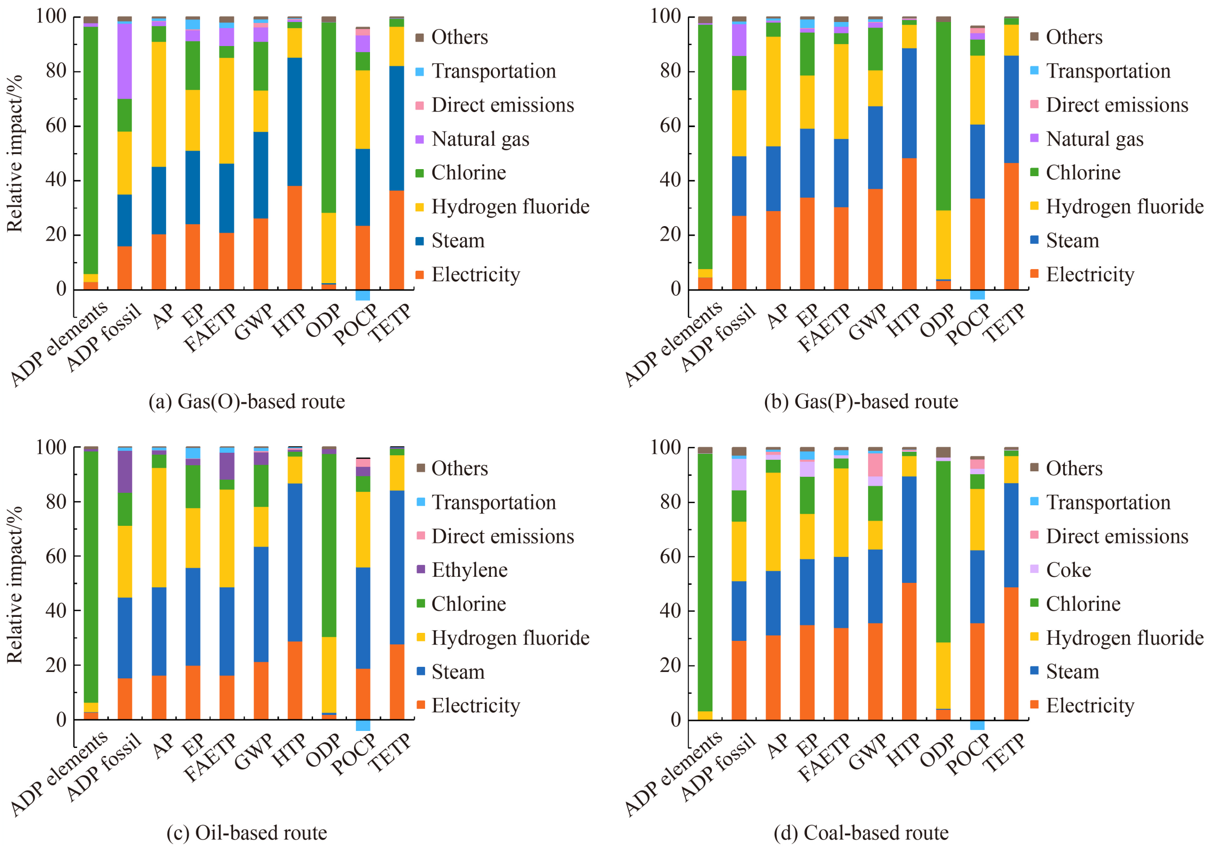

Fig. 5 Relative contribution of each process to the environment in (a) gas(O)-based, (b) gas(P)-based, (c) oil-based and (d) coal-based routes.

to the environment in the four HFC-134a production routes. ADP elements and ODP categories were mainly contributed by chlorine. In addition to these two impact categories, in the gas(O)-based, gas(P)-based and coal-based routes, the electricity had the highest contribution to the remaining impact categories, followed by steam. The oil-based route was different, with steam contributing the most to these impact categories, followed by electricity. Moreover, hydrogen fluoride had a significant impact on the AP, FAETP, ODP and POCP categories in the four production routes. The contribution of direct emissions, transportation stages, and other processes to each impact category were relatively small. Therefore, it is important to reduce the consumption of electricity, steam, and hydrogen fluoride for decreasing the environmental impacts of HFC-134a production. Since electricity generation and steam production both consume large amounts of coal, using clean energy to replace coal is also one of the important future directions for improving the enviromental benefits of HFC-134a production.

It can be seen from the normalization results (Fig. 6) that, in the four HFC-134a production routes, the contribution of each impact category to the normalized environmental performance exhibited similar variation trend. HTP category contributed the most to the normalized environmental performance, and accounted for 43%–48%, followed by ADP fossil, GWP, AP and POCP, which accounted for 17%–22%, 11%–13%, 10%–12%, and ~6%, respectively, while the remaining categories only accounted for ca.7%.

The coal-based route had the largest normalized value for each impact category, followed by the gas(P)-based route (except for ADP fossil category). Because these two routes consumed large amounts of electricity (more than 6100 kWh of electricity), which was 1.8 times that of the gas(O)-based route, and 2.7 times that of the oil-based route. For the ADP fossil category, the environmental burdens of the gas(O)-based route was second only to the coal-based route, and was approximately 6495 MJ higher than the gas(P)-based route. Since nearly 70% of natural gas was burnt to provide heat energy for the remaining natural gas cracking in the gas(O)-based route, the route consumed a lot of natural gas. For the categories of ADP elements, ADP fossil and ODP, the environmental burdens of the gas(O)-based route were slightly higher than those of the oil-based route. However, for the remaining impact categories, the environmental burdens of the gas(O)-based route were smaller than that of the oil-based route. Therefore, in order to facilitate the comparison of the environmental benefits of each HFC-134a production route, these ten impact categories were weighted to get a comprehensive index, as shown in Fig. 7. It can be seen that, under the current energy structure, the gas(O)-based route had the most favourable environmental benefits, followed by the oil-based, gas(P)-based and coal-based routes.

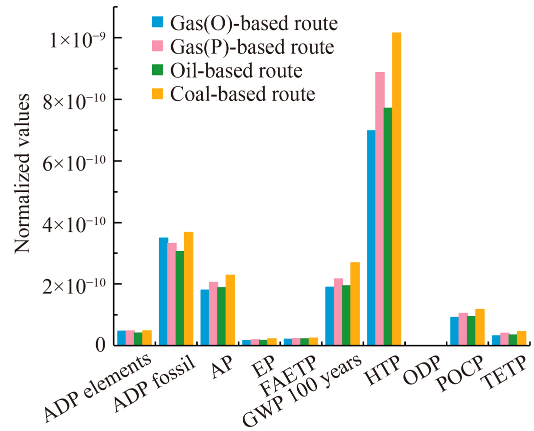

Fig. 6 Comparison of normalized results for different HFC-134a production routes.

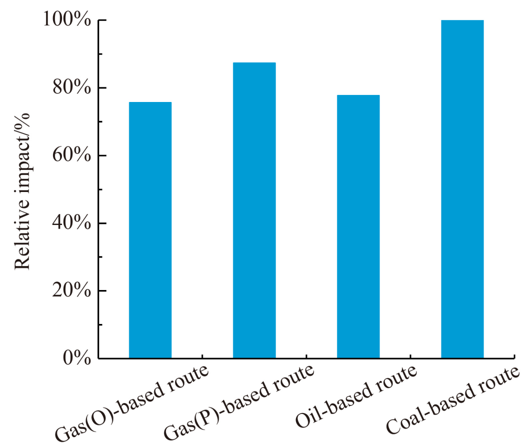

Fig. 7 Comparison of weighted results for different HFC-134a production routes.

3.1.2 Impact of China's energy transition

It can be observed from the above results that electricity and steam were the key factors impacting the environment in HFC-134a production. The large-scale utilization of fossil resources in China results in large amounts of CO_2 emissions, and serious air pollution [27]. In this regard, the 14th Five-Year Power Plan pointed out [5] that China should further advance the energy transition, and vigorously promote the application of electric heating equipment (such as electric steam generators and electric heat-conduction oil furnaces) in the industrial field to replace traditional fossil-based heating equipment, which is of great significance for achieving carbon neutrality and mitigating air pollution. Moreover, it was also predicted the installed power generation capacity and their proportion in 2025−2050 (Appendix A2). China's power generation capacity will grow rapidly in the next 30 years. The proportion of coal-based power will gradually decrease from 64.8% in 2019 to 5.7% in 2050, and the clean energy power generation will develop into China's main energy source. Therefore, according to the future power deployment in the policy, a scenarios analysis of HFC-134a production was conducted. In the basic scenario, electricity situation was assumed as that of 2019 state grid; steam was produced by coal. In other scenarios, both the electricity and the steam were generated from the state grid of the year, which were respectively recorded as scenario 2019, scenario 2025, scenario 2035, and scenario 2050.

The results in Table 6 show that, compared with the basic scenario, the fossil resource consumption of the four production routes in scenario 2019 increased by 3.8×10^4, 3.2×10^4, 3.4×10^4 and 4.3×10^4 MJ, respectively,

Table 6 Fossil resource consumption and CO_2 equivalent emissions of different HFC-134a production routes in different scenarios

Category	Scenario	Gas(O)-based route	Gas(P)-based route	Oil-based route	Coal-based route
ADP fossil/MJ	Basic scenario	1.33×10^5	1.26×10^5	1.16×10^5	1.40×10^5
	Scenario 2019	1.64×10^5	1.61×10^5	1.59×10^5	1.78×10^5
	Scenario 2025	1.55×10^5	1.43×10^5	1.43×10^5	1.60×10^5
	Scenario 2035	1.27×10^5	1.11×10^5	1.11×10^5	1.22×10^5
	Scenario 2050	1.01×10^5	8.12×10^4	8.10×10^4	8.78×10^4
GWP/kg CO_2 eq.	Basic scenario	8.00×10^3	9.12×10^3	8.21×10^3	1.13×10^4
	Scenario 2019	1.11×10^4	1.25×10^4	1.24×10^4	1.51×10^4
	Scenario 2025	1.00×10^4	1.06×10^4	1.06×10^4	1.30×10^4
	Scenario 2035	7.17×10^3	7.33×10^3	7.37×10^3	9.27×10^3
	Scenario 2050	4.62×10^3	4.42×10^3	4.44×10^3	5.90×10^3

and the CO_2 equivalent emissions increased by 3.7, 3.1, 3.4 and 4.2 t, respectively. The increase was very significant, which means that the performance of electric steam was significantly inferior to coal-fired steam in terms of fossil resource consumption and CO_2 equivalent emissions, when the electricity used in HFC-134a production was from 2019 state grid.

In scenarios 2019, 2025, 2035 and 2050, the fossil resource consumption and CO_2 equivalent emissions of the four production routes gradually decreased, indicating that the higher the proportion of clean energy power generation, the more conducive to reducing fossil resource consumption and CO_2 equivalent emissions. Starting from scenario 2035, the fossil resource consumption and CO_2 equivalent emissions of the four production routes became lower than those of the basic scenario. Especially in scenario 2050, compared with the basic scenario, the fossil resource consumption of the four production routes was reduced by 23%–38%, and the CO_2 equivalent emissions were reduced by 42%–52%. Additionally, in this scenario, the gas(P)-based route had the least carbon emissions, which were reduced by 4.7 t as compared to basic scenario. In addition, the CO_2 equivalent emissions of the coal-based route in the five scenarios were much higher than the other three production routes, which was in part due to the direct CO_2 emissions during the calcium carbide production stage that reached 1.37 t and accounted for 12.1%, 9.1%, 10.5%, 14.8% and 23.2% of the CO_2 equivalent emissions in basic scenario and scenarios 2019, 2025, 2035 and 2050, respectively.

It can be seen from Fig. 8 that the overall environmental benefits of the four production routes in basic scenario were far better than scenario 2019. In these two scenarios, electricity was both from 2019 state grid, and the difference lied in the types of steam used. Therefore, it can be inferred that the environmental benefits of electric steam were inferior to that of coal-fired steam. The reason was that coal-based power played a leading role in 2019 state grid, and the chemical energy of coal was first converted into electric energy, and then into heat energy, which lowered the energy utilization efficiency as compared to that of the direct conversion of chemical energy of coal into heat energy. With the decrease in the proportion of coal-based power, and the increase in the proportion of clean energy power generation, the environmental burdens of each production route gradually decreased. It can be seen that the overall environmental burdens of coal-based power were higher than those of the clean energy power [28–31]. By scenario 2035, the proportion of coal-based power dropped to 26.0%, whereas the overall environmental benefits of each production route were better than that of the basic scenario. In scenario 2050, the order of environmental benefits of each route were found in the following descending order: gas(P)-based route = oil-based route > gas(O)-based route > coal-based route, while the overall environmental burdens of the gas(P)-based and oil-based routes were 11.8% less than those of the coal-based route.

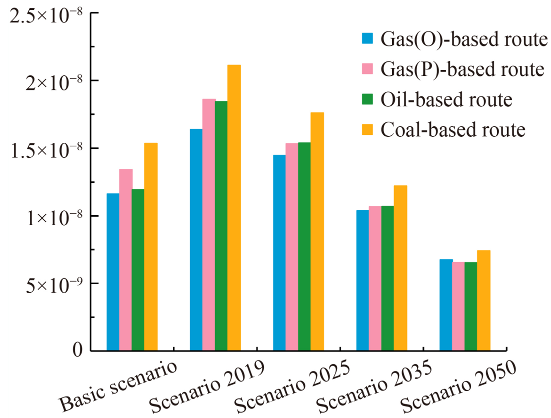

Fig. 8 Comparison of weighted results of different HFC-134a production routes in different scenarios.

In short, changes in the energy structure have a profound impact on the environmental performance of HFC-134a production. Only under the condition that the proportion of coal-based power is reduced to about 26%, the overall environmental burdens of HFC-134a production can be reduced when electric heating equipment is used to replace fossil-based heating equipment. In the process of energy transition, manufacturers should be encouraged to give priority to using green electricity to heat equipment.

3.2 Comparison of economic performance

3.2.1 PC

Acetylene was the intermediate raw material for HFC-134a production using the gas(O)-based, gas(P)-based and coal-based routes, whereas the difference in PC of the three routes mainly stemmed from the acetylene production stage. The results presented in Table 7 show that the PC of the gas(O)-based route was the highest with 17187 CNY·$t_{HFC\text{-}134a}^{-1}$. In addition, its raw material cost was significantly higher than those for the other routes, mainly because large amounts of natural gas were consumed in the partial oxidation process of natural gas, and the price of natural gas has been rising in China in recent years, thus resulting in a high natural gas raw material cost that reached 3860 CNY·$t_{HFC\text{-}134a}^{-1}$. The PC of the coal-based route was 16574 CNY·$t_{HFC\text{-}134a}^{-1}$, second to the gas(O)-based route. In this route, the raw material cost of coke and electrode paste consumed was only 538 CNY·$t_{HFC\text{-}134a}^{-1}$, which was much lower than the gas(O)-based route. Meanwhile, this route had the highest utility cost due to a great amount of electricity consumed in the calcium carbide production stage. The PC of the gas(P)-based route was 15212 CNY·$t_{HFC\text{-}134a}^{-1}$, which was 1362 CNY·$t_{HFC\text{-}134a}^{-1}$ less than the coal-based route. Furthermore, its natural gas raw material cost was 2515 CNY·$t_{HFC\text{-}134a}^{-1}$ lower than the gas(O)-based route due to the reason that its natural gas consumption was about one-third of the gas(O)-based route. Moreover, natural gas cracking via plasma required vast quantities of electricity. Therefore, its utility cost was relatively high, and second only to the coal-based route. Among all the HFC-134a production routes, the PC of the oil-based route was the lowest with 14780 CNY·$t_{HFC\text{-}134a}^{-1}$.

In addition to the main product, by-products were also produced. The economic values of by-products of the gas(O)-based and gas(P)-based routes were significantly higher than those of the other two routes, mainly because a great quantity of syngas or hydrogen were produced in the acetylene production stage.

Table 7 PC of 1 t HFC-134a produced by different routes

Item	Gas(O)-based route	Gas(P)-based route	Oil-based route	Coal-based route
C_R/CNY	12090	9605	10726	8929
C_U/CNY	2797	3647	2185	4395
C_{OM}/CNY	2066	1868	1480	2088
C_D/CNY	1370	1049	943	1160
C_O/CNY	1034	944	742	1056
C_M/CNY	344	304	296	332
C_S/CNY	344	304	296	332
C_B/CNY	–2856	–2509	–1887	–1716
PC/CNY	17187	15212	14780	16574

3.2.2 Sensitivity analysis

Sensitivity analysis is an effective method to determine the impact of various uncertain factors on the economic evaluation index of a project. A sensitivity analysis of the PC was carried out in this study, as shown in Fig. 9. It can be seen from Fig. 9(a), the most significant impact on the PC of the gas(O)-based route was the raw material cost, followed by the utility cost, and operation and maintenance cost. When the raw material cost, utility cost, and operation and maintenance cost varied by ±20%, the PC of the gas(O)-based route varied by ±14.07%, ±3.25%, and ±2.45%, respectively. Similar to the gas(O)-based route, these three types of costs had a significant impact on the PC of the other production routes, as shown in Figs. 9(b–d). The by-product cost, which was just the opposite of other types of costs, also had relatively large impact on PC. When the variation was +20%, the PCs of the gas(O)-based, gas(P)-based, oil-based and coal-based routes changed by –3.32%, –3.30%, –2.55% and –2.07%, respectively. The remaining costs had little effect on the PC of the four production routes, which varied by less than ±2%. Therefore, in order to reduce the PC, efforts should be made to reduce the raw material cost, followed by the utility cost, and operation and maintenance cost, as well as efforts to increase the value of by-products.

3.2.3 Impact of raw material prices on production cost

As mentioned in Section 3.2.2, raw material cost had the most significant impact on the economic performance of HFC-134a production compared to other types of costs. Therefore, the authors further investigated the impact of the price of important raw materials on the production cost, as shown in Fig. 10. Figure 10(a) shows that the PC of the four production routes would increase significantly with the increase in hydrogen fluoride price. When the price of hydrogen fluoride changed from 6000 to 11000 CNY·t^{-1}, the PC of the four production routes increased by 4175 CNY·$t_{HFC\text{-}134a}^{-1}$. As shown in Fig. 10(b), when the natural gas price increased from 1 to 5 CNY·m^{-3}, the PC of 1 t HFC-134a using the gas(O)-based and gas(P)-based routes increased from 14871 to 21047, and 14405 to 16557 CNY, respectively. It was clear that the impact of change in the price of natural gas on the PC of the gas(O)-based route was more significant than that of the gas(P)-based route, which mainly depended on the consumption of natural gas in the production stage of acetylene. When the price of ethylene increased to 11000 CNY·t^{-1}, the PC of the oil-based route increased to 16304 CNY·$t_{HFC\text{-}134a}^{-1}$, which was still lower than the coal-based route. Furthermore, only

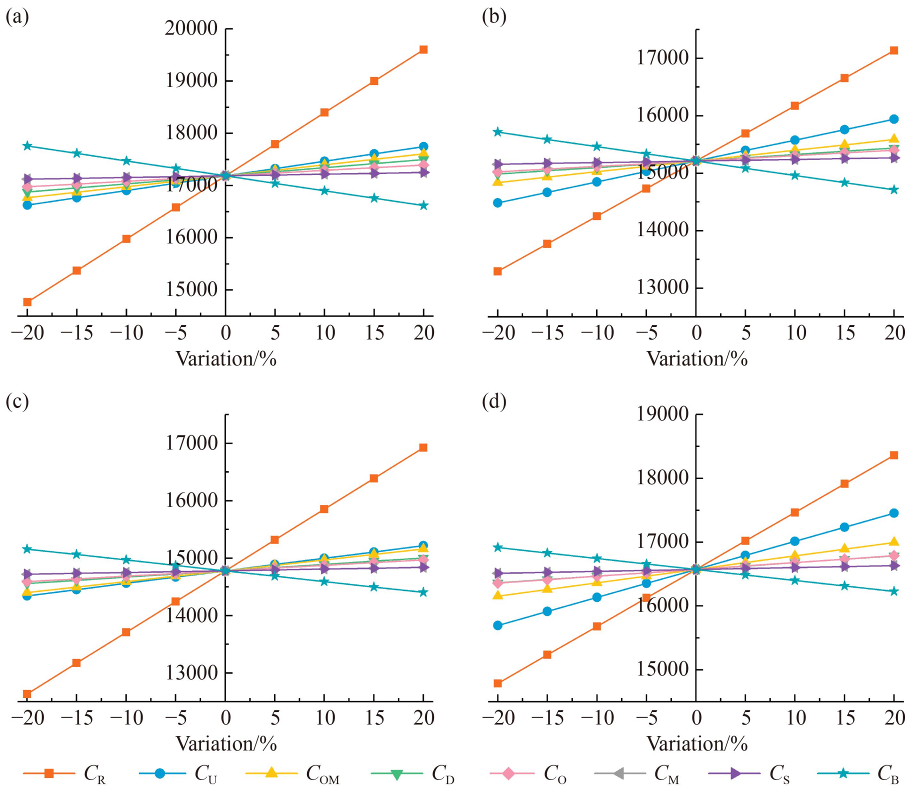

Fig. 9 Sensitivity analysis of production cost of HFC-134a produced by (a) gas(O)-based, (b) gas(P)-based, (c) oil-based and (d) coal-based routes.

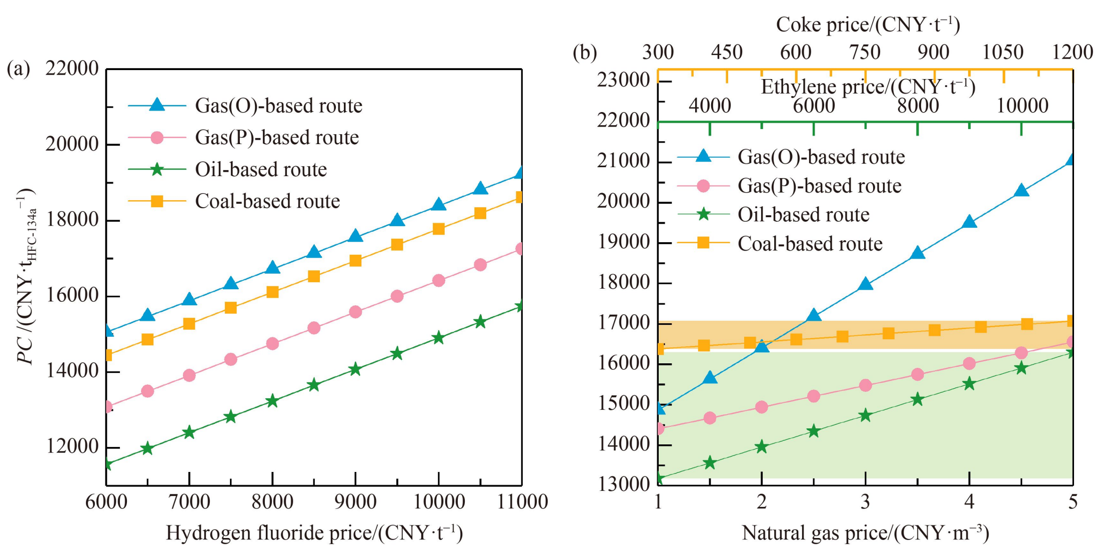

Fig. 10 Impact of different raw material prices on PCs: (a) hydrogen fluoride; (b) natural gas, ethylene and coke.

when the price of natural gas was lower than 1.93 and 4.53 CNY·m^{-3}, the PC of gas(O)-based and gas(P)-based routes was lower than the oil-based route, respectively. When the coke price fluctuated within the range of 300–1200 CNY·t^{-1}, the PC of the coal-based route changed by a maximum of 691 CNY·t$_{HFC-134a}^{-1}$, which had little impact on its PC. In addition, only when the price of natural gas was lower than 1.98 and 4.68 CNY·m^{-3}, respectively, it could be assured that the finished PC of the gas(O)-based and gas(P)-based routes were lower than the coal-based route. However, the price of natural gas in China has been increasing in recent years, and the current average price has reached 2.5 CNY·m^{-3}. It can be seen that the economic performance of the gas(P)-based route was better than that of the gas(O)-based and coal-based routes.

4 Conclusions

In this study, the environmental and economic performances of HFC-134a production using the gas(O)-based, gas(P)-based, oil-based and coal-based routes were studied. Based upon the results obtained, following conclusions are drawn.

Electricity and steam were the key factors impacting the environmental performance of the four production routes. The gas(O)-based route had the most favourable overall environmental benefits, followed by the oil-based, gas(P)-based and coal-based routes.

The environmental burdens of gas(P)-based and oil-based routes were the smallest, both being 11.8% less than the coal-based route in scenario 2050. Moreover, only under the condition that the energy structure is profoundly changed (the proportion of clean energy power generation was significantly increased), the overall environmental burdens of HFC-134a production could be reduced when electric heating equipment was used to replace the fossil-based heating equipment.

With regards to the economic performance, the PC of the gas(O)-based route was the highest with 17187 $CNY \cdot t_{HFC\text{-}134a}^{-1}$, followed by the coal-based, gas(P)-based and oil-based routes. The impact analysis of raw material price showed that the gas(P)-based route was less affected by the change of natural gas price than the gas(O)-based route, and its economic performance was better than the gas(O)-based and coal-based routes. Only when the price of natural gas was lower than 4.53 $CNY \cdot m^{-3}$, the competitiveness of gas(P)-based route was equivalent to that of the oil-based route.

HFC-134a is not only used in the automotive industry, but also has important applications in other fields. Research on the environmental and economic performance of HFC-134a production provides valuable insights for decision-makers in the face of diversified process technology choices.

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Appendix

Table A1 Allocation method and allocation factors involved in each route

Item	Acetylene production stage	Trichloroethylene production stage	HFC-134a production stage
Gas(O)-based route	Economic value allocation, acetylene 65.2%, syngas 34.8%	Mass allocation, trichloroethylene 73.3%, tetrachloroethylene 2.7%, 31% hydrochloric acid 24.0%	Economic value allocation, HFC-134a 95.1%, HFC-143a 0.5%, 31% hydrochloric acid 4.4%
Gas(P)-based route	Economic value allocation, acetylene 75.3%, H_2 24.7%		
Coal-based route	–	Mass allocation, trichloroethylene 73.8%, tetrachloroethylene 2.2%, hydrogen chloride 20.1%, high-boiling product 2.4%, low-boiling product were 1.5%	
Oil-based route	–	Mass allocation, trichloroethylene 76.6%, tetrachloroethylene 12.5%, hydrogen chloride 10.9%	

Table A2 China's different types of installed power generation capacity (TWh) and their proportion in 2025–2050[a)]

Category	2025		2035		2050	
	Power generation	Proportion	Power generation	Proportion	Power generation	Proportion
Coal	4515.5	48.9%	3045.8	26.0%	815.5	5.7%
Hydro	1483.2	16%	1915.7	16.4%	2248.4	15.7%
Wind	1019.3	11%	2413.3	20.6%	4357.8	30.5%
Nuclear	511.6	5.5%	872.3	7.4%	1228.8	8.6%
Natural gas	589.2	6.4%	605.5	5.2%	486.3	3.4%
Solar photovoltaic	853.3	9.2%	2342.5	20.0%	4305.7	30.1%
Solar thermal	30.0	0.3%	130.5	1.1%	352.9	2.5%
Biomass and others	253.9	2.7%	388.5	3.3%	503.5	3.5%
Total	9256.0	100%	11714.1	100%	14298.9	100%

a) Due to data limitations, solar thermal power generation was modeled as solar photovoltaic power generation, and biomass and others were modeled as biomass power generation.

References

1. Alam M S, Jeong J H. Thermodynamic properties and critical parameters of HFO-1123 and its binary blends with HFC-32 and HFC-134a using molecular simulations. International Journal of Refrigeration, 2019, 104: 311–320
2. Bell I H, Domanskib P A, McLindena M O, Linterisb G T. The hunt for nonflammable refrigerant blends to replace R-134a. International Journal of Refrigeration, 2019, 104: 484–495
3. CBG. China refrigerant industry analysis report 2021. China Bao Gao Website, 2021
4. Wang H, Ma F, Tong X, Liu Z, Zhang X, Wu Z, Li D, Wang B, Xie Y, Yang L. Potential and exploration direction of unconventional natural gas resources in the middle Yangtze Region. Petroleum Exploration and Development, 2016, 43(06): 850–862
5. Zhang S, Li J, Li G, Nie Y, Qiang L, Bai B, Ma X. Life cycle assessment of acetylene production from calcium carbide and methane in China. Journal of Cleaner Production, 2021, 322: 129055
6. Wang X. A strategic cooperation agreement about the largest domestic single set of natural gas plasma acetylene equipment was signed in Xinjiang. Natural Gas Chemical Industry, 2020, 45: 128 (in Chinese)
7. Maiorino A, Llopis R, Duca M, Aprea C. Environmental impact assessment of R-152a as a drop-in replacement of R-134a in a domestic refrigerator. International Journal of Refrigeration, 2020, 117: 132–139
8. Wu M, Yuan X R, Xu Y J, Qiao X G, Han X H, Chen G M. Cycle performance study of ethyl fluoride in the refrigeration system of HFC-134a. Applied Energy, 2014, 136: 1004–1009
9. Zhang S, Li J, Nie Y, Qiang L, Bai B, Peng Z, Ma X. Life cycle assessment of HFC-134a production by calcium carbide acetylene route in China. Chinese Journal of Chemical Engineering, 2022, 42: 236–244
10. ISO 14040, Environmental Management—Life Cycle Assessment—Principles and Framework. Genève: International Organization for Standardization, 2006
11. ISO 14044, Environmental Management—Life Cycle Assessment—Requirements and Guidelines. Genève: International Organization for Standardization, 2006
12. An J. Actuality and thoughts of natural gas to acetylene technology. Modern Chemical Industry, 2013, 33: 5–8 (in Chinese)
13. Bovea M D, Cabello R, Querol D. Comparative life cycle assessment of commonly used refrigerants in commercial refrigeration systems. International Journal of Life Cycle Assessment, 2007, 12(5): 299–307
14. DEEXUAR. Methanol hydrogen emergency project due to natural gas supply limit. Department of Ecology and Environment of Xinjiang Uygur Autonomous Region Website, 2019
15. McCulloch A, Lindley A A. From mine to refrigeration: a life cycle inventory analysis of the production of HFC-134a. International Journal of Refrigeration, 2003, 26(8): 865–872
16. Wang W. Production technology improvement of trichloroethylene. Dissertation for the Master's Degree. Zhejiang: Zhejiang University of Technology, 2012, 5–8 (in Chinese)
17. Xiong G, Li J, Chen X. Feasibility analysis of acetylene production via pyrolysis of natural gas in plasma at the condition of atmospheric pressure and low temperature. Polyvinyl Chloride, 2017, 45: 17−19 (in Chinese)
18. Mushtaq Z, Wei W, Jamil I, Sharif M, Chandio A A, Ahmad F. Evaluating the factors of coal consumption inefficiency in energy intensive industries of China: an epsilon-based measure model. Resources Policy, 2022, 78: 102800
19. Yang Q, Zhang J, Chu G, Zhou H, Zhang D. Optimal design, thermodynamic and economic analysis of coal to ethylene glycol processes integrated with various methane reforming technologies for CO_2 reduction. Energy Conversion and Management, 2021, 244: 114538
20. Guinée J B, Gorrée M, Heijungs R, Huppes G, Kleijn R, Wegener Sleeswijk A, Huijbregts M A J. Handbook on Life Cycle Assessment Operational Guide to the ISO Standards. New York: Springer, 2002
21. Cucurachi S, Seager T P, Prado V. Normalization in comparative life cycle assessment to support environmental decision making. Journal of Industrial Ecology, 2017, 21(2): 242–243
22. Ren J, Ren X, Liang H, Dong L, Zhang L, Luo X, Yang Y, Gao Z. Multi-actor multi-criteria sustainability assessment framework for energy and industrial systems in life cycle perspective under uncertainties. Part 1: Weighting method. International Journal of Life Cycle Assessment, 2017, 22(9): 1397–1405
23. Chen W, Geng Y, Hong J, Yang D, Ma X. Life cycle assessment of potash fertilizer production in China. Resources, Conservation and Recycling, 2018, 138: 238–245
24. Chen Q, Gu Y, Tang Z, Sun Y. Comparative environmental and economic performance of solar energy integrated methanol production systems in China. Energy Conversion and Management, 2019, 187: 63–75
25. Orfanos N, Mitzelos D, Sagani A, Dedoussis V. Life-cycle environmental performance assessment of electricity generation and transmission systems in Greece. Renewable Energy, 2019, 139: 1447–1462
26. Yang Q, Yang Q, Xu S, Zhu S, Zhang D. Technoeconomic and environmental analysis of ethylene glycol production from coal and natural gas compared with oil-based production. Journal of Cleaner Production, 2020, 273: 123120
27. Lu Y, Shao M, Zheng C, Ji H, Gao X, Wang Q. Air pollutant emissions from fossil fuel consumption in China: current status and future predictions. Atmospheric Environment, 2020, 231: 117536
28. Chang Y, Huang R, Ries R J, Masanet E. Life-cycle comparison of greenhouse gas emissions and water consumption for coal and shale gas fired power generation in China. Energy, 2015, 86: 335–343
29. Mahmud M A P, Huda N, Farjana S H, Lang C. Life-cycle impact assessment of renewable electricity generation systems in the United States. Renewable Energy, 2020, 151: 1028–1045
30. Orhan M F, Dincer I, Naterer G F. Cost analysis of a thermochemical Cu–Cl pilot plant for nuclear-based hydrogen production. International Journal of Hydrogen Energy, 2008,

33(21): 6006–6020

31. Zhao X, Cai Q, Zhang S, Luo K. The substitution of wind power for coal-fired power to realize China's CO_2 emissions reduction targets in 2020 and 2030. Energy, 2017, 120: 164–178