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Influencing Factors of Carbon Emission from Typical Refining Units: Identification, Analysis, and Mitigation Potential

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Abstract: As the global third-largest stationary source of carbon emissions, petroleum refineries have attracted much attention. Many investigations and methodologies have been used for the quantification of carbon emissions of refineries at the industry or enterprise scale. The granularity of current carbon emissions data impairs the reliability of precise mitigation, so analysis and identification of influencing factors for carbon emissions at a more micro-level, such as unit level, is essential. In this paper, four typical units, including fluid catalytic cracking, Continuous Catalytic Reforming, delayed coking, and hydrogen production, were chosen as objects. A typical 5-million-ton scale Chinese petroleum refinery was selected as an investigating object. The Redundancy analysis and multiple regression analysis were utilized to explore the relationship between the process parameters and carbon emissions. Three types of influencing factors include reaction conditions, processing scale, and materials property. The most important mitigation of carbon emission, in this case, can be summarized as measures of improving energy efficiency via optimizing equipment parameters or prompting mass efficiency by upgrading the scale for material and energy flow.

Keywords: a petroleum refinery; process unit scale; carbon emission; influence factors; pathway of mitigation

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1. Introduction

Greenhouse gases (GHGs) mainly include CO_2, CH_4, N_2O, hydrofluorocarbons, perfluorocarbons, sulfur hexafluoride, and nitrogen trifluoride [1]). GHG emissions cause changes in net radiation flux in the troposphere or atmosphere, which can lead to climate change. The production and use of fossil fuels mainly contribute to global GHG emissions [2]. As the third-largest stationary source, the cumulative GHG emissions from global petroleum refineries from 2000 to 2021 are approximately 3.41 billion tons, with an average annual growth rate of 0.7% [3]. Carbon dioxide (CO_2) and methane (CH_4) are the primary species emitted by refineries [4]. At present, many investigations and methodologies have been used to explore carbon emissions from refineries at the industry or enterprise scale. The current granularity of carbon emissions data impairs the reliability of precise mitigation, so analysis and identification of influencing factors for carbon emissions at a more micro-level, such as unit level, is an urgent task for effective carbon reduction.

Different process units in a petroleum refinery show various intensities and patterns of carbon emission [5]. The main process units include a crude distillate unit and vacuum distillate unit (CD and VD), fluid catalytic cracking unit (FCC), catalytic reforming unit (CR), hydrocracking unit (HC), hydrofining unit (HF), solvent deasphalting unit (SD), and delayed coking unit (DC). According to Jia et al. [6], FCC, DC, HC, and hydrotreatment (HT) are the main carbon emission sources. FCC is the most important unit for increasing the processing depth of crude oil in petroleum refining enterprises, accounting for 24.3% of the total emissions in a refinery. According toAl-Salem [7], the burn of catalyst coke in the regenerator's stack within FCC can produce 40% of the total CO_2 in a refinery. Steam methane reforming (SMR) is the most widely used process to produce hydrogen. About 20% of the total CO_2 emission could be attributed to hydrogen production (HP) units. Stockle et al. [8] raised that a ton of hydrogen produced via SMR produced about 10 tons of CO_2. DC is an important way for the thermal treatment of heavy oil. Large amounts of energy are consumed to provide reaction heat for the coking process, resulting in high carbon emissions [9]. As for CR units, a lot of heaters should be used to maintain the reaction due to the endothermic property of the reforming reaction [4].

In the research on influencing factors of carbon emission, the factorial decomposition method is one of the more widely used methods [10]. It mainly consists of structural decomposition analysis (SDA) and index decomposition analysis (IDA) [11]. Compared to the SDA method, which needs to be established on the basis of input–output models, the IDA method has been more widely used due to its characteristics of easier data acquisition and easy operation [12]. However, the exponential decomposition method also has certain drawbacks, such as being represented as a product of several factor indicators by the explanatory variable while ignoring the dependence between the multiplied factors. Moreover, the influencing factors that are artificially selected to enter the model are subjective. SDA or IDA can be carried out at the international level, national level, and sectoral levels but rarely at the enterprise and process level [13]. Therefore, more suitable methods are needed for identifying influencing factors of carbon emission at the micro level.

Based on various carbon emission characteristics, Li et al. [14] divided the abatement technologies of CO_2 in the petroleum refining industry into the following six categories: (1) Waste-heat recovery and over-bottom pressure recovery technology. (2) New materials technology. (3) Process optimization technology. (4) Intelligent system scheduling optimization technology. (5) Circulating water system energy-saving technology. (6) New equipment technology. For example, Liu et al. [15] suggested that upgrading process heaters has been a priority in recent years, but heat recovery and advanced process control systems will gradually begin to dominate the technological marketplace in the long term. The use of renewable energy to produce renewable hydrogen via electrolysis for HT unit, which replaces the steam methane reform, and to provide oxygen for oxy-combustion or capture CO_2 in FCC units can mitigate up to 22.11% of the GHG emissions in the petroleum refineries [16]. The carbon-based methods emit large quantities of CO_2, which motivates the need to develop alternative and sustainable methods of generating hydrogen, such as the thermochemical Cu-Cl cycle [17]. In addition, new equipment technologies have delivered the greatest contribution to CO_2 emissions reduction (more than 50%), while new material technology only offers the lowest contribution to CO_2 emissions reduction (less than 1%). Xie et al. [18] suggested paying more attention to the research and development of energy-saving technology, as well as the clean transformation of energy structure, by investigating the driving factors of energy-related CO_2 emissions in China's petroleum refinery industry. Morrow et al. [19,20] developed a refinery model that consisted of 12 process units for the U.S. petroleum refining sector, and they classified CO_2 emissions reduction technologies by process unit. Recently, the carbon capture, utilization, and storage (CCUS) for industrial flue gases has become an important issue in the petroleum industry [21–24]. It includes carbon capture, carbon transport, CO_2-enhanced energy recovery, and comprehensive utilization of CO_2 [25]. The CCUS could mitigate the emissions from refining operations and reduce the refining sector's share of global CO_2 emissions by 4% [26]. Berghout et al. [27] evaluated the combination of mitigation options at a complex refinery, including energy efficiency, CCUS, and the introduction of biomass feedstock. Reasonable optimization of device parameters is a low-cost means of achieving carbon emission reduction. Zhang et al. [28]

configured the optimal parameters for the driving of steam and power systems to reduce the carbon emissions of the device.

From above, previous studies made valuable contributions to our understanding of carbon emissions and the mitigation of petroleum refineries from macroscopic aspects. However, few studies have focused on exploring influencing factors of carbon emissions from petroleum refineries at the process unit level. The impact of process parameters on carbon emissions is still unclear because the influencing parameters are complex and diverse. In addition, the carbon emission reduction technologies used for process units are generally selected based on expert experience, which usually involves some general knowledge and principles. The lack of specific analysis methods and data support generates ambiguous suggestions for carbon emission reduction.

In response to these key issues, four typical process units of a certain refinery, including FCC, Continuous Catalytic Reforming (CCR), HP, and DC, are chosen as objects. A typical 5-million-ton scale Chinese petroleum refinery was selected as an investigating object. Redundancy analysis (RDA) and multiple regression analysis (MRA) were employed to identify the key influencing factors of carbon emissions. The carbon reduction pathway aiming at the identified influencing factors is further proposed for the target refinery. The rest of this paper is organized as follows: Section 2 describes the main process units of the refinery case, identifies the main process units of carbon emission, and describes the RDA and MRA methods; Section 3 analyses and discusses the results of RDA and MRA, and proposed carbon emission reduction pathways on the basis of results; Section 4 presented the conclusions and some relevant suggestions

2. Data and Methods

2.1. Case Study

A petroleum refinery in China is taken as an example to conduct carbon emission and mitigation-related analysis at process unit level. The enterprise can process up to 5 million tons of crude oil annually. Mixed crude oil, methanol, and natural gas are used as the primary raw materials to produce gasoline, diesel oil, liquefied gas, propylene, naphtha, benzene, and other refined products. The carbon emission contribution of target refinery is calculated on the basis of process classification (Figure 1). Refinery "off-site" (e.g., utilities such as steam and electricity generation and hydrogen production) are neglected here.

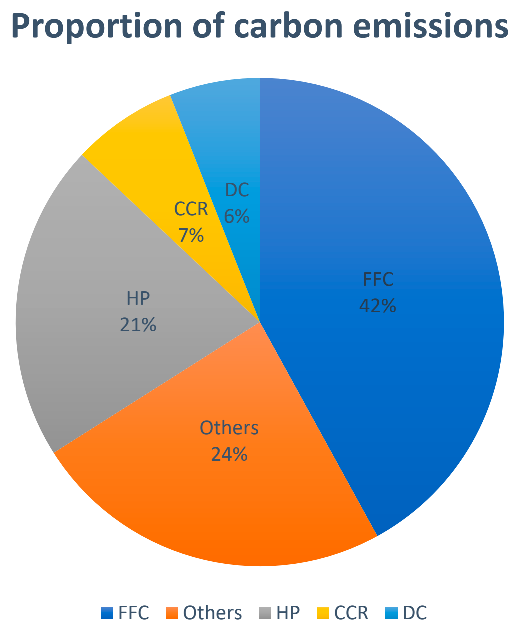

Figure 1. Proportion of carbon emissions from refinery processes. Notes: FCC—fluid catalytic cracking; DC—delayed coking; CCR—Continuous Catalytic Reforming; HP—Hydrogen production.

From Figure 1, process units such as FCC, CCR, DC, and HP are the main sources of carbon emission, accounting for 76% of the total carbon emissions of the enterprise. Compared with other units, FCC has a large amount of raw material processing, longer process flow, and more equipment. Thus, the scale of corresponding power and steam consumption is larger [5]. The carbon emission of FCC and HP units exceeds that of other production units. FCC is usually the processing unit with the highest carbon emission in heavy oil treatment due to the complex reaction conditions and the requirement for catalyst regeneration [29–32]. The main product of the HP unit is hydrogen. After purifying hydrogen through pressure swing adsorption (PSA), impurities such as CO_2 will be discharged in the form of waste gas [33]. Hydrogen is required as a raw material in each hydrogenation process, and the carbon emissions of the HP unit in case study accounted for 21% of the total carbon emissions of process discharges. The carbon emission from CCR and DC units mainly comes from the heating process, and the combustion of the coke part of the DC unit is also the main source of their carbon emissions [34].

Identification of specific sources is conducted for four process units. Process units can be decomposed into subunits according to their technological processes. GHG species of each subunit are further analyzed (Table 1). As for refineries, the emissions of CO_2, CH_4, and N_2O account for 98%, 2.25%, and 0.08% of the total GHG emissions. Facilities that do not have FCC and HP units will tend to have higher fraction of their total GHG emissions released as CH_4 [4]. Thus, species analysis of GHG in refinery focuses on CO_2 and CH_4. Additionally, GHG emission is mainly in the form of organized and unorganized emissions. Due to the randomness and dispersibility of unorganized emission sources, organized emission is emphatically discussed based on subunits.

Table 1. Identification results of emission source and compositions of GHG in a petroleum refinery.

Process Unit	Process Subunit	Emission Source of GHG	Compositions of GHG
FCC	Reaction-regeneration	Catalyst-coking exhaust emissions	CO_2
	Fractionation	Unorganized escape	CH_4
	Absorption and stabilization	Unorganized escape	CH_4
CCR	Pre-hydrogenation	Pre-hydrogenation furnace combustion, unorganized emission	CO_2, CH_4
	Reforming	Heating furnace combustion, unorganized emission	CO_2, CH_4
	Extraction system	unorganized emission	CH_4
	Regeneration	Catalyst-coking exhaust emissions	CO_2
DC	Reaction and fractionation	Heating furnace combustion, unorganized emission	CO_2, CH_4
	Absorption and stabilization	unorganized emission	CH_4
	Cold coke, coke water reuse	unorganized emission	CH_4
HP	Loading system	Pre-heating furnace combustion emission	CO_2, CH_4
	hydrodesulfurization	unorganized emission	CH_4
	Conversion furnace	Fuel combustion, unorganized escape	CO_2, CH_4
	PSA	unorganized emission	CO_2

Notes: FCC—fluid catalytic cracking; DC—delayed coking; CCR—Continuous Catalytic Reforming; HP—hydrogen production.

The FCC includes reaction-regeneration, fractionation, and absorption stabilization subunits. In reaction-regeneration subunit, the feedstock is cracked under high-temperature catalyst, and the coke is deposited on the catalyst, which reduces its catalytic activity. The spent catalysts are sent to regeneration system to burn off the deposited coke, producing large amount of flue gas mainly consisting of CO_2. The resulting effluent from reaction-regeneration sub-unit is processed in fractionators, which separate the effluent based on various boiling points into several intermediate products. Absorption and rectification methods are used in absorption stabilization systems to separate rich gas and crude gasoline [35]. Carbon emission of fractionation and absorption stabilization subunits is mainly attributed to CH_4 leakage from components or devices.

CCR includes three subunits: pre-treatment, reforming, and catalyst continuous regeneration. Impurities, such as heavy metals, S, N, are removed to refine the raw material of naphtha in pre-hydrogenation, and oil productions with a high content of aromatics are generated in reforming subprocess, in which combustion emission of pre-hydrogenation furnace and reforming heating furnace emits CO_2 and not fully burned CH_4. The used catalysts are regenerated by oxychlorination, drying, and chemical reduction in continuous regeneration sub-process [36]. Coke burning oxidizes the carbon on the surface of catalysts, leading to CO_2 emission.

DC mainly includes reaction and fractionation, absorption and stabilization, cold coke, and coke water reuse [37]. This thermal cracking unit rapidly heats heavy residual oil to high temperatures under intense heat conditions through the heating furnace tube. The oil reaches the temperature for coking reaction within a short period of time and quickly leaves the heating furnace, entering the coke tower. Combustion of heating furnace generates CO_2 and CH_4. After pyrogenic reaction, the coke tower needs to be cooled with water. During this process, oil and gas together with water vapor, enter the cold coke water vent system, absorbing the oil and gas after contacting the circulating cooling water. When the temperature of the coke tower is high, poor adsorption of oil and gas causes vent emission of CH_4.

Steam methane reforming (SMR) technology is generally used in HP unit, which includes loading system, hydrodesulfurization, conversion furnace, and PSA subunits. Feedstocks are heated to appropriate temperature by preheating furnace, and unsaturated hydrocarbons are converted to saturated hydrocarbons in the hydrogenation reactor. The hydrogenated gas and water vapor undergo a conversion reaction in a certain proportion. Combustion of preheating furnace and conversion furnace produces CO_2 and CH_4. Then, conversion gas undergoes heat exchange, condensation, and other processes, allowing the gas to pass through a PAS device equipped with various adsorbents under automated control. Impurities such as carbon monoxide and carbon dioxide are adsorbed by the adsorption tower, obtaining the final product, hydrogen [38]. Desorption of PAS devices leads to lots of CO_2 emissions.

2.2. Data Sources

The process data adopts the monthly GHG emission monitoring data and monthly monitoring process parameters from 2021 to 2023. The data come from self-monitoring of the refinery in this study. Other technical reports sponsored by the United States Government are sourced from online downloads. There are a total of 128 process parameters related to carbon emissions in the FCC unit, mainly including data items about reaction regeneration, pressure swing adsorption (PSA), fractional distillation, absorption-stabilization, desulfurization, mercaptan removal, flue gas desulfurization and denitrification, catalyst dosage, properties, and processed product volume. There are a total of 43 process parameters related to carbon emissions in the DC unit, mainly including data regarding hydrogen production, PSA, hydrogen balance, heating furnace, and consumption of raw materials and intermediate products. The HP unit has 36 process parameters associated with hydrogen production, PS, hydrogen balance, heating furnace section, and consumption of raw materials and intermediate products. There are 45 process parameters related to carbon emissions in CCR, mainly including that of pre-hydrogenation, reforming, regeneration, lye dissolving tank (V-901), heating furnace, and consumption of raw materials and intermediate products.

2.3. Methods

2.3.1. Redundancy Analysis

In this study, CO_2 and CH_4 were considered as two response variables, and the other parameters were set as explanatory variables. In this situation, correspondence analysis (CA) was used to explore the relationship between process parameters and carbon emissions within each production unit. Redundancy analysis (RDA) and Canonical Correspondence

Analysis (CCA) are both CA-based sequencing methods [39]. RDA is a linear model, while CCA is a unimodal model. The nonlinear model of CCA can accommodate the linear model, and the results of RDA will be more accurate in the case of shorter gradient length [40]. Another method of method selection can be judged by the lengths of gradient value result of Detrending Correspondence Analysis (DCA); if its maximum value is less than 3, the RDA analysis is more accurate. If it is greater than 4, CCA analysis should be selected. Between 3–4, both methods can be used [41]. The results of DCA analysis of FCC, DC, HP, and CCR are shown in Table 2.

Table 2. DCA analysis results of four process units.

Name	**FFC**	**DC**	**HP**	**CCR**
Data (Monthly)	January 2021–January 2023	January 2021–March 2023	January 2021–February 2023	January 2021–March 2023
Maximum gradient length	0.15	1.05	0.06	0.22
Suitable method	RDA	RDA	RDA	RDA

The results indicate that RDA analysis is more suitable for this study than CCA analysis, and the data changes of carbon emissions are gentle without significant fluctuations. Therefore, using a linear model is more suitable. Redundancy analysis (RDA) is a sorting method that combines regression analysis with principal component analysis. RDA is a principal component analysis for the fitting value matrix of multiple linear regression between the response variable matrix and the explanatory variable matrix. It simplifies the number of variables by screening the eigenvalues and then intuitively reflects the relationship between the explanatory variable and the response variable on the same coordinate axis. At the same time, RDA can provide the contribution of each explanatory variable to the response variable, identifying variables that have a significant impact on carbon emission [42].

The calculation of RDA method is to first perform multiple regression between each response variable in the centralized response variable matrix (Y) and all explanatory variable matrix (X) in order to obtain the vector of fitted value ($\hat{y}$) of each response variable and the vector of residual (y_{res}). The vectors of all fitted values form a matrix of fitted values ($\hat{Y}$). Then, principal component analysis was applied to the matrix ($\hat{Y}$) to obtain the canonical eigenvector matrix (U). Two sets of sorting coordinates were calculated based on matrix YU and $\hat{Y}U$, which represents the sorting coordinates of Y space and that of X space, respectively. All calculations related to the DCA and RDA were performed based on Canoco 5.0 software, and its significance was evaluated by using the Monte Carlo permutation test [43].

2.3.2. Multiple Regression Analysis

The carbon emission can be regarded as one response variable for CO_2 dominates to the point where other gases can be ignored. Therefore, the multiple regression analysis is used to identify the link between the dependent variable (y)'value of a CO_2 emission and many known independent variables (x). The unknown dependent variable can be determined in a predictive model if all parameters have been evaluated. The model for the MRA can be described as follows [44]

$$y_i = \beta_0 + \beta_1 x_{i1} + \beta_2 x_{i2} + \cdots + \beta_k x_{ik} \tag{1}$$

where y_i: dependent variable; $x_{i1}, \cdots, x_{ik}$: independent variables; β_0: constant; $\beta_1, \cdots, \beta_k$: coefficients of variables. All calculations for parameter estimation and validation are based on IBM SPSS Statistics 27 software.

3. Results

3.1. Influencing Parameters and Reducing Pathways of FCC Unit

Through RDA analysis, a total of five relevant influencing factors with a contribution of 87.2% to CO_2 and CH_4 emissions were identified, as shown in Figure 2 and Table 3. It shows that the angle between the middle circulation reflux (L6) and the CO_2 axis is small, and the length is the longest, indicating that it has the highest positive correlation on CO_2 emission. At the same time, catalyst surface area (SA) and slurry (P7) also have strong positive correlations on CO_2 emission. The main factors affecting CH_4 emission mainly include C-5002 pressure (PR11) and bottom loose steam (VF6).

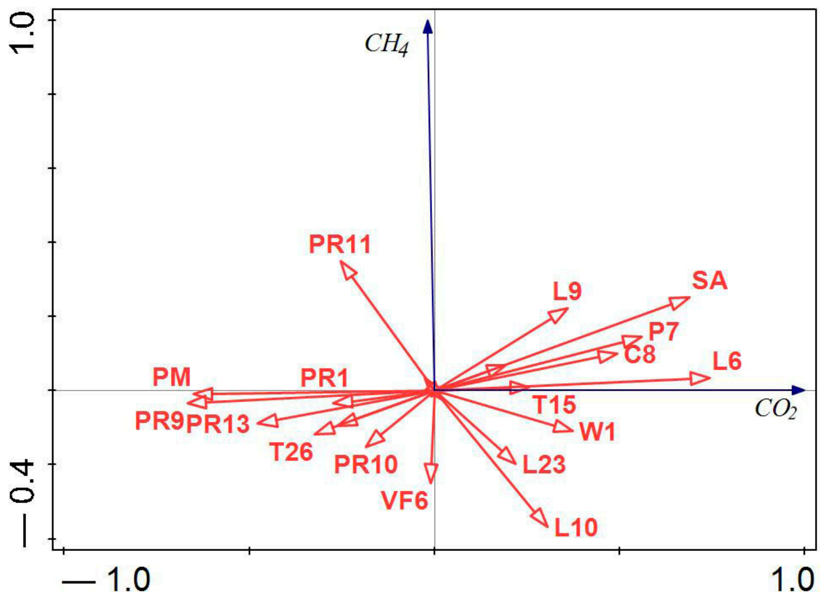

Figure 2. Diagram of the redundancy analysis (RDA) presenting the correlations between the carbon emission (CO_2, CH_4) and process parameters of the FCC unit.

Table 3. Testing significances of process variables to GHG emissions of FCC.

Factor Name	Abb.	Explains (%)	Contribution (%)	*p*-Value
Middle Circulation Reflux (t/h)	L6	54.8	54.8	0.002
Slurry (kg)	P7	17.5	17.5	0.002
Catalyst surface area (m^2/g)	SA	6.6	6.6	0.020
C-5002 pressures (MPa)	PR11	5.8	5.8	0.022
Bottom loose steam (kg/h)	VF6	2.5	2.5	0.016

Testing significances of process variables to carbon emissions are shown in Table 3. The contribution of L6 is 54.8% of the total variance of the response variable matrix. That of P7 ranks second, accounting for 17.5% of the total variance. The *p*-values of L6 and P7 are less than 0.01, indicating that the significance of these two factors is high. The *p*-values of other parameters, such as SA, PR11, and VF6, are all less than 0.05, indicating that these factors are significant.

The parameters in Table 3 can be classified into three categories based on their characters: processing scale, reaction condition, and material property, as shown in Table 4. L6 is regarded as the processing scale as it is usually used as the heat source for the absorption tower, in which a large amount of energy is consumed during the heat-up process. The increase in L6 results in an increase in carbon emissions. PR11 and VF6 are parameters related to reaction conditions. Thermodynamic and chemical kinetic considerations establish pressures and temperatures required to maximize the yield of desirable products. The temperature and pressure will jointly affect the reaction process. The P7 reflects the scale of refinery processing. The output of the oil slurry is proportional to the circulating volume in the fractionation tower. The larger the output of the oil slurry, the greater the energy consumption required, and the carbon emissions will increase [45]. The properties of SA usually lead to coke deposition into the catalyst particles or matrix pores. During this process, carbon emissions will increase as a result [46].

Table 4. Types of influencing factors and emission reduction pathways of FCC unit.

Factor Name	Abb.	Factor Type	Emission Reduction Pathways
Middle Circulation Reflux (t/h)	L6	processing scale	(1) Changing the composition of raw oil (2) Slow heating up
C-5002 pressures (MPa)	PR11	reaction conditions	(1) Optimize process parameters
Bottom loose steam (kg/h)	VF6	processing scale	
Catalyst surface area (m^2/g)	SA	Material property	(1) Improving the properties of raw oil (2) Controlling temperature (3) Increasing catalyst pore size
Slurry (kg)	P7	processing scale	(1) Recycling and filtration

Based on the 21 indicators identified by RDA analysis, multiple regression analysis (MRA) was conducted, and the stepwise method was used to screen independent variables. The results obtained are shown in Table 5. The adjusted R^2 of the model reached 0.761, indicating a high fitting effect and significant *t*-test for independent variables.

Table 5. Coefficients and *t*-test of regress model for FCC.

Model	Unstandardized Coefficient		Standardized Coefficient	*t*	Significance
	B	Standard Error	Beta		
Constant	5.455	3.603		1.514	0.149
L6	0.07	0.009	1.031	8.225	0
P7	1.21×10^{-6}	0	0.538	4.29	0.001

The regression model is shown in Formula (2), which is as follows:

$$y = 0.07x_1 + 1.21 \times 10^{-6}x_2 + 5.455 \quad (2)$$

where y—CO_2 emissions, mg/m^3; x_1—Intermediate circulation volume, t/h; x_2—slurry, kg. The equation indicates that carbon dioxide emissions can be explained or predicted by the intermediate circulation volume (L6) and oil slurry (P7). The results are basically consistent with that of the RDA analysis.

3.2. Influencing Parameters and Reducing Pathways of DC Unit

Through RDA analysis, a total of 9 relevant influencing factors with a contribution of 82.5% to carbon emissions were identified, as shown in Figure 3 and Table 6.

It shows that the heat efficiency of the furnace (JC) has the highest negative correlation on CO_2 emission, followed by the temperature at the bottom of the desorption tower (XA) and sealing oil pressure (FAA). At the same time, Heating furnace outlet pressure (FM), Heating furnace feed rate (FO), dry gas (G5), heating furnace oxygen content (JA), Excess air coefficient (JB) and heating furnace temperature (FR) have strong positive correlations on CH_4 emission.

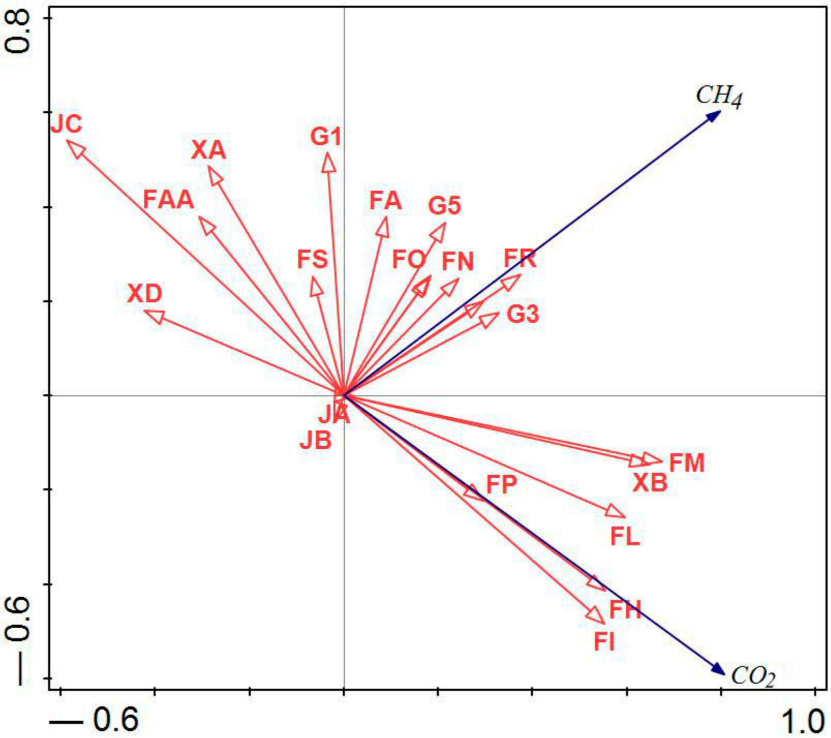

Figure 3. Diagram of the redundancy analysis (RDA) presenting the correlations between the GHG emission (CO_2, CH_4) and process parameters of the DC unit.

Table 6. Testing significances of process variables to GHG emissions of DC.

Name	Abbas.	Explains %	Contribution %	*p*-Value
Heat efficiency of the furnace (%)	JC	32.6	32.6	0.002
Heating furnace outlet pressure (MPa)	FM	12.3	12.3	0.036
Heating furnace temperature (°C)	FR	8.1	8.1	0.068
Excess air coefficient	JB	6.1	6.1	0.05
Heating furnace oxygen content (%)	JA	5.8	5.8	0.09
Temperature at the bottom of the desorption tower (°C)	XA	5.0	5.0	0.084
Heating furnace feed rate (t)	FO	4.8	4.8	0.153
Dry gas (t)	G5	4.4	4.4	0.125
Sealing oil pressure (MPa)	FAA	3.4	3.4	0.076

Types of influencing factors and emission reduction pathways of DC units are shown in Table 7. The influencing factors are classified into two categories: reaction condition and processing scale. The main influencing factors related to reaction conditions are the operating parameters related to the heating furnace. Improving the thermal efficiency of the heating furnace will improve energy efficiency and reduce carbon emissions. The excess air coefficient will affect the thermal efficiency of the heating furnace. If the coefficient is too small, it will cause incomplete combustion of fuel in the heating furnace, resulting in more coke production. The pressures and temperatures are prerequisites for many physical and chemical reactions based on thermodynamic and chemical kinetic considerations. The changes of them will change the yield of intermediate, final products, and wastes. Its establishment also requires energy consumption, thereby affecting carbon emissions. The temperature change at the bottom of the desorption tower will affect the amount of desorbed gas, which in turn affects the absorption effect of the absorption tower. An increase in the bottom temperature of the analytical tower will lead to an increase of the C3 component in the dry gas, resulting in a decrease in the absorption efficiency and an increase in the carbon emission.

Table 7. Types of influencing factors and emission reduction pathways of DC unit.

Name	Abbas.	Factor Type	Emission Reduction Pathways
Heat efficiency of the furnace (%)	JC	reaction conditions	Improving heat efficiency
Heating furnace outlet pressure (MPa)	FM	reaction conditions	Appropriate pressure
Heating furnace temperature (°C)	FR	reaction conditions	Reduce the temperature
Excess air coefficient	JB	reaction conditions	Reduce excess air coefficient while ensuring complete combustion
Heating furnace oxygen content (%)	JA	reaction conditions	Appropriate oxygen content
Temperature at the bottom of the desorption tower (°C)	XA	reaction conditions	Reduce the temperature
Heating furnace feed rate (t)	FO	processing scale	Choose the appropriate recycle ratio in delayed coking
Dry gas (t)	G5	processing scale	Choose the appropriate recycle ratio in delayed coking
Sealing oil pressure (MPa)	FAA	reaction conditions	Optimize the pressure to reduce carbon emissions

Based on the 22 indicators identified by RDA analysis, MRA was conducted, and the stepwise method was used to screen independent variables. The results obtained are shown in Table 8. The adjusted R^2 of the model reached 0.801, indicating a high fitting effect and significant *t*-test for independent variables.

Table 8. Coefficients and *t*-test of regress model for DC.

Model	Unstandardized Coefficient		Standardized Coefficient	*t*	Significance
	B	Standard Error	Beta		
Constant	354.4	51.022		6.946	<0.001
JC	−2.609	0.466	−0.636	−5.598	<0.001
XA	−0.377	0.087	−0.591	−4.342	<0.001
JB	−61.448	17.040	−0.365	−3.606	0.002
FR	0.036	0.016	−0.297	2.293	0.033

The regression model is shown in Formula (3), which is as follows:

$$y = -2.609x_1 - 0.377x_2 - 61.448x_3 + 0.036x_4 + 354.4 \quad (3)$$

where y—CO_2 emissions, mg/m^3; x_1—heat efficiency of the furnace, %; x_2—temperature at the bottom of the desorption tower, °C; x_3—excess air coefficient; x_4—heating furnace temperature, °C. The equation indicates that carbon dioxide emissions can be explained or predicted by the JC, XA, JB, and PR. The results are basically consistent with that of the RDA analysis.

3.3. Influencing Parameters and Reducing Pathways of HP Unit

Through RDA analysis, a total of five relevant influencing factors with a contribution of 81.5% to GHG emissions were identified, as shown in Figure 4 and Table 9. The mixed excess air coefficient of the heating furnace (JB) has the highest positive correlation and the greatest impact on CO_2 emission, followed by conversion furnace feed flow (ZW). The converter outlet temperature (ZJ) has the highest negative correlation to CH_4 emission.

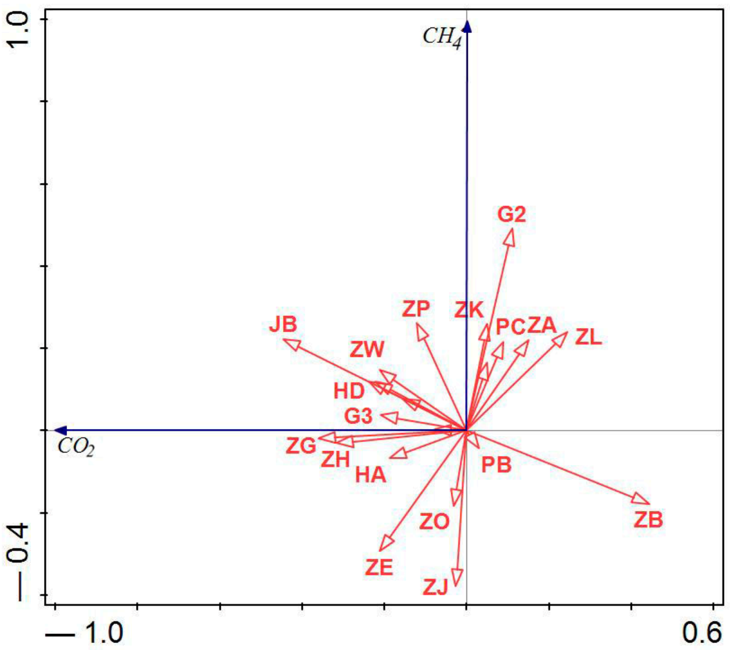

Figure 4. Diagram of the redundancy analysis (RDA) presenting the correlations between the GHG emission (CO_2, CH_4) and process parameters of HP unit.

Table 9. Testing significances of process variables to GHG emissions of HP.

Factor Name	Abb.	Explains%	Contribution%	*p*-Value
Converter outlet temperature (°C)	ZJ	27.1	27.1	0.026
Excess air coefficient of heating furnace	JB	26.3	26.3	0.014
Conversion furnace feed flow (Nm^3/h)	ZW	17.9	17.9	0.010
Product hydrogen flow rate (Nm^3/h)	HD	10.4	10.4	0.078

Testing significances of influencing factors are shown in Table 9. It can be seen that the explained variance of ZJ, JB, and ZW accounts for 27.1%, 26.3%, 17.9%, and 10.4%, respectively. The p values of ZJ, JB, and ZW are all less than 0.05, indicating the significance of these factors.

Types of influencing factors and emission reduction pathways of HP units are shown in Table 10. The conversion of natural gas steam to hydrogen will produce carbon emissions, mainly including process carbon emissions caused by the conversion reaction of methane steam and indirect carbon emissions caused by energy consumption during the hydrogen production process [47]. The significant indicators related to process scale will increase or decrease the load of the conversion furnace and heating furnace, thereby affecting fuel consumption and device emissions. Regarding reaction conditions, mainly about temperature and excess air coefficient, there is a significant impact on energy and thermal efficiency during chemical reaction process, further affecting carbon emissions.

Table 10. Types of influencing factors and emission reduction pathways of HP unit.

Factor Name	Abb.	Factor Type	Emission Reduction Pathways
Converter outlet temperature (°C)	ZJ	reaction conditions	Optimize temperature control to reduce energy consumption
Excess air coefficient of heating furnace	JB	reaction conditions	Optimize oxygen content to increase energy efficiency
Conversion furnace feed flow (Nm^3/h)	ZW	Process scale	Decrease water/carbon ratio
Product hydrogen flow rate (Nm^3/h)	HD	Process scale	Decrease water/carbon ratio

Based on the 22 indicators identified by RDA analysis, MRA was conducted, and the stepwise method was used to screen independent variables. The results obtained are shown in Table 11. The adjusted R^2 of the model reached 0.637, indicating a high fitting effect and significant *t*-test for independent variables.

Table 11. Coefficients and *t*-test of regress model for HP.

Model	Unstandardized Coefficient		Standardized Coefficient	*t*	Significance
	B	Standard Error	Beta		
Constant	−132.556	52.997		−2.501	0.020
JB	34.684	8.948	0.874	3.876	0.001
ZJ	0.167	0.060	0.625	2.772	0.011

The regression model is shown in Formula (4), which is as follows:

$$y = 34.684x_1 + 0.167x_2 - 132.556 \quad (4)$$

where y—CO_2 emissions, mg/m^3; x_1—excess air coefficient of a heating furnace; x_2—converter outlet temperature, °C. The equation indicates that carbon dioxide emissions can be explained or predicted by the excess air coefficient of a heating furnace (JB) and converter outlet temperature (ZJ). The results are basically consistent with that of the RDA analysis.

3.4. Influencing Parameters and Reducing Pathways of CCR Unit

Through RDA analysis, a total of 7 factors with a significant impact on GHG emissions (contributing to 81.9% explained variances of GHG emissions) were identified, as shown in Figure 5 and Table 12.

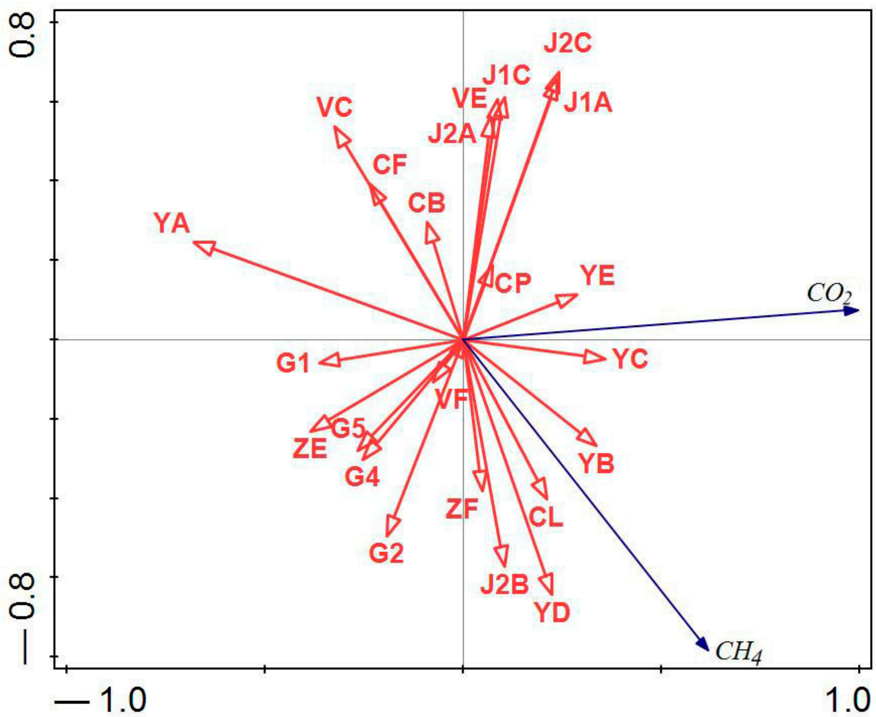

Figure 5. Diagram of the redundancy analysis (RDA) presenting the correlations between the GHG emission (CO_2, CH_4) and process parameters of CCR unit.

Table 12. Testing significances of process variables to GHG emissions of CCR.

Name	Abb.	Explains %	Contribution %	*p*-Value
Pre-hydrogenation feed volume (t/h)	YA	42.8	42.8	0.002
Oxygen content in box furnace (%)	J_2C	11.1	11.1	0.02
Excess air coefficient	J_1A	10.4	10.4	0.018
Regenerated oxygen content (%)	ZF	7.7	7.7	0.014
The amount of hydrogen mixed (m^3/h)	CB	4.6	4.6	0.056
Yield of C_6 (t)	G_2	3.1	3.1	0.08
Gas-liquid separation pressure (MPa)	YC	2.2	2.2	0.12

According to Table 12, the contribution of YA is much higher than that of other devices, accounting for a 42.8% variance contribution. The *p*-values of J_1A, J_2C, ZF, and CB are about less than 0.05, indicating significant factors.

The identified factors can be categorized into reaction conditions and processing scale, as shown in Table 13. The parameters that have the most obvious impact on carbon emissions are mainly related to temperature, which not only affects the catalytic process but also affects the composition of the product. As the temperature increases, carbon emissions will increase [48]. The YA will have an impact on the hydrogen oil ratio. The high YA will increase the steam consumption of the recycled gas compressor, resulting in higher energy consumption. The oxygen content and excess air coefficient are both related to the heating furnace, and the oxygen content of the heating furnace determines whether the internal fuel can be completely burned, which is an important parameter to measure the energy efficiency of the heating furnace. The ZF needs to be controlled within a certain level for both high or low is not good. Compared with C7, the conversion rate of C6 straight-chain alkanes in the raw materials is much lower, and the conversion of C6 straight-chain alkanes into benzene in the reforming raw materials is more difficult, resulting in increased energy consumption.

Table 13. Types of influencing factors and emission reduction pathways of CCR unit.

Name	Abb.	IMPACT TYPE	Emission Reduction Pathways
Pre-hydrogenation feed volume (t/h)	YA	processing scale	Control the feeding speed of materials
Oxygen content in box furnace (%)	J2C	reaction conditions	Determine the optimal oxygen content based on the coke temperature gradient in the regeneration coke zone
Excess air coefficient	J1A	reaction conditions	
Regenerated oxygen content (%)	ZF	reaction conditions	
Hybrid gasoline and Hydrogen (m^3/h)	CB	processing scale	Optimizing the hydrogen/carbon ratio
Yield of C6 (t)	G2	processing scale	Optimizing components and the Initial Distillation Point of raw Materials

Based on the 24 indicators identified by RDA analysis, MRA was conducted, and the stepwise method was used to screen independent variables. The results obtained are shown in Table 14. The adjusted R^2 of the model reaches 0.732, indicating a high fitting effect and significant *t*-test for independent variables.

Table 14. Coefficients and *t*-test of regress model for CCR.

Model	Unstandardized Coefficient		Standardized Coefficient	*t*	Significance
	B	Standard Error	Beta		
Constant	67.138	13.696		3.816	0.001
YA	−0.315	0.057	−0.723	−5.799	0
J2C	8.368	1.65	1.075	3.585	0.002
J1A	−47.9	12.581	−0.859	−2.591	0.017

The regression model is shown in Formula (5), which is as follows:

$$y = -0.315x_1 + 8.368x_2 - 47.9x_3 + 67.138 \quad (5)$$

where y—CO_2 emissions, mg/m^3; x_1—pre-hydrogenation feed rate, t/h; x_2—oxygen content of box furnace, %; x_3—excess air coefficient. The equation indicates that carbon dioxide emissions can be explained or predicted by the YA, J_2C, and J_1A. The results are basically consistent with that of the RDA analysis.

4. Discussions

Decomposition analysis has been widely used to quantify driving factors of changes in an indicator over time [12]. Xie et al. [18] decomposed the CO_2 emissions changes of China's petroleum refining and coking industry (PRCI) into five factors and compared their diverse contributions by using the Logarithmic Mean Divisia Index (LMDI) decomposition method. The results show that industrial activity is the dominant driving force of the growth of CO_2 emissions, followed by industrial scale and energy intensity. Liu et al. [49] combined the structural decomposition analysis method and the input–output subsystem analysis method to construct a decomposition model of the factors influencing the amount of change in carbon dioxide emissions in China. However, due to methodological limitations, factor decomposition methods focus on a small number of highly comprehensive driving force indicators, making it difficult to provide driving force analysis of core parameters at the critical process level.

A few recent studies aim to assess CO_2 mitigation potential for a complex refinery by using a bottom-up method, in which the studies of the oil industry process-chain (production, transport, and refining) were used to identify energy efficiency measures (EEM) based on operational data at the process unit level [50]. The first step of the general approach is identifying an inventory of existing facilities and key parameters of the core process of the refinery (e.g., CO_2 emissions, reaction parameters, material and energy flows). Morrow et al. [19,20] identified energy efficiency-related measures and CO_2 emissions reduction potential for the U.S. refining industry by dividing petroleum refining into 12 process units. Jia et al. [6] established a modeling framework to address the petroleum and its derivatives, energy, and CO_2 emissions nexus at the process unit-level based on energy flow analysis and bottom-up method when refining paraffin-based crude oil in China. Although the bottom-up approach starts from process-level data of petroleum refining, it lacks the ability to objectively identify influencing factors. The energy flow analysis-based bottom-up approach can only identify the influencing factor of flux or scale type and cannot analyze the influencing factors of chemical reactions and material properties types. Therefore, the integrated RDA and MRA method proposed in this article can deal with all kinds of factors to one or multiple response variables, providing a quantitative method for identifying significant influencing factors and expanding the application scope of "Decomposition Analysis".

FCC, CCR, DC, and HP units are selected as the object of study according to the proportion of carbon emissions. The results of four main units indicate that the main types of influencing factors are energy consumption, reaction conditions, processing scale, and catalyst-related factors. In the reaction conditions, regardless of the device, any part that involves heating will have a significant impact on carbon emissions. In most processes, the fractionation parts are the main factors that influence the GHG emission. It is probable that continuous heating sources are required, which results in a significant amount of energy consumption and carbon emissions. The impact of process scale is reflected in the production load. If other parameter conditions remain unchanged, an increase in load leads to higher carbon emissions. The coke burning of catalyst regeneration produces a large amount of greenhouse gases. Any factor that affects the carbon deposition on the catalyst will have a significant impact on carbon emissions.

5. Conclusions

When estimating or reducing carbon emissions in a refinery, researchers often focus on carbon emissions at industries and enterprise levels, neglecting that of process or equipment. This reduces the resolution of the estimation and the operability of the measures. Taking a certain petroleum refinery in China as an example, the study identified the relationship between the parameters of each operating device and carbon emissions through process analysis combined with statistical analysis of MRA and RDA and provided more targeted suggestions for reducing carbon emissions in the refinery.

The proposed method, compared to the factorial decomposition method, can analyze the factors affecting carbon emissions at a more microscopic level and provide more detailed information, such as analyzing the factors affecting carbon emissions of an enterprise or equipment. The proposed method is easy to understand, simpler to calculate, and can identify significant factors affecting carbon emissions from numerous production process parameters, avoiding the subjective selection of research factors. The proposal method provides a higher resolution factor identification method, but it is still qualitative, based on multi-objective optimization and multi-objective experimental design methods. The influencing factors can be further studied to obtain the optimal values while balancing the economy, environment, and other issues.

Potential carbon mitigating pathways for FCC unit after analyzing significant influencing factors include changing the composition of raw oil and improving catalyst performance to reduce the amount of produced coke. Optimizing process parameters and strengthening the circulation and recovery of heat and steam to improve energy efficiency. Potential carbon mitigating pathways for DC unit is to optimize process parameters to improve the thermal efficiency of the heating furnace. In the HP unit, optimizing the reaction conditions and inlet and outlet loads of the conversion furnace and heating furnace are main ways to reduce carbon emissions. The potential emission reduction methods of the CCR device are mainly through optimizing the raw material composition, controlling reaction parameters, and optimizing the reaction load.

In this case, the most mitigations of carbon emission can be classified as implementing energy or mass efficiency measures. It can be implied by operational control measures and scale control measures. The former mainly involves the optimization of equipment parameters, while the latter mainly involves the optimization of scale for material and energy flow. This paper mainly concentrated on proposing mitigation pathways based on identified influencing factors that have a negative effect on the GHG emission of certain refinery units. The discussion of current trends in novel carbon reduction technologies for the petroleum refining industry, including combined heat and power (CHP), carbon capture, utilization, and storage (CCUS), and the potential introduction of biomass energy and Green Hydrogen [51], are not addressed in this paper. These opportunities are recommended for further research and analysis. Moreover, this study is based on data from only one refinery, so the sample size is not large. If the study could use more data from more refineries, the results would be more objective. Due to the complexity of the petroleum refining process, only the main carbon emission equipment was selected for this study, and further research is needed on the remaining carbon emission equipment.

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