Carbon flow analysis and Carbon emission reduction of FCC in Chinese oil refineries

Fengrui Jia¹, Na Wei¹, Danzhu Ma¹, Guangxin Liu¹, Ming Wu¹, Qiang Yue²

¹College of Petroleum Engineering, Liaoning Shihua University, Fushun, Liaoning, 113001, China
²Institute of metallurgy, Northeastern University, Shenyang, Liaoning, 110819, China

The corresponding author’s e-mail: jfrjfr_1983@163.com

Abstract. The major problem of the energy production in oil refineries is the high emission of CO₂ in China. The fluid catalytic cracking unit (FCC) is the key source of carbon emission in the oil refineries. According to the statistical data, the carbon emission of FCC unit accounts for more than 31% for the typical oil refineries. The carbon flow of FCC in the typical Chinese oil refineries were evaluated and analysed, which aimed at the solution of CO₂ emission reduction. The method of substances flow analysis (SFA) and the mathematical programming were used to evaluate the carbon metabolism and optimize the carbon emission. The results indicated that the combustion emission of the reaction-regeneration subsystem (RRS) was the major source of FCC. The quantity of CO₂ emission of RSS was more than 90%. The combustion efficiency and the amount of residual oil affected the carbon emission of RRS most according to the optimized analysis of carbon emission reduction. Moreover, the fractionation subsystem (TFS) had the highest environmental efficiency and the absorption-stabilization subsystem (ASS) had the highest resource efficiency (approximately to 1) of carbon.

1. Introduction

Under the situation of serious environmental pollution, the implementation of the industrial CO₂ emissions reduction has become a very urgent task [1-2]. Petrochemical industry is one of the sixth largest energy-consuming and CO₂ emitter industry in China, especially the oil refinery process which consumes a large amount of energy and releases a great deal of CO₂. In other words, the oil refinery process contributes most to CO₂ emission in petrochemical industry. According to the statistics, the emission of CO₂ has increased 20% with a little increasing in refining capacity (6.96%) in Chinese oil refineries from 1999 to 2009[3,4]. So, the CO₂ emission reduction in Chinese oil refineries, which needs the characteristics of CO₂ emission and the rules of Carbon flow, plays an important role to the mitigation of climate change. Moreover, quantitative evaluation of Carbon flows, stocks and its environmental effects is beneficial for CO₂ emission reduction.

In this paper, the characteristics of CO₂ emission, the rules of Carbon flows and the main factors on CO₂ emission reduction were conducted concerning oil refinery in China. Focusing on the production process and its Carbon emission, the emission characteristics was analyzed based on the statistical data. Additionally, the Carbon flows were investigated using SFA for FCC in oil refinery. Also, the impact factors of CO₂ emission reduction were determined by mathematical programming.
2. Methods

2.1. Substance Flow Analysis

Substance flow analysis (SFA) [5-7] is an extensive utilized and valuable tool, which can be efficiently used to support environment management decisions and sustainable development evaluation and analysis. SFA can be defined as an analytical method used to systematically assess the flows and stocks of Carbon within a given oil refinery unit [8]. And it’s always concerned with identifying environmental problems associated with Carbon flows. It can be used to estimate the losses and gains of Carbon from a refinery system of study and the environmental impacts during various processes in its life cycle. The SFA monitors Carbon flows and evaluates the environmental interactions that raise particular concerns regarding the environmental risks associated with its production and consumption. It uses the principle of “mass conservation” to analyze the relationships between Carbon flows, refining process and environmental changes. So, the results of SFA should be viewed as a tool for sustainability assessment for climatic environment and petrochemical industry development.

| Nomenclature                  | Definition                                                                 |
|-------------------------------|---------------------------------------------------------------------------|
| \( E_{CO_2} \)               | the total CO\(_2\) emission into environment, including all the direct carbon emission (t/t) |
| \( E_c \)                    | the total carbon content (t/t)                                            |
| \( C \)                      | the content of carbon element of different substance, such as the material, the product, the outsourcing fuel, the waste and so on (t) |
| \( P \)                      | the product output of the target unit or subsystem (t)                     |
| \( W_c \)                    | the outsourcing carbon from the outside of a target unit (t/t)            |
| \( Re_c \)                   | the resource efficiency of carbon for the target unit or subsystem (t/t)  |
| \( Ec_e \)                   | the environmental efficiency of carbon for the target unit or subsystem (t/t) |
| \( M_{i, in, m} \)           | the mass of input material or fuel for \( m \) material of \( i \) subsystem (t) |
| \( M_{i, out, n} \)          | the mass of output products for \( n \) product of \( i \) subsystem (t)   |
| \( c_{i, in, m} \)           | the conversion coefficient of carbon for \( m \) material of \( i \) subsystem |
| \( c_{i, out, n} \)          | the conversion coefficient of carbon for \( n \) product of \( i \) subsystem |

2.2. Definition of evaluation indicators

The carbon emissions of the oil refinery were divided into two types, including direct emission and indirect emission, according to its resources and importance. The emissions from the stationary combustion, the refinery processes and the gases escape were all considered in the direct emission. The indirect part is the carbon emission caused by power consumption. Based on statistic data of Chinese oil refinery enterprises, the direct emission takes more than 96% in the total emission. The indirect emissions is affected by many factors, such as technology, working condition, equipment condition and so on, which is less than 4% and very difficult to determine accurately. In this paper, the direct carbon emission was analysed by SFA.

In order to evaluate the flow of carbon, four indicators were introduced as following:

\[
E_{CO_2} = E_c \times \frac{44}{12} = \left[ \sum C_{in} - \sum C_{out} \right] \times \frac{44}{12} \tag{1}
\]

\[
W_c = \frac{\sum C_{outsourcing}}{\sum P_{product}} \tag{2}
\]

\[
Re_c = \frac{\sum C_{product}}{\sum C_{material}} \tag{3}
\]
\[ E_{e} = \sum P_{\text{product}} / \sum C_{\text{waste}} \]  

(4)

2.3. FCC unit

Base on the production data of a certain oil refinery enterprise, the carbon emissions of FCC unit accounts for more than 31% in the oil refinery enterprises. It is the key sources of carbon emissions. FCC includes RRS, TFS and ASS, as shown in Figure 1, and the capacity is 130 t/h. The heating load of heating furnace is $34.74 \times 10^6$ kJ/h. And the compositions of products are as follow in Table 1.

![FCC unit diagram](image)

**Table 1.** The compositions of products of FCC.

| Products                      | Share/% | Carbon content/% |
|-------------------------------|---------|------------------|
| Dry gas                       | 5       | 77               |
| Liquefied gas                 | 11      | 82.3             |
| Stabilized gasoline           | 48      | 86               |
| Light diesel oil              | 20      | 83               |
| heavy diesel oil              | 1.2     | 89               |
| Slurry oil                    | 6       | 75               |
| Other loser                   | 8.8     | 60               |

The mathematical programming method was used to optimize the carbon emission of FCC. The objective function is shown as:

\[ E_{CO_2} = \sum_{i=1}^{n} C' \times X_i + E'_{CO_2} \]  

(5)

And the constraint conditions of the optimization included the heat load of heating furnace, the elements equilibrium constraints (N, C, S), the material balance constraint, the environment constraint and non-negativity constraint.

3. Results and discussion

3.1. Carbon flow analysis

The carbon flows into FCC unit, starting with RRS. After a series of metabolic processes, such as migration and transformation, then the carbon output the unit from ASS. The carbon output includes two parts, the carbon emission and the carbon products. All the carbon emissions in different forms were converted into CO$_2$ emission in the carbon flow analysis, as shown in formula (6):
\[
E_{CO_2} = \left[ \sum_{j=1,2,3} M_{i,in,m} \times c_{i,in,m} - \sum_{i=1,2,3} M_{i,out,n} \times c_{i,out,n} \right] \times \frac{44}{12}
\]  

Table 2 gives the results of evaluation indicators of carbon flow in FCC unit. 

| System | Combustion emission/% | Process emission/% | \(W_c/t/t\) | \(R_e/t/t\) | \(E_e/t/t\) | \(E_{CO_2}/t/t\) | Emission percentage/% |
|--------|-----------------------|--------------------|------------|------------|------------|-----------------|----------------------|
| RRS    | 68.96                 | 31.04              | 0.90       | 0.903      | 9.67       | 0.367           | 91.29                |
| TFS    | <47.89                | >52.11             | -          | 0.99       | 116.91     | 0.033           | 8.21                 |
| ASS    | -                     | -                  | -1         | -          | -          | 0.002           | 0.50                 |
| FCC    | 68.40                 | 31.6               | 0.61       | 0.88       | 8.67       | 0.402           | 100                  |

As shown in Table 2, the major form of carbon emission comes from the combustion of fuels and the combustion emission contributes more than two times of the process emission for FCC. RRS is the main carbon outsource in FCC, includes the input of raw oil and power fuels. And it is also the main carbon emission source in FCC, more than 90%, due to the fuel combustion in the heating furnace. The main process for TFS is the fractionation of hot oil-gas mixture, and output different carbon products which separation by boiling point. So, TFS has a very high environmental efficiency, means it has very small impact on environment. The carbon emission of TFS can be recycled and reused by recycling the oil slurry to RRS. For ASS, the resource efficiency of carbon is approximately equal to 1, means carbon provides all the services to products, no carbon pollution. Thus, the crux of the carbon emission reduction for FCC is to reduce the combustion emission of RRS.

### 3.2. Carbon reduction impacts

The factors of the amount of residual oil, the combustion efficiency, the C/H ratio of fuel and the excess air coefficient were investigated to optimize the carbon emission of RRS. And the influencing factors were explored through univariate analysis, in order to determine the key factors affecting carbon emission of RRS.

![Figure 2. The relationships between the combustion efficiency, the amount of residual oil and the CO₂ emission.](image)

The relationship curves between the combustion efficiency, the amount of residual oil and the CO₂ emission were derived, as shown in figure 2. The combustion efficiencies of RRS heating furnace from 86% to 96% were investigated. According to the analysis result, it imitated a monotone increasing function of the combustion efficiency and the CO₂ emission. The CO₂ emission included the carbon emission with flue gas and waste residue. The carbon emission of flue gas increased with the increasing of combustion efficiency, while the carbon emission of waste residue decreased. Means the carbon fuel burnt more fully under higher combustion efficiency. From an overall view, the CO₂ emission increased 11.51% when the combustion efficiency increased from 86% to 96%. For the residual oil, it is one of the raw materials for RRS, which is recycled from TFS. The influencing of the
amount of residual oil was also studied. The mass flow rate of the residual oil also showed a significant and similar effect on CO$_2$ emission. With 9.56% increasing of the mass flow rate of residual oil, the carbon emission grown 9.62% and 7.86% for flue gas and waste residue, respectively.

![Figure 3. The relationships between the excess air coefficient, the C/H ratio of fuel and the CO$_2$ emission.](image_url)

Figure 3 gives the optimization analysis results of the excess air coefficient and the C/H ratio. As shown in figure 3, with the excess air coefficient increased from 1.10 to 1.30, the CO$_2$ emission reduced 0.13% for RRS. In theory, the complete combustion of fuel and air can be achieved when the excess air coefficient is 1.00. And when it is 1.10, the consumption of fuel can achieve the minimum. With the increasing of C/H ration, the CO$_2$ emission increased from 6359.5 m$^3$/h to 6554.6 m$^3$/h (3.07% growth). This shown that the changes of the excess air coefficient and the C/H ratio have a certain impact on CO$_2$ emission, but they are not the main factors.

4. Conclusion
The model of carbon flow analysis was established, and the carbon flow were tracked and evaluated. The result shows that RRS is the key point of carbon emission for FCC. The carbon emission of RRS is more than 90% of FCC. And the analysis of carbon emission for RRS shows that the combustion emission is the most part of it. So the carbon reduction of FCC should focus on the combustion emission of RRS.

The carbon reduction analysis was optimized for RRS. The results shows that the combustion efficiency and the amount of residual oil are the main factors affecting the carbon emission of RSS, and there must have optimal and matched values between them to achieve the aim of carbon reduction for RRS.

Acknowledgments
The research was conducted with financial support from the National Natural Science Foundation of China (No. 71373003) and the Scientific Research Project of Department of education of Liaoning Province (No. L2014146).

References
[1] Burnham A, Han J, Corrie E C 2012 *Environ. Sci. Technol* 46 619.
[2] Gutowski T G, Allwood J M, Herrmann C 2013 *Annu. Rev. Environ. Resour* 38 81.
[3] Bing Y, Xiao L, Lei S, Yi Q 2015 *J. Clean Prod* 103 801.
[4] Yibin W, Guangxu Y, Yu L, Shaohui G 2015 *J. Clean Prod* 105 1.
[5] Chu-Long, H, Hwong-Wen M, Chang-ping Y 2014 *Total Environ* 499 265.
[6] Donald, Huisingh, Zhihua, Zhang, John, C, Moore, Qi Qiao, Li Qi 2015 *J. Clean. Prod* 103 1.
[7] West J J, Smith S J, Silva R A 2013 *Nat. Clim. Change* 3 885.
[8] Hirshfeld D S, Kolb J A, 2012 *Environ. Sci. Technol* 46 3697.