

# Study on Emission Factors of FCC Flue Gas Pollutants in Petroleum Refineries

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## Research Article

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# Abstract

Fluid Catalytic cracking (FCC) unit is one of the means to lighten heavy oil in refineries, and its regenerated flue gas is also the main source of air pollutants from refinery. However, it is not clear about the type and amount of pollutants discharged from FCC units. The emissions of regenerated pollutants in the stack flue gases of three typical FCC units in China were investigated in this study, including a partial regeneration unit without a CO boiler (U1), a partial regeneration unit with a CO boiler (U2) and a full regeneration unit (U3). Different monitoring methods were used to analyze the concentration of sulfur dioxide (SO<sub>2</sub>) and nitrogen oxides (NO<sub>x</sub>), and the results showed that Fourier Transform Infrared Spectroscopy (FTIR) monitoring results of SO<sub>2</sub> and NO<sub>x</sub> are approximately 10 times and 5 times larger than that of the Continuous Emission Monitoring System (CEMS) data, respectively. Also, the contents of characteristic pollutants such as NH<sub>3</sub>, C<sub>6</sub>H<sub>6</sub>, HCN, C<sub>8</sub>H<sub>8</sub>, C<sub>2</sub>H<sub>4</sub>, CH<sub>4</sub> and CO were also monitored by FTIR, and the emission factors based on coke burn-off rate and throughput were investigated. The pollutants in U1 exhibited relatively higher contents with the NH<sub>3</sub>, HCN and C<sub>6</sub>H<sub>6</sub> of 116.99, 71.94 and 56.41 mg/Nm<sup>3</sup> in flue gas, respectively. The emission of regenerated pollutants in U2 and U3 are significantly different from U1. Regeneration processes (including coke properties, operating modes and presence or absence of CO boilers) affected pollutants emission factors in varying degree. At last, reasonable emission factors based on the different FCC regeneration processes contributes to the prediction, assessment and control for the pollutants emission.

## 1. Introduction

The FCC is the core process technology for lightening heavy oil in petroleum refining enterprises, and it is also one of the key monitoring sources for the petroleum refining industry. Normally, the FCC catalyst regenerator vent might be the biggest single source of air pollution in an oil refinery. Previous research (Evans and Quinn, 1993) has shown the gaseous flue gas pollutants emitted by the FCC unit are mainly SO<sub>2</sub>, NO<sub>x</sub> and CO, and most units are emitting 300 to 600 ppm for SO<sub>2</sub> as well as generally less than 200 ppm for NO<sub>x</sub> and the CO levels are well under 500 ppm when most units had added a CO incineration boiler to the flue gas system. In recent years, with the increasing proportion of oil refineries processing high-sulfur crude oil and heavy crude oil, the concentration of SO<sub>2</sub>, NO<sub>x</sub> and particulate matter in the regeneration flue gas of catalytic cracking units has been increasing. The FCC is a catalytic process used to upgrade (crack) heavy distillates to form lighter, more useful distillates such as heating oils or gasoline. As a by-product of the cracking reactions, coke is deposited on the catalyst particles. The coke reduces the activity of the catalyst, and the spent catalyst is returned from the FCC reactor is regenerated continuously by burning off coke in the FCC catalyst regenerator. The FCC catalyst regenerator vent releases a wide variety of pollutants, including particulate matters (PM), SO<sub>2</sub>, NO<sub>x</sub>, CO, VOCs, metal hazard air pollutants (HAPs), organic HAPs, and ammonia (US EPA, 2015). These pollutants could have an impact on population health. Despite this critical scenario, few studies have been developed with the objective of fully evaluating pollutant emissions of the FCC catalyst regenerator vent, especially regarding the quantification of pollutant emission sources.

Comprehensive investigations have been performed to evaluate the emission of regenerated pollutants from FCC units in North America and Europe (US EPA, 1995/2008/15; US EPA, 2015; CONCAWE, 2019). The US refinery emission factor method is derived from the EPA's Compilation of Air Pollution Emission Factors (AP-42), which was first published in 1972 and their Emissions Estimation Protocol for Petroleum Refineries in 2015. The basic data established by the air pollutant emission factors of its FCC unit are mainly derived from enterprise survey data, measured data and automatic monitoring data, which are checked and updated every three years. In AP-42, a series of emission factors with different quality levels have been established for users' reference in accordance with the combustion mode, operating conditions, and control technology of FCC unit. The research on the emission factors of atmospheric pollutants in EU refineries began in the 1990s. Its emission factors that has been widely adopted by various member states of the European Union are derived from the European Monitoring and Evaluation Programme/The European Union (EU) emission inventory programme (EMEP/CORINAIR) Air Pollutant Emission Inventory Guide published by the European Environment Agency (EEA) (EEA, 2019). It was the first version in 1996, which has been updated irregularly since then, and has now been updated to the 2019 version. EEA mainly uses data input models such as FCC feed rate, coke combustion rate, and control technology to calculate its air pollutant emission factors. In recent years, with the promotion of some experts and scholars, domestic emission inventories have also begun to be constructed and improved. However, there are only a few researches on the emission factors of refineries, most of which are involved in the study of regional air pollutant emission inventories (Pan et al., 2014; Lu et al., 2018; Sha et al., 2019). These inventories are mainly based on industry emissions, regional or urban emission inventories based on enterprises, and rarely fall into the level of device activity in terms of accuracy. Therefore, the inventories are not dynamic and high-resolution, which is not conducive to traceability and pollutant identification of pollutants. In order to achieve effective control and identification and prediction of pollutants, obtaining characteristic pollutant emission lists based on the reaction device, reaction mechanism models and process conditions is a development trend of environmental monitoring and a major demand for controlling pollutant emissions. A.H. Bhatt et al. (Bhatt et al., 2020) quantifies emission estimates from co-processing raw bio-oil in existing FCC units, which makes our work more significant. It is necessary to figure out the pollutants emission in existing refineries as things are moving towards renewable energy and petroleum refineries would struggle to survive owing to fossil energy.

The formation of these unintentionally produced regenerating pollutants in the FCC unit may be affected by many factors, including properties of feedstocks, catalyst properties, process conditions in the riser-reactor, regeneration types, operating conditions and control devices, etc. To understand influencing factors of pollutants formation progress in a FCC regenerator it is essential to distinguish between the two possible modes of operation: full burn and partial burn. Full burn units run with an excess of air to the regenerator and have low CO emissions. The main species leaving the regenerator are CO<sub>2</sub>, H<sub>2</sub>O, SO<sub>2</sub>, N<sub>2</sub> and NO. Partial burn units run with a deficit of air to the regenerator to produce CO which is subsequently burned in a CO boiler. This boiler usually has supplementary fuel firing. It has been shown that the combustion mode (full regeneration or partial regeneration) of the regenerator and the control device (such as CO boiler) are the main factors that stimulate the formation of regeneration pollutants

(CONCAWE et al., 2009). Also, feedstock, catalyst properties, process conditions in the riser-reactor can affect type and amount of emissions to a certain extent, but analyze all of them in a simultaneous way is very difficult. B. Behera et al. (Behera et al., 2007) have shown in their classic paper that the coke obtained from FCC refineries can be termed as soft and hard coke depending on its solubility, and the nature of these coke species is different depending on feed characteristics, catalyst used as well on process conditions. Thus, for the sake of simplicity, the method used in this study is to summarize the main influencing factors and discuss the impact of these factors on various characteristic pollutants. Three factors are summarized in this study, including coke properties, regeneration types and CO boiler.

Generally, a partial regeneration unit also needs to be equipped with a CO boiler, but according to preliminary investigations, this is not the case. Details on emissions of regenerated pollutants in these installations have not been clearly investigated. Therefore, in this study, the emissions of pollutants from a complete regeneration unit, a partial regeneration unit, and a CO-free boiler regeneration unit were studied.

The effects of different spent catalyst and regeneration type from combustion process on the formation of regenerated pollutants were also compared. And emission factors of regenerated pollutants based the coke burn-off rate and the processing rate in the three FCC units were developed, respectively. The development of emission factors for regenerated pollutants is to accurately estimate the emissions of these regenerated pollutants during the production of FCC units in China. The results may help our understanding the emission of the regenerated pollutants from the FCC units in China, along with the benefits of the possible strategies and techniques to control regenerated pollutants releases during the FCC process.

## **2. Materials And Methods**

### **2.1. FCC Process and basic information concerning the Petroleum Refineries**

Figure 1 presents the reaction scheme of a circulating fluidized bed FCC process. Fresh feedstock oil is mixed with refining oil after heat exchange, heated to 300 ~ 400°C by a heating furnace, and then enters the nozzle in the lower part of the riser reactor. The mixed oil enters the lower part of the riser after being atomized by steam, and contacts the high-temperature catalyst (650 ~ 760°C) from the regenerator, and then gasifies and reacts. The residence time of oil and gas in the riser is very short, usually 2 to 4 seconds. The reacted oil and gas enter the plenum after passing through the cyclone separator, and enter the fractionation system through the top outlet of the settler. Coke-accumulated spent catalyst enters the stripping section underneath the settler, and strips with superheated steam to remove a small amount of oil and gas adsorbed on the surface of the catalytic catalyst, and then passes through the inclined tube. The single-acting sliding valve enters the regenerator and contacts with the air from the bottom of the regenerator to restore the catalyst's activity and release a large amount of heat.

There are two regeneration modes: full regeneration and incomplete regeneration. Among them, complete regeneration refers to the complete combustion of coke under oxygen-enriched, high-temperature conditions. The higher oxygen content in the regenerator is about 3%, and the lower CO content is usually less than 1%. Incomplete regeneration usually exists in a two-stage regeneration process. One of the regeneration processes is carried out under oxygen-depleted and low-temperature conditions. Most of the hydrogen and carbon on the coke react in this zone. The oxygen content in the flue gas is low (usually below 0.5%) and the CO content is high (usually 3% ~ 6%). This process is to ensure that the catalyst will not be hydrothermally deactivated under secondary high temperature conditions. In the industry, incomplete regeneration is usually used in conjunction with CO boilers to achieve complete oxidation of CO and recovery of reaction heat. If there is no CO boiler, it is necessary to use a full regeneration method. By increasing the main air volume and adding CO combustion improver to achieve complete CO oxidation, otherwise it will cause CO combustion in the flue to damage the equipment (Wang et al., 2007). Therefore, three typical FCC units are selected to evaluate the emission factors, and the basic information of these FCC units was shown in Table 1.

Table 1  
Basic information of three typical FCC units

Unit type	Process type	Purification device	Mass flow of feedstock oil (t/h)	Sulfur content in feedstock (g/kg)	Nitrogen content in feedstock (g/kg)	Volume flow of flue gas (m <sup>3</sup> /h)
U1	RFCC	WGS <sup>a</sup>	177	2.40	2.55	184490
U2	ARFCC	WGS + SCR <sup>b</sup>	109	2.87	2.87	177749
U3	MIP	WGS + SCR	142	2.61	3.00	276355

U1: 1.4 million tons / year partially regenerated FCC unit without CO boiler

U2: 1.2 million tons / year partially regenerated FCC unit with CO boiler

U3: 1.6 million tons / year fully regenerated FCC unit

a: Wet Gas System

b: Selective Catalytic Reduction

U1 is the residue fluidized catalytic cracking (RFCC) process, which is a typical FCC process. U2 is the auxiliary riser fluidized catalytic cracking (ARFCC) process, while U3 is the maximum isoparaffin (MIP) FCC process. The RFCC process is basically used for heavy oil cracking, whose heavy fraction, nitrogen and sulfur contents are relative high, leading to high coking degree on catalyst. Compared with the typical FCC process, the ARFCC process reduces the olefin content of catalytic gasoline, and the octane number is basically unchanged or slightly reduced (Guo et al., 2013); MIP can reduce olefin, benzene and sulfur

contents and increase the octane number (Cui et al., 2010). In addition, in the second reaction zone of the MIP process, olefins are converted to more aromatics through hydrogen transfer reactions (Xu, 2002).

## **2.2. Sampling procedures and Instrumental analyses**

In order to obtain accurate monitoring data, during the monitoring period, it is required that the working conditions are stable, whose production load is above 75%, and the environmental protection facilities are operating normally. When the production load is less than 75%, the monitoring staff stops monitoring to ensure the validity of the monitoring data. The whole process quality assurance is implemented in the flue gas detection, and the organized emission source detection technology requires the implementation of the corresponding regulations. The sampling instruments are checked for air tightness and flow calibration before use.

The selected three sets of FCC device exhaust cylinders were chosen for sampling and monitoring. According to the FTIR method, the Gaset Dx-4000 equipment was used to monitor three points twice a day, and the effective monitoring time was 60 minutes each time. It is worth noting that when using the Gaset Dx-4000 device, a particle filter is required to prevent particles from entering the analyzer during sampling, but like most traditional analyzers, there is no need to remove water in the gas cooler. However, the analyzer needs to be heated to prevent condensation. Sick Maihak S810 instrument is used as continues emission monitoring system (CEMS) to monitor the on-line data of FCC flue gas. Nitrogen content is conducted by chemiluminescence method and sulfur content is conducted by ultraviolet fluorescence method. Elemental analysis on spent catalysts was characterized by using Vario EL III elemental analyzer from Elementar, Germany. The Vario EL III is a fully automatic analyzer for C, H, N, S and O elements. Multi-element simultaneous determination and single-element determination can be performed separately by utilizing unique dynamic design and changing different modes. Instrument working conditions: decomposition temperature: 900 ° C ~ 1200 ° C; analysis time: 6 ~ 12 min; sample weighing: 0.02 ~ 1000 mg.

## **3. Results And Discussion**

### ***3.1. Emissions of regeneration flue gas from three typical FCC units***

#### ***3.1.1 FTIR results***

FTIR method could avoid the effect of CO and water vapor with high concentration, and are applicable for the complex compositions flue gas (Luan et al., 2020). In order to find out the emissions of FCC regenerated pollutants, such as whether the pollutant concentration exceeds the limitation, whether the online monitoring data is accurate and whether there are unknown pollutants, the on-site monitoring of typical FCC unit regenerated flue gas was carried out by using the FTIR method. The emission concentrations of regenerated pollutants in the stack flue gases of three typical FCC units are shown in Table 2.

**Table 2 FTIR Monitoring Results of Regenerated Pollutants [mg/m<sup>3</sup>]**

Pollutants		NO <sub>x</sub>	SO <sub>2</sub>	NH <sub>3</sub>	C <sub>6</sub> H <sub>6</sub>	HCN	C <sub>8</sub> H <sub>8</sub>	C <sub>2</sub> H <sub>4</sub>	CH <sub>4</sub>	CO
Projects										
Hourly mean	U1	66.71	86.41	116.99	56.41	71.94	27.79	12.50	164.14	1.48%
	U2	52.22	31.65	5.50	7.13	3.46	9.95	0.98	3.91	0.78%
	U3	60.93	11.96	1.14	0.04	0.01	0.06	0.55	0.00	0.08%

U1: 1.4 million tons / year partially regenerated FCC unit without CO boiler

U2: 1.2 million tons / year partially regenerated FCC unit with CO boiler

U3: 1.6 million tons / year fully regenerated FCC unit

As seen from Table 2, the NO<sub>x</sub> and SO<sub>2</sub> content of U1 are 66.71 and 86.41, respectively, which are the highest among three units. In addition, the FTIR data of three typical FCC units shows that not only SO<sub>2</sub> and NO<sub>x</sub>, which are already well-known pollutants, are present in the catalytic regeneration flue gas, but also find that the FCC flue gas contains methane, ethylene, benzene, styrene, hydrogen cyanide, ammonia and other pollutants. It is noted that the content of NH<sub>3</sub> and HCN are 116.99 mg/m<sup>3</sup> and 71.94 mg/m<sup>3</sup>, respectively, which are much higher than expected. Moreover, some pollutant concentrations have seriously exceeded the limitation. At present, only SO<sub>2</sub>, NO<sub>x</sub> and particles are monitored manually or on-line in most enterprises. Obviously, few kinds of pollutants are monitored, so it is difficult to meet the control requirements of national regulations on pollutant emissions from refineries. But this on-site monitoring results found that there were many unpredicted pollutants of FCC flue gas in these three units, which was a quite noteworthy issue. VOCs are organic compounds that participate in atmospheric photochemical reactions or bring about odor complaint. VOCs are important precursors to form PM<sub>2.5</sub> and O<sub>3</sub>, which can lead to the higher atmospheric oxidizing ability and adversely impair the air quality and human health, meanwhile, FCC units were identified as the largest contributor (Wei et al., 2014). In the process of denitration treatment, a large proportion of excessive ammonia spraying in pursuit of NO<sub>x</sub> emission indicators directly leads to a gas-phase reaction between the gaseous NH<sub>3</sub> evaporating from the ammonia water and the SO<sub>2</sub> in the flue gas, which form a large amount of aerosol discharging into the atmosphere (Huang et al., 2016; Bao et al., 2017). In addition, HCN is acutely toxic via inhalation. Acute oral doses of cyanide cause cardiovascular, respiratory, and neurophysiological changes, and may even damage the brain (IPCS, 2004). Emission factors were developed from the measured HCN emissions from FCC units undertaken by the US EPA in 2011 and performed by Concawe in 2016, respectively (US EPA, 2015; Concawe, 2019). The results confirm that the FCC unit will emit a certain amount of HCN. In addition, FCC units in other refineries in China have hardly carried out similar on-site monitoring, and have not developed the emission inventory of FCC regenerated pollutants. Therefore, it is not clear whether these pollutants exist in other FCC units and what their emission concentrations are. It is worth pondering

whether the "white plume" of FCC unit after flue gas desulfurization which is becoming increasingly public concern is clean or not.

### 3.1.2 SO<sub>2</sub> and NO<sub>x</sub> results

It is found that the on-site monitoring data of FTIR method differed greatly from the online monitoring data of CEMS. Specific data are shown in Table 3.

**Table 3 Monitoring results of SO<sub>2</sub> and NO<sub>x</sub> by FTIR and CEMS [mg/m<sup>3</sup>]**

Project	FTIR	CEMS	
SO <sub>2</sub>	U1	86.41	9.75
	U2	31.65	3.35
	U3	11.96	1.10
NO <sub>x</sub>	U1	66.71	17.50
	U2	52.22	11.39
	U3	60.93	14.98

U1: 1.4 million tons / year partially regenerated FCC unit without CO boiler

U2: 1.2 million tons / year partially regenerated FCC unit with CO boiler

U3: 1.6 million tons / year fully regenerated FCC unit

From the table, the SO<sub>2</sub> and NO<sub>x</sub> content of U1 from FTIR are 86.41 mg/m<sup>3</sup> and 66.71 mg/m<sup>3</sup>, respectively, which are approximately 9 times and 4 times higher than the CEMS data, respectively. Similar results are found for the other two units. The compositions of the exhaust gas are complex and the humidity is high, which will affect the online measurement results of sulfur dioxide and nitrogen oxides. After investigation, all of these three FCC units used wet desulfurization processes (WGS), and the flue gas humidity was about 10 ~ 30%. The measuring principle of the equipment is all cold-dry straight extraction. During the condensation and water removal pretreatment process, most of the sulfur dioxide was absorbed by the ammonia gas and condensate in the flue gas, which caused the sulfur dioxide online monitoring data to be low, or even undetectable. The Ion chromatographic analysis of the condensate water generated during the condensation process of the flue gas confirmed our conjecture later. Detailed studies have been described in our previous works (Luan et al., 2020). In addition, some catalytic regeneration process uses two stages of incomplete regeneration, and there is no supporting construction of CO boiler, resulting in the presence of a large amount of other pollutants such as HCN, NH<sub>3</sub>, CO and VOCs in the flue gas. Due to the presence of many components to be measured in the infrared region, the respective characteristic spectra may overlap when using non-dispersive infrared on-

line measurement, so these pollutants will cause a certain degree of interference to the online monitoring results of  $\text{SO}_2$  and  $\text{NO}_x$ , making the measurement results low. According to the survey (Li, 2013), all of the online monitoring equipment used in FCC units in China are cold-dry straight extraction methods, resulting in that the online monitoring data is much lower than the on-site monitoring data. This makes it difficult for on-site monitors to judge the FCC flue gas emissions.

The analysis results obtained through these monitoring processes show that the FCC flue gas has the risk of exceeding the pollutant emission standard; the online monitoring data of the FCC flue gas is not accurate, and there is a risk of being identified as fraud; there is a risk of incomplete monitoring and unclear number of regenerated pollutants. Therefore, it is necessary to further study the emissions of regenerated pollutants from FCC units and establish emission factors for regenerated pollutants from FCC units.

### ***3.2. Emission factors of Regeneration Pollutants***

The role of emission factors is to provide relatively accurate estimates of the emissions of pollutants when the online monitoring data is inaccurate and incomplete and there is no on-site monitoring data, especially to provide an informative data basis for the development of regional emission inventories. Therefore, it is critical to accurately calculate the emission factor, which is attributed to the issue of a baseline selection, which needs to be highly correlated with the emissions of pollutants. The emission factors of regeneration pollutants in the stack gases from these FCC units were investigated, which will benefit the regeneration pollutant emission inventories of FCC unit.

#### ***3.2.1 Calculation of emission factors***

Generally, all regenerated pollutants production is more closely related to coke burn rate than feed rate, and coke yield varies with feed characteristics; however, if FCC unit feed and operating conditions do not vary significantly, throughput-based emissions factors may be used. Therefore, the two types of emission factors of regeneration pollutants in the stack gases from the individual FCC unit could be calculated separately, one is based on the measured emissions rate (kg/h) of regeneration pollutants divided by the coke burn-off rate (t/hr), the other is based on the measured emissions rate (kg/h) of regeneration pollutants divided by the processing rate (throughput/h). The calculation of the coke burn-off rate is based on the main air flow and dry flue gas composition. First, the main air flow is calculated as the flue gas flow using nitrogen balance, and the dry flue gas volume is calculated by considering the molecular humidity of the air. Then, the coke burn-off rate is calculated by using the composition of the regenerator outlet flue gas. Only two elements of coke and hydrocarbon are considered here, and the combustion rate of carbon and hydrogen are calculated, respectively. Sum of carbon burning rate and hydrogen burning rate is the coke burn-off rate. The corresponding calculation results are shown in Table 4 and Table 5.

#### **Table 4 Emission factors based on the coke burn-off rate of regeneration pollutants (kg/t)**

Pollutants		NO <sub>x</sub>	SO <sub>2</sub>	NH <sub>3</sub>	C <sub>6</sub> H <sub>6</sub>	HCN	C <sub>8</sub> H <sub>8</sub>	C <sub>2</sub> H <sub>4</sub>	CH <sub>4</sub>	CO
Projects										
Emission Factors	U1	1.09	1.41	1.91	0.92	1.17	0.45	0.20	2.68	301.72
	U2	1.54	0.93	0.16	0.21	0.10	0.29	0.03	0.12	287.08
	U3	1.74	0.34	0.03	1.1E-3	3.0E-4	1.7E-3	1.6E-2	0.00	28.49

**Table 5 Emission factors based on the processing rate of regeneration pollutants (kg/t)**

Pollutants		NO <sub>x</sub>	SO <sub>2</sub>	NH <sub>3</sub>	C <sub>6</sub> H <sub>6</sub>	HCN	C <sub>8</sub> H <sub>8</sub>	C <sub>2</sub> H <sub>4</sub>	CH <sub>4</sub>	CO
Projects										
Emission Factors	U1	0.070	0.090	0.122	0.059	0.075	0.029	0.013	0.171	19.3
	U2	0.114	0.069	0.012	0.016	7.58E-3	0.022	2.15E-3	8.57E-3	21.4
	U3	0.151	0.030	0.003	9.93E-5	2.48E-5	1.49E-4	1.37E-3	0	2.48

U1: 1.4 million tons/ year partially regenerated FCC unit without CO boiler

U2: 1.2 million tons/ year partially regenerated FCC unit with CO boiler

U3: 1.6 million tons/ year fully regenerated FCC unit

The emission factors of different pollutants vary greatly for different units, and the emission factors of each pollutant are affected under different degrees by different factors, or these factors have different effects on the pollutant emission factors. By comparing the differences between these three FCC units, the factors that affect the differences in emission factors can be classified into three categories, namely coke properties, regeneration processes and the presence or absence of CO boilers. The specific impact analysis will be discussed in detail in next section.

According to the US EPA AP-42, fifth edition, Vol. 1, Chapter 5: Petroleum industry, Emissions estimation protocol for petroleum refineries -Version 3.0 and the Report No. 4/19 published by CONCAWE, emission factors of regeneration pollutants in the stack gases from FCC unit in the refinery are shown in Table 6:

**Table 6 Emission factors of regeneration pollutants (US EPA, 1995/2008/15; CONCAWE, 2019)**

Pollutants		NO <sub>x</sub>	SO <sub>2</sub>	NH <sub>3</sub>	C <sub>6</sub> H <sub>6</sub>	HCN	NM	CO
Projects							VOC	
Emission Factors	K1	-	-	0.57	1.10E-3	0.43	-	-
	K2	0.235 <sup>a</sup>	1.63 <sup>b</sup>	0.043	5.96E-5	0.023	0.729	45.4
	K3	0.204 <sup>c</sup>	1.41 <sup>d</sup>	0.155	-	-	0.630	39.2

K1 Emission factors calculated based on coke combustion rate (kg/t)

K2 Emission factors calculated based on feedstock mass flow rate (kg/t)

K3 Emission factors calculated based on feedstock volume flow rate (kg/m<sup>3</sup>)

a: The value range is 0.123 ~ 0.481

b: The value range is 0.331 ~ 1.740

c: The value range is 0.107 ~ 1.416

d: The value range is 0.286 ~ 1.505

Among the emission factors for FCC unit regeneration pollutants given in Table 6, the emission factors for NO<sub>x</sub> and SO<sub>2</sub> do not distinguish between the presence and absence of a CO boiler. NH<sub>3</sub>, C<sub>6</sub>H<sub>6</sub>, NMVOC, and CO are considered to be controlled to a negligible level of pollutants after the CO boiler is installed. HCN is relatively special. Europe and the United States have specifically investigated and developed the emission factors of FCCU HCN. For the US EPA, the sets of individual unit emission factors, irrespective of mode of operation, were therefore averaged to provide the final published factors of 0.43 kg HCN/t coke burn and 0.023 kg HCN/kg 1000 unit feed (US EPA, 2015). According to the European Pollutant Release and Transfer Register (E-PRTR) report they developed an emission factor for FCCU HCN of 0.58 kg HCN / t coke burn for full regeneration units and 0.042 kg HCN / t coke burn for partial regeneration units (CONCAWE, 2019). These results indicate that reasonable emission factors should be developed for different pollutants under different conditions. This conclusion is consistent with the above research.

Fig. 2 shows the emission factors based on throughput of regeneration pollutants from investigative three FCC units and AP-42. From the Fig. 2 it can be seen that emission factors of three FCC units and AP-42 are different. This is normal because different raw materials, different reaction-regeneration processes, and differences in downstream pollutant emission control devices can significantly affect the final pollutant emissions. Therefore, the next research should investigate more samples and perform corresponding statistical analysis to obtain a reasonable classification and uncertainty range of emission factors.

### 3.2.2 Effect of regeneration process on emission factors

Fig. 3 shows the emission factors based on the coke burn-off rate and the processing rate of regenerated pollutants from three FCC units, respectively. Different regeneration processes can affect emission factors significantly. The emission factors of the partial regeneration unit without the CO boiler (U1) are generally significantly higher than those of the other two units, and in these two units, the emission factors of the complete regeneration unit (U3) are generally lower than those of the partial regeneration unit with a CO boiler (U2). Generally speaking, a wide range of variables, to varying degrees, affect the regeneration pollutant emissions, such as the refinery crude throughput, coke properties, the process units installed and type of equipment in use, etc. Therefore, this cannot be distinguished only by the presence or absence of CO boilers, but also by the differences in their operation modes and coke properties. The reasons for the different emission levels of each pollutant need to be discussed separately. Here, the typical pollutants  $\text{SO}_2$ ,  $\text{NO}_x$ ,  $\text{NH}_3$ ,  $\text{HCN}$ ,  $\text{CH}_4$ , and  $\text{CO}$  are discussed separately.

To better understand the relationship between pollutant emissions and pollutant precursors on the spent catalysts, the elements contents on the spent coke are analyzed, which is shown in Table 7. From the table, it can be seen that the content of sulfur and nitrogen of C1 are 0.32wt.% and 0.74wt.%, respectively, which is the highest among three catalysts. This means sulfur-containing and nitrogen-containing pollutants from the U1 flue gas may be much higher than the other two. In addition, the emission level of  $\text{SO}_2$  has a significant correlation with the sulfur content in coke, this can easily explain the reason for the high  $\text{SO}_2$  emission factor in U1. As for why the sulfur content of C2 is lower than C3, but the  $\text{SO}_2$  emission in the flue gas in U2 is greater than that of U3. For this phenomenon, it is related to the form of regeneration of U3. U3 is fully regenerated, and Luan et al. (Luan et al., 2020) believes the amount of  $\text{SO}_2$  generated in fully regenerated process is significantly reduced.

**Table 7 Results of spent FCC catalyst elemental analysis**

Contents(wt.%)	C	N	H	S
Sample NO.				
C1	0.84	0.32	0.71	0.74
C2	1.38	0.06	0.41	0.06
C3	1.45	0.09	0.27	0.14

C1: spent catalyst from U1

C2: spent catalyst from U2

C3: spent catalyst from U3

However, the  $\text{NO}_x$  emission factor for U1 is lower than that of the other two devices. This is because most of the coke nitrogen is converted to molecular nitrogen ( $\text{N}_2$ ), even though the presence of coke nitrogen is

an important source of FCC  $\text{NO}_x$  (Concawe, 2009). This means changes in the nitrogen content in the feed and coke will not affect  $\text{NO}_x$  emissions significantly. What really affects  $\text{NO}_x$  emissions is the regeneration type and the presence or absence of a CO boiler. Partial regeneration usually exists in the two-stage regeneration process, which is repeatedly performed under low temperature and oxygen-depleted conditions. The oxygen content is usually less than 0.5%. Most of the hydrogen and carbon on the coke react in this zone, which inhibits the formation of  $\text{NO}_x$  and favours the formation of  $\text{N}_2$  and of more reduced S and N species such as COS,  $\text{H}_2\text{S}$ ,  $\text{NH}_3$  and HCN (Babich et al., 2005; Ju et al., 2020). From Table 4 and Table 5,  $\text{NO}_x$  emission factors of U3 is the highest among three modes, which are 1.74 kg  $\text{NO}_x$ /t coke burn and 0.151 kg  $\text{NO}_x$ /t throughput, respectively. This also confirms that full regeneration will produce more  $\text{NO}_x$ . Previous research (Ju et al., 2020) has shown that pyridinic nitrogen (N-6), pyrrolic nitrogen (N-5), and quaternary nitrogen (N-Q) are the main precursors of nitrogen-containing species, including NO,  $\text{NH}_3$  and HCN etc., during FCC regeneration, different regeneration conditions, such as regeneration temperature and oxygen concentration, could cause these nitrogen-containing compounds to transform into each other. In addition, due to partial regeneration, it produces less  $\text{NO}_x$ , and there is no CO boiler downstream, resulting in that  $\text{NH}_3$ , HCN and other gases cannot be converted to  $\text{NO}_x$  under conditions of high temperature, excess oxygen, and long residence time, and eventually lead to lower  $\text{NO}_x$  emissions in U1. It also explains that the  $\text{NH}_3$  and HCN emission factors of the device are large.

Table 7 shows that the H/C ratio of the three catalysts is 0.85, 0.30, and 0.19, respectively, which is mostly consistent with the literature (Cerqueira et al., 2008) that the coke component on the catalyst usually has an H/C ratio of 0.3 ~ 1.0. The H/C ratio can represent its coking degree because a substance with low H/C ratio may have more condensed rings than that with high H/C ratio (Cerqueira et al., 2008; Behera et al., 2013). So it believes that Cat2 and Cat3 may have more condensed rings. Since aromatic carbon is more stable than aliphatic carbon, during the combustion of coke, it is not easy to decompose into small molecules of hydrocarbons. Thus, U2 and U3 emit less hydrocarbons. From the perspective of regeneration process, on the other hand, VOCs, CO and  $\text{CH}_4$  are formed as the coke is burned in partial burn units. These species leave the regenerator and enter the CO boiler where they are largely converted to  $\text{CO}_2$ . It can be seen from the monitoring results that although there is a CO boiler downstream during partial regeneration, the CO emission concentration in the flue gas may not reach a non-negligible level (< 500 ppm). Under fully regeneration conditions, most of the C and H substances on the coke will be completely burned to form  $\text{CO}_2$  under sufficient oxygen conditions, resulting in less VOCs, CO and  $\text{CH}_4$ . Thus, the VOCs, CO and  $\text{CH}_4$  content in U1 is high, while U2 has less VOCs, CO and  $\text{CH}_4$  and U3 has the least.

To sum up, the emission factors of FCC unit regeneration pollutants need to be distinguished from the types of coke properties, regeneration modes, and pollutant control devices. The emission factors of each pollutant are also affected by each type of impact differently. Reasonable emission factors need to be developed based on the specific circumstances.

## 4. Conclusions

The emission concentrations and emission factors of regenerated pollutants from three typical FCC units in China have been investigated. Overall, the emissions of SO<sub>2</sub> and NO<sub>x</sub> vary greatly by different monitoring methods. FCC flue gas contains lots of non-regular pollutants, such as methane, ethylene, benzene, styrene, hydrogen cyanide, ammonia, etc., and the emission concentrations of these pollutants exhibited obvious differences among the tested three FCC units. In addition, the emission factors of pollutants based on coke burn-off rate and throughput in the three FCC units were also estimated for emission inventory in China. The results showed that SO<sub>2</sub> emission factor, take SO<sub>2</sub> as an example, based on coke burn-off ranged from 0.34 kg/t to 1.41 kg/t and the factor based on throughput ranged from 0.030 kg/t to 0.090 kg/t, which suggested that FCC types affected emission factor significantly. According to the results of emission factors, it is found that emission of these pollutants had correlations with FCC regeneration process (coke properties, operating mode and presence or absence of CO boiler). Sulfur contents and H/C ratio of coke can significantly affect the emissions of SO<sub>2</sub> and hydrocarbons in FCC flue gas, respectively. Different regeneration processes also have a significant impact on the pollutant emission factors. There are more NO<sub>x</sub> emissions during full regeneration, more HCN and NH<sub>3</sub> emissions during partial regeneration, and coke burning intensity of the partial regeneration is much larger, so VOCs emitted are also relatively high. CO boiler is sure to reduce emissions of most pollutants to a certain extent. It suggested that the refinery should try to match the CO boiler to reduce the emissions of pollutants such as CO, VOCs, HCN and NH<sub>3</sub>. Also, the emission factors developed in this study can help refineries quantify emission estimates for FCC process optimization such as co-processing raw bio-oil activities.

## Declarations

**Authors' contributions** Hui Luan: conceptualization, writing - original draft, methodology. Cong Wu: writing - original draft, methodology, visualization. Feng Ju: revision, resources, funding acquisition. Guangli Xiu: conceptualization, project administration, writing - review & editing. Hao Ling: formal analysis. Helin Pan: formal analysis.

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**Data availability** Not applicable for that specific section.

**Compliance with ethical standards**

**Conflict of interest** The authors declare that they have no competing interests.

**Ethical approval** This article does not contain any studies with human participants or animals performed by any of the authors.

**Consent to participate** The authors declare consent to participate.

**Consent to publish** The authors declare consent to publish.

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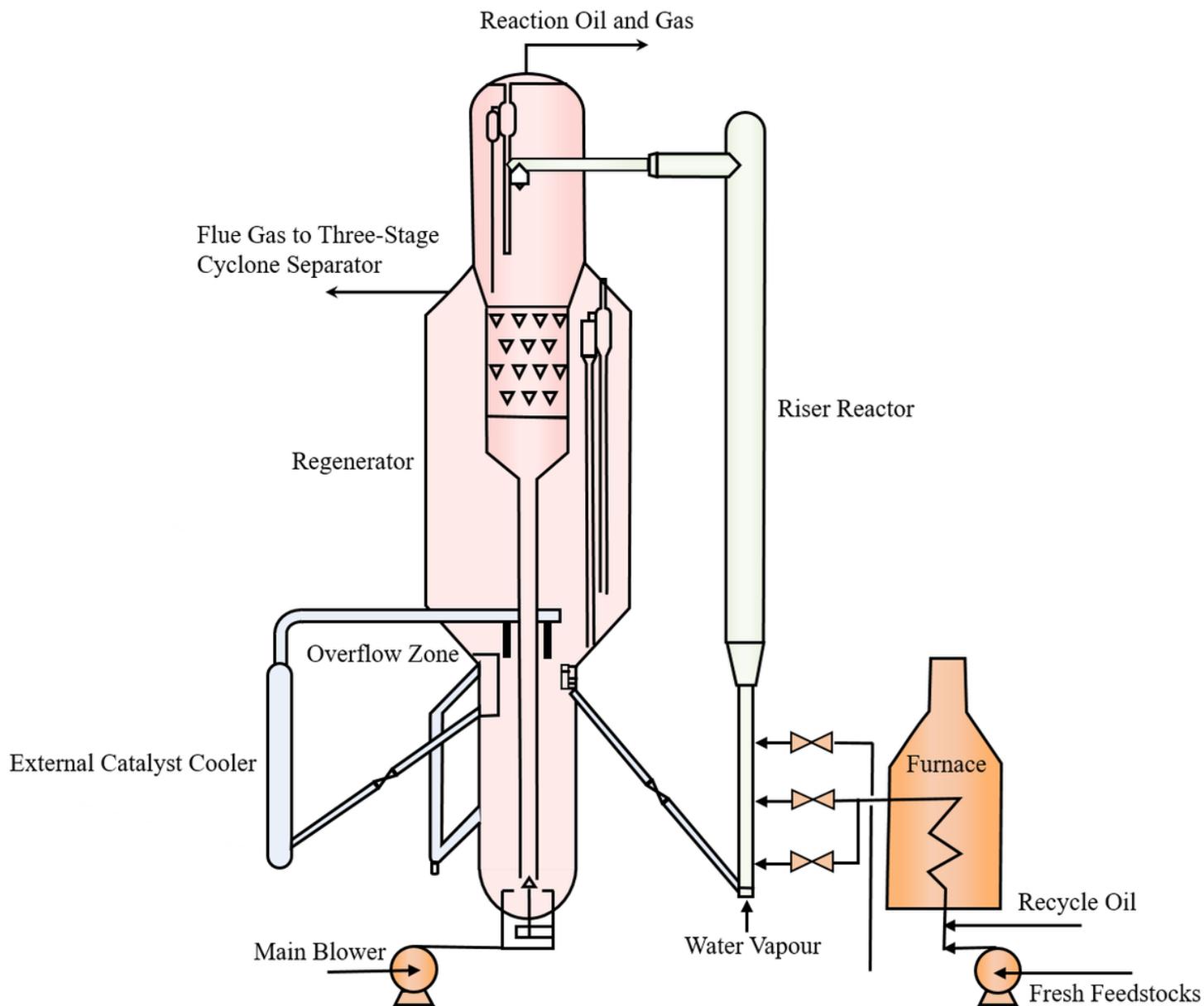
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## Figures



**Figure 1**

the reaction scheme of a circulating fluidized bed FCC process

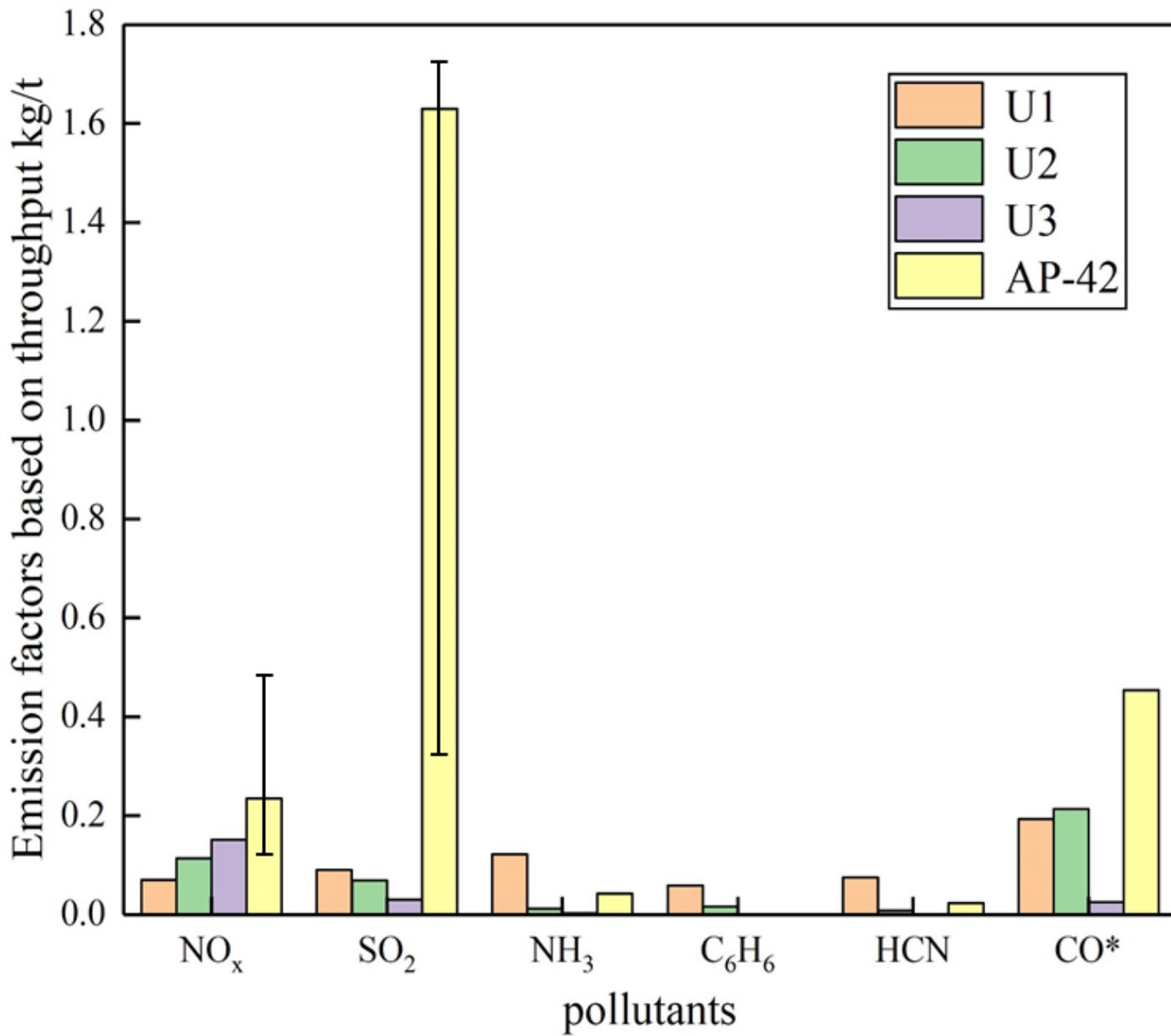
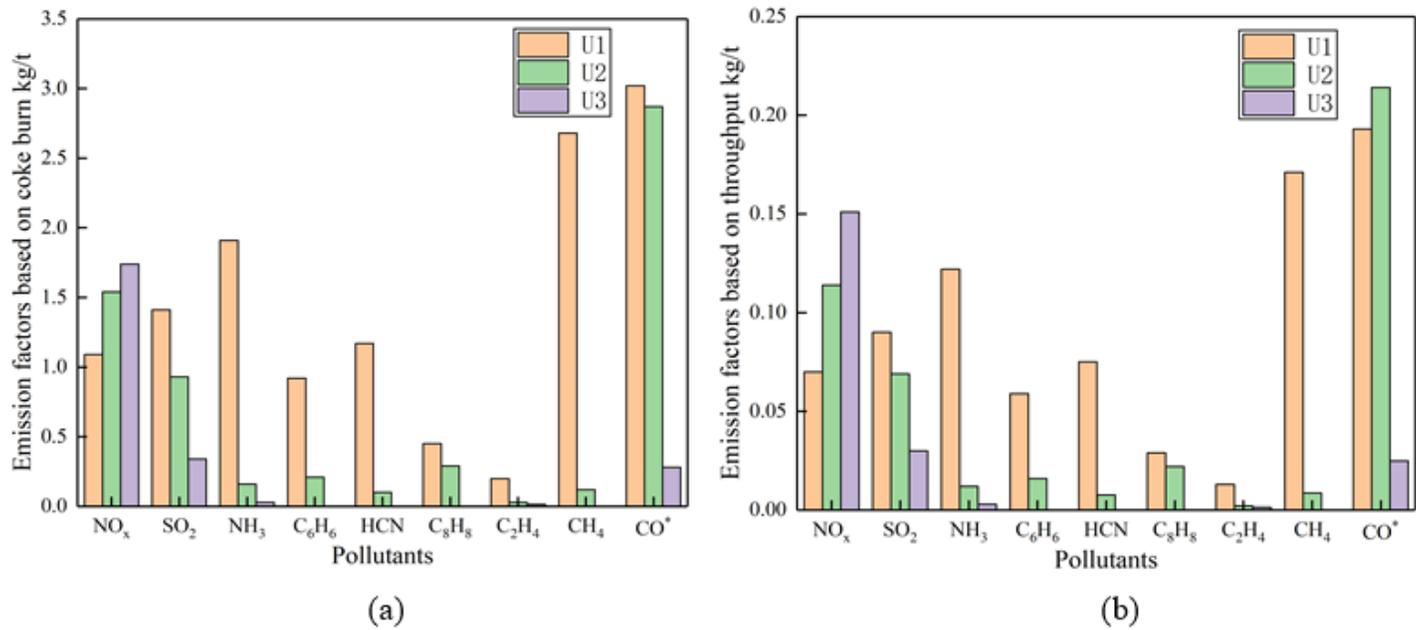


Figure 2

Emission factors of regeneration pollutants based on throughput (kg/t)



**Figure 3**

Emission factors of regeneration pollutants: (a) Based on coke burn (b) Based on throughput U1: 1.4 million tons/ year partially regenerated FCC unit without CO boiler U2: 1.2 million tons/ year partially regenerated FCC unit with CO boiler U3: 1.6 million tons/ year fully regenerated FCC unit \*: It notes that the emission factor of CO is reduced by a factor of 100