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Characteristics and ozone formation potential of volatile organic compounds in emissions from a typical Chinese coking plant

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ABSTRACT

Coking industry is an important volatile organic compounds (VOCs) emission source in China, however, detailed information on VOCs emissions is lacking. Therefore, we selected a typical mechanized coking plant and collected air samples according to the Emission Standard of Pollutants for Coking Chemical Industry (GB16171-2012). Using gas chromatography-mass spectrometry method, we analyzed the VOCs in the air samples, and applied maximum increment reactivity (MIR) rule to estimate ozone formation potential (OFP) of the VOCs emitted from the coke production. More than 90 VOCs species were detected from the coking plant, including alkanes, alkenes, alkynes, aromatic hydrocarbons, halogenated hydrocarbons and oxygenated VOCs. The concentrations of VOCs ($\rho(\text{VOCs})$) generated at different stages of the coking process are significantly different. $\rho(\text{VOCs})$ from coke oven chimney had the highest concentration (87.1 mg/m³), followed by coke pushing (4.0 mg/m³), coal charging (3.3 mg/m³) and coke oven tops (1.1 mg/m³). VOCs species emitted from the coke production processes were dominated by alkanes and alkenes, but the composition proportions were different at the different stages. Alkenes were the most abundant emission species in flue gases of the coke oven chimney accounting for up to 66% of the total VOCs, while the VOCs emissions from coke pushing and coal charging were dominated by alkanes (36% and 42%, respectively), and the alkanes and alkenes emitted from coke oven top were similar (31% and 29%, respectively). Based on above results, reduction of VOCs emissions from coke oven chimney flue gases is suggested to be an effective measure, especially for alkenes.

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Introduction

Volatile organic compounds (VOCs) are a class of organic compounds that do not have a uniform worldwide definition. VOCs usually refers to all organic compounds that have melting

points below room temperature and boiling temperatures less than 50–260°C on the standard atmospheric pressure. They include alkanes, alkenes, alkynes, aromatics, alcohols, aldehydes, ethers, ketones, esters, halogenated hydrocarbons, and others (State Council of the People's Republic of China, 2017). Ambient VOCs contribute substantially to the formation of ozone and secondary organic aerosols (Guo et al., 2017; Zhang et al., 2017, 2015; Chen and Luo, 2012; Zhou et al., 2011; Geng et al., 2008) and have a negative impact on human health (Gong et al., 2017; Ramfrezn et al., 2012; Goldstein, 2010;

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Parra et al., 2006). For example, 1,3-butadiene and benzene are known carcinogens. Rapid economic and industrial development in past decades has caused serious air pollution in China. In addition to the primary pollutants directly emitted, air quality in China today is also seriously affected by fine particles ($PM_{2.5}$) and photochemical smog (O_3), which are formed by secondary reactions. VOCs have also received increased attention, and the Chinese Central Government has implemented a system of countermeasures to improve ambient air quality and protect human health. China's "13th Five-Year Plan" requires total VOCs emissions to be reduced by 10% between 2015 and 2020 (State Council of the People's Republic of China, 2017). VOCs are emitted into the atmosphere from anthropogenic and biogenic sources (Scientific Assessment of Ozone Depletion, 1994; Guenther et al., 1995, 2000; Sawyer et al., 2000; Placet et al., 2000). Anthropogenic emission sources include solvent utilization, vehicles, and incomplete combustion etc., but a very important emission source is industrial processes (McCarthy et al., 2013; Yang, 2012; The Coke Oven Managers' Association, 2007). Coke production is a major source of emissions (Wang, 2014; Wang et al., 2008), and contributes more than 10% of the total industrial VOCs emissions in China (Wu et al., 2016). Previous studies have demonstrated the harmful effects VOCs emissions from the coking industry have on human health (He et al., 2015; Bieniek, 2010; Contini, 2006; Strunk et al., 2002; Blanka et al., 1998). In China the coking industry is well developed, and is the largest coke supplier in the world, accounting for more than 70% of global production (National Statistics Bureau of the People's Republic of China, 2017; Ministry of Ecology and Environment of the People's Republic of China, 2017). Reducing VOCs emissions from the coking industry is vital to achieving the 2020 emission reduction targets to improve air quality, and China has taken integrated measures to reduce air pollutant emissions from the coking industry. For example, the emission standards for air pollutants including VOCs from coke production in China were published in 2012 and strict emission standards were implemented in the Beijing-Tianjin-Hebei region (GB 16171-2012). Yet few studies have analyzed the characteristics of VOCs from coke production, and so our main research objective is to characterize these emissions and to evaluate ozone formation potential so that more efficient pollution control measures for reducing VOCs emissions can be scientifically supported.

VOCs are emitted from both stationary and fugitive emission sources of coke production (Shi et al., 2015), and the concentration and species of VOCs are very important to characterize their emissions (Bo et al., 2008). Scholars in China and elsewhere have studied VOCs emission characteristics from coke production. He et al. (2005) analyzed VOCs in the atmosphere outside a mechanical coking plant using the gas chromatography-mass spectrometry (GC/MS) method, and detected 17 VOCs including benzenes, alkanes, halogenated hydrocarbons, and terpenes. VOCs concentration was 0.2285 mg/m^3 , and benzene was the most abundant species. Aries et al. (2007) tested the fugitive emissions from coke oven tops and coal charging in Dawes Lane Coking Plant, UK and detected 16 VOCs, mainly aromatic hydrocarbons, of which benzene was the most abundant specie. For a JN43-80 coke oven, Jia et al. (2008) analyzed VOCs fugitive emissions by the GC/MS method, and detected 68 VOCs species. The VOCs concentration with concentrations in coal charging of about 4.185 mg/m^3 . Ciaparra et al. (2009) used DOAS technology to monitor benzene, toluene and xylene in the air of the Corus Coking Plant, UK, and found mean concentrations of benzene, toluene and xylene of about 0.0280, 0.0145 and 0.0057 mg/m^3 , respectively. Li et al. (2014) analyzed VOCs from fugitive emission and coal charging flue gas in a

Mechanized-Coke Wet Quenching (CWQ) Coking Plant, identifying 55 VOCs species, including alkanes, alkenes, aromatic hydrocarbons and alkynes. VOCs concentration on the coke oven tops were about $0.9028 \pm 0.1671 \text{ mg/m}^3$, and in the flue gas from both coal charging and coke discharging were about $2.233 \pm 0.534 \text{ mg/m}^3$. Dong et al. (2016) studied VOCs fugitive emissions in a coking plant by GC/MS combined with a portable VOCs detector, and recorded 51 VOCs species including alkanes, alkenes, halogenated hydrocarbons, benzenes, and oxygenated compounds. Li et al. (2019) systematically sampled and analyzed the industrial process in a Coke Dry Quenching (CDQ) Coking Plant and identified 102 VOCs including alkanes, alkenes and halogenated hydrocarbons by GC/MS. VOCs concentration in the coke oven flue gas was the highest (527.5 mg/m^3), followed by coal charging (237.6 mg/m^3), coke pushing (235.5 mg/m^3) and dry quenching (188.8 mg/m^3).

Current studies mainly focus on ambient air fugitive emissions, and less on flue gas in chimney emissions. According to GB 16171-2012 "Emission Standards for Pollutants for Coking Chemical Industry" (Ministry of Ecology and Environment of the People's Republic of China, 2007a), VOCs emissions from coal charging, coke pushing, coke oven chimneys and coke oven tops are the most important. In summary, until now, only Li et al. (2019) systematically monitored the industrial process in a CDQ coking plant, and from 17 to 102 VOCs species have been identified. Therefore, we selected a CWQ coking plant, and systematically sampled coke oven chimney, coal charging, coke pushing and coke oven top emissions according to GB 16171-2012, and conducted a multi-species analysis using the GC/MS method, to provide scientific data for VOCs emission reduction and control in the current Chinese coking industry.

1. Materials and methods

1.1. Sampling and analysis

Sampling was carried out at a representative coke plant in Hebei province, China, located approximately 400 km south of Beijing. The plant has a large production capacity with an annual coke output of 3180 Gg. It has a typical Side-mounted tamping CWQ Furnace and possesses four coke ovens with coke wet quenching. The plant is equipped with coke and dust removal equipment used in the process of coal charging and pushing, and has a ground observation station. The sampling site and the studied coking plants are illustrated in Fig. 1. According to the Emission Standard of Pollutants for Coking Chemical Industry (GB16171-2012), four air sampling points were established, including the flue gas in the coke oven chimney, coal charging, coke pushing, and also the fugitive emission on the coke oven top. Sampling was carried out based on the "Technical specifications for emission monitoring of stationary source (HJ/T 397-2007)" (Ministry of Ecology and Environment of the People's Republic of China, 2007b). Collection of the flue gas samples in the chimney was based on the "Emission from stationary sources-Sampling of volatile organic compounds-Bags method (HJ 732-2014)" (Ministry of Ecology and Environment of the People's Republic of China, 2019). For ease of transportation, air sampling bags were replaced by 3.2 L stainless steel SUMMA canisters (Entech Instrument, Inc., USA). When VOCs sampling was carried out in the coke oven chimney, coal charging and coke push, a portable pump (libra plus-7, BUCK, USA) was used to extract the air, and simultaneously some quartz cotton was added at the front of the filter to remove dust in the flue gas air. The air sampling flow was controlled at about 2 L/min by a flow restrictor. As coke pushing and coal charging are discontinu-

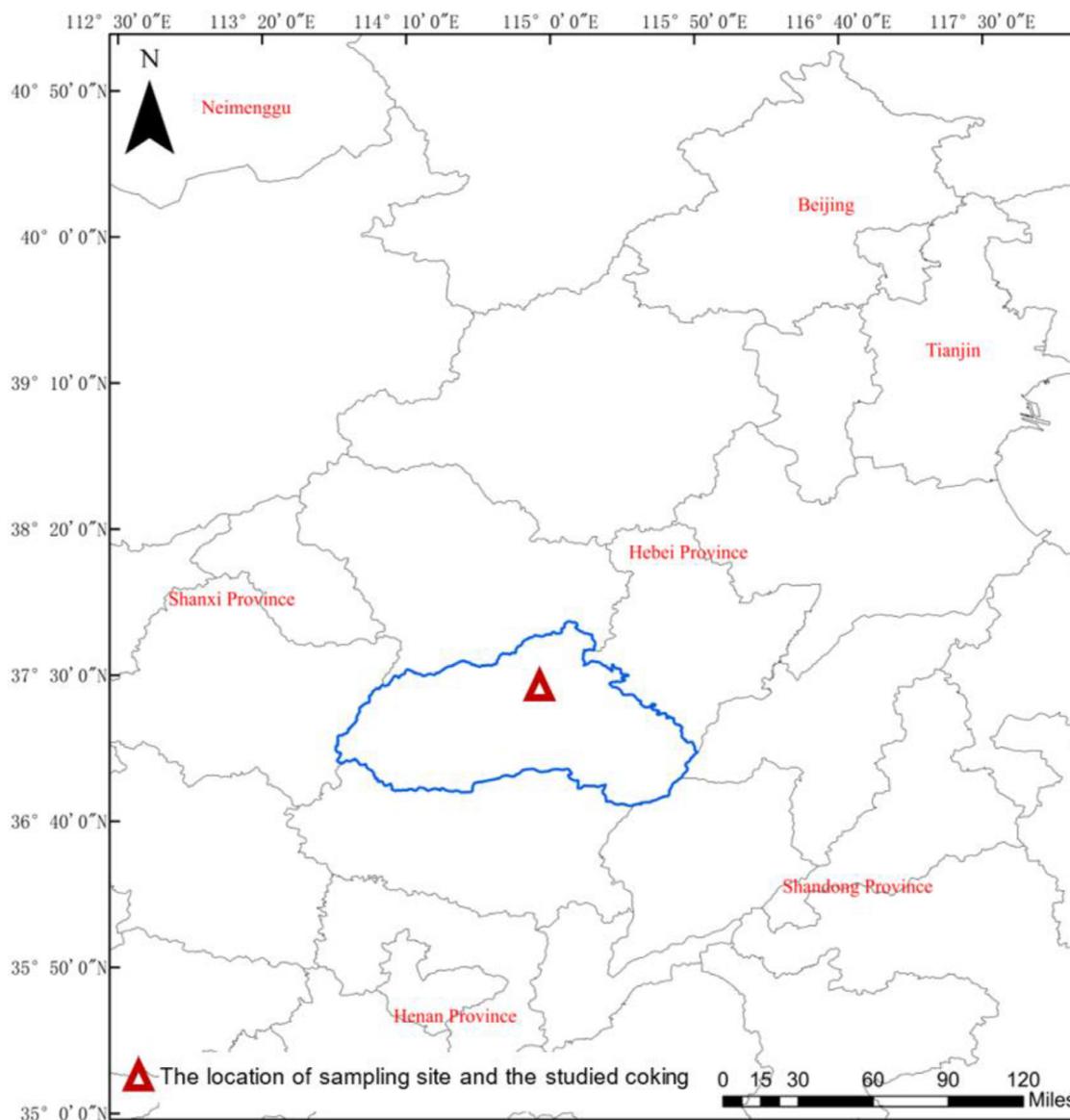


Fig. 1 – Location of sampling site and the studied coking plant.

ous discharges, a flue gas comprehensive analyzer (Testo 350-Pro, Testo Company, Germany) was used to measure observed flue gas changes. The VOCs sample on the coke oven top was collected using a transient method. To be representative, the air samples were collected on a day when the operational capacity of the plant exceeded 85% of the rated value. Sampling was carried out from 23 to 29 August 2018 when the ambient air quality was good. The wind speed was less than 2 m/sec, and the air temperature was between 20 and 32°C. Using the GC/MS method, we analyzed the VOCs in the air samples.

1.2. VOCs analysis

VOCs analysis was conducted according to the methods of “Determination of volatile organic compounds in ambient air - Tank sampling / gas chromatography - mass spectrometry (HJ759-2015)” (Ministry of Ecology and Environment of the People’s Republic of China, 2015). Whole samples were pre-treated on an Entech concentrator (7100A, Simi Valley, USA) at a constant rate manipulated by a mass flow controller (MFC). After removing water and CO₂ from the air samples, VOCs

species were separated by gas chromatography (7890, Agilent, USA) and quantified by a quadruple mass spectrum detector (MSD, 5975C, Agilent, USA) with a total ion scanning mode. The 56 USA Photochemical Assessment Monitoring Stations (PAMS) target hydrocarbons and the 64 VOCs species determined by the TO-15 method were identified and quantified by GC-MSD using a gas mixture (TO-15, Spectra gases Inc., USA). Overall, 102 species of VOCs in the air samples were recognized (Table 1). Rigorous quality control and assurance procedures were adopted. To qualify the species of VOCs, two standard gases were used, and they are, respectively. For instrument, the format is (Model, Company, Nation) and TO-15 from the Scott Specialty gases company in USA, and the deviations of GC-MSD sensitivities for the same VOCs species were within 20%. At the same time four internal standards (1,4-difluorobenzene, bromochloromethane, bromofluorobenzene, and chlorobenzene-d₅, from the Environmental Technology Center, Canada) were used too. For each species, the range of the method detection limit of the online GC-MSD was within 0.004–0.070 ppbV. Details of the analysis system can be found elsewhere (Li et al., 2019).

Table 1 – Species of VOCs measured in this study.

No.	Species	No.	Species	No.	Species
Alkanes (29)					
1	Ethane	36	Isopropylbenzene	71	Methyl methacrylate
2	Propane	37	<i>n</i> -Propylbenzene	72	Hexanal
3	Isobutane	38	3-Ethyltoluene	73	<i>n</i> -Butyl acetate
4	<i>n</i> -Butane	39	4-Ethyltoluene	Halocarbons (27)	
5	Cyclopentane	40	1,3,5-Trimethylbenzene	74	CF ₂ Cl ₂
6	Isopentane	41	2-Ethyltoluene	75	C ₂ F ₄ Cl ₂
7	<i>n</i> -Pentane	42	1,2,4-Trimethylbenzene	76	Chloromethane
8	2,2-Dimethylbutane	43	1,2,3-Trimethylbenzene	77	Chloroethylene
9	2,3-Dimethylbutane	44	1,3-Diethylbenzene	78	C ₂ F ₃ Cl ₃
10	3-Methylpentane	45	1,4-Diethylbenzene	79	1,1-Dichloroethylene
Alkenes (11)					
11	2-Methylpentane	46	Ethene	80	Dichloromethane
12	<i>n</i> -Hexane	47	Propene	81	1,1-Dichloroethane
13	Cyclohexane	48	<i>trans</i> -2-Butene	82	<i>cis</i> -1,2-Dichloroethylene
14	Methylpentane	49	1-Butene	83	Chloroform
15	2-Methylhexane	50	<i>cis</i> -2-Butene	84	1,1,1-Trichloroethane
16	2,4-Dimethylpentane	51	1,3-Butadiene	85	Carbon tetrachloride
17	2,3-Dimethylpentane	52	1-Pentene	86	1,2-Dichloroethane
18	3-Methylhexane	53	<i>trans</i> -2-Pentene	87	Trichloroethylene
19	2,2,4-Trimethylpentane	54	Isoprene	88	1,2-Dichloropropane
20	2,3,4-Trimethylpentane	55	<i>cis</i> -2-Pentene	89	Dichlorodibromomethane
21	Methylcyclohexane	56	1-Hexene	90	<i>trans</i> -1,3-Dichloropropene
Oxygenated VOCs (17)					
22	<i>n</i> -Heptane	57	Acrolein	91	1,1,2,2-Tetrachloroethane
23	2-Methylheptane	58	Propanal	92	Tetrachloroethylene
24	3-Methylheptane	59	Acetone	93	1,4-Dichlorobenzene
25	Octane	60	Ethyl acetate	94	Chlorobenzene
26	<i>n</i> -Nonane	61	Methyl tert-butyl ether (MTBE)	95	Bromoform
27	<i>n</i> -Decane	62	Methacrolein	96	1,1,2-Trichloroethane
28	<i>n</i> -Undecane	63	Vinyl acetate	97	1,3-Dichlorobenzene
29	Dodecane	64	<i>n</i> -Butanal	98	1,2-Dibromoethane
Aromatics (16)					
30	Benzene	65	Methyl vinyl ketone	99	Benzylchloride
31	Toluene	66	Methylethylketone	100	1,2-Dichlorobenzene
32	Ethylbenzene	67	Ethyl acetate	Alkyne (1)	
33	<i>m</i> -Xylene / <i>p</i> -Xylene	68	2-Pentanone	101	Ethyne
34	<i>o</i> -Xylene	69	<i>n</i> -Pentanone	Nitriles (1)	
35	Styrene	70	3-Pentanone	102	Acetonitrile

2. Results and discussion

2.1. VOCs emission characteristics from coke production

A total of 93 VOCs species including 28 alkanes, 11 alkenes, 16 aromatics, 27 halocarbons, 1 alkyne and 13 oxygenated VOCs in the air samples were detected (Fig. 2). VOCs concentrations, in descending order, were coke oven flue (87.1 mg/m³), followed by coke pushing (4.0 mg/m³), coal charging (3.3 mg/m³), and fugitive emission on the coke oven top (1.1 mg/m³). Li et al. (2014) found VOCs concentrations of coal charging and coke oven flue gas were 2.233 ± 0.534 mg/m³, and that of the coke oven top was 0.903 ± 0.167 mg/m³. Furthermore, Li et al. (2019) found VOCs concentration of coke oven flue gas, coal charging and coke pushing were 527.5, 237.6 and 235.5 mg/m³, respectively. Our results are in the middle of the above reported studies owing to the different industrial production process and pollution control countermeasures of the three tested companies.

VOC species concentrations were calculated for all of the air samples. VOC species emitted from the coke production processes were dominated by alkanes and alkenes, but the composition proportions were different at the different stages (Fig. 3). Alkenes were the most abundant emission species in flue gases of the coke oven chimney accounting for up

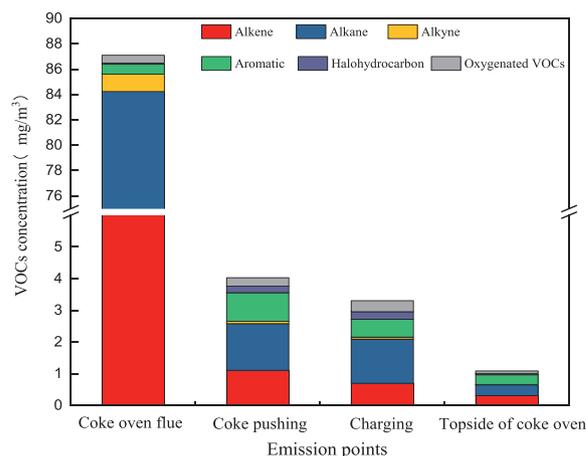


Fig. 2 – Comparison of VOCs concentration levels during the coking process.

to 66% of the total VOCs, while the alkanes accounted for 30%, and other species (alkynes, aromatic hydrocarbons, oxygenated VOCs and halogenated hydrocarbons) were relatively rare.

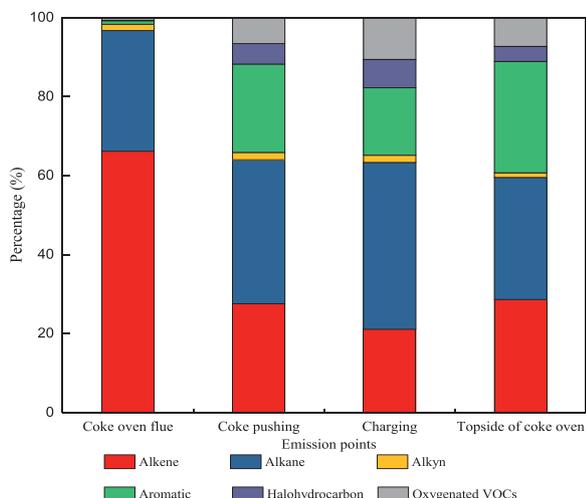


Fig. 3 – VOCs species composition in different stages of the coking process.

VOCs species composition in coke pushing, coal charging and coke oven top were similar. VOCs in coke pushing and coal charging are mainly alkanes (42% and 36%, respectively), of which alkanes > alkenes > aromatics > oxygen VOCs > halogenated hydrocarbons > alkynes, while the proportion of alkanes, alkenes and aromatic hydrocarbons in VOCs at the top of coke ovens was close to 31%, 29% and 28%, respectively. These differences indicate that the flue gas emitted from the coal charging and coke pushing is derived from the decomposition

combustion of coal and the hot coke emissions introduced by the carbonization chamber. Moreover, the proportion of alkanes in the coal loading is greater than that in the coke pushing, while for alkenes and aromatic hydrocarbons the proportion is reversed. This is mainly caused by the pyrolysis of alkanes into alkenes or aromatization into aromatic hydrocarbons after high-temperature combustion in the carbonization chamber.

2.2. Identification of VOCs characteristic pollutants at different stages of the coking process

The top 6 VOC species emission from coke oven chimney, coke pushing, coal charging and coke oven top are alkanes, alkenes and aromatic hydrocarbons, respectively (Fig. 4). The main alkanes are ethane and propane, alkenes are ethylene and propylene, and aromatic hydrocarbons are benzene and toluene, in addition to alkyne (acetylene) and oxygenated VOCs (acetaldehyde, acetone). In the coal charging, dichlorobromomethane and 1,1-dichloroethylene were the unique VOCs species detected, and subsequent experiments will be carried out for verification.

Some studies have identified the main sources of VOCs by means of the mass concentration ratio BTEX (combined of benzene (B), toluene (T), ethylbenzene (E) and xylene (X)). When B/T ($\rho(\text{benzene})/\rho(\text{toluene})$, the same below) is 0.5, VOCs are mainly from motor vehicle exhausts (Pfeffer, 1994). In our study, the B/T of coke oven chimney, coke pushing, coal charging and coke oven top are 8.10, 1.63, 2.10, 5.33, respectively. These B/T ratios in all coking process stages are all greater than 1, which is much higher than that of a vehicle emission source. Among them, the B/T of the coke oven top is 5.33, which is in good agreement with previous research results. Additionally, in view of the abundant emissions of ethylene,

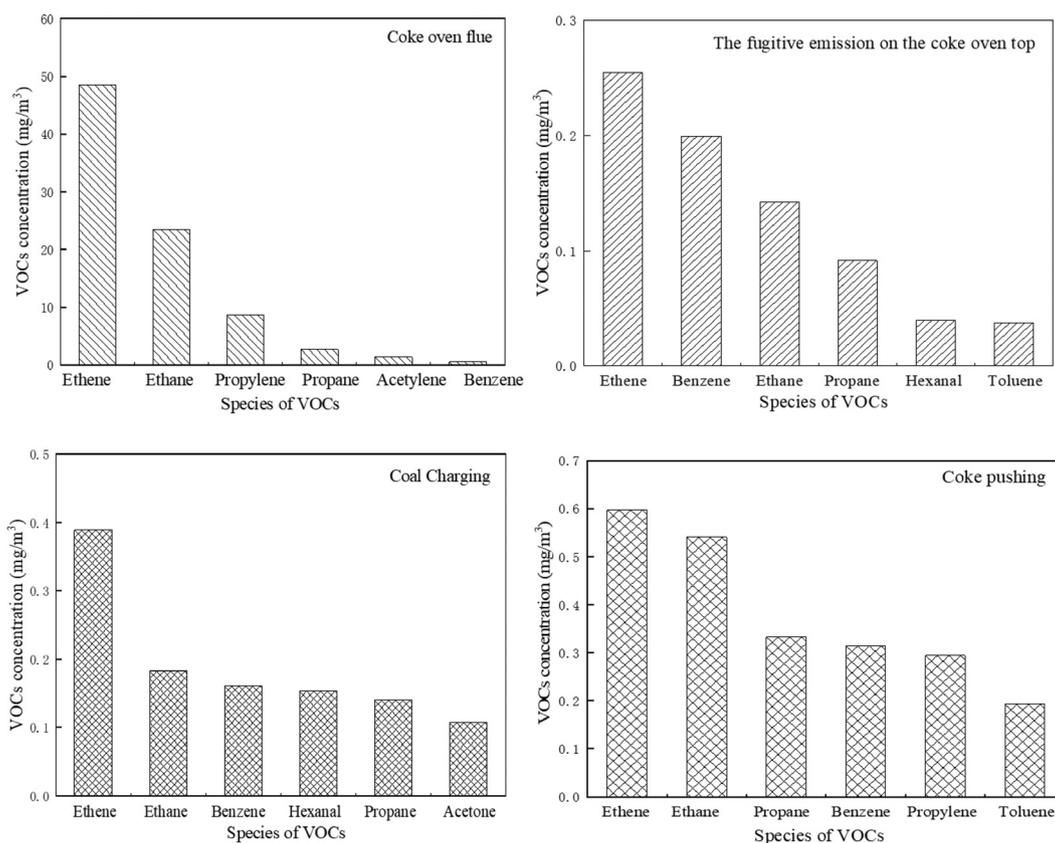


Fig. 4 – Top 6 kinds of VOCs emitted from different stages of the coking process.

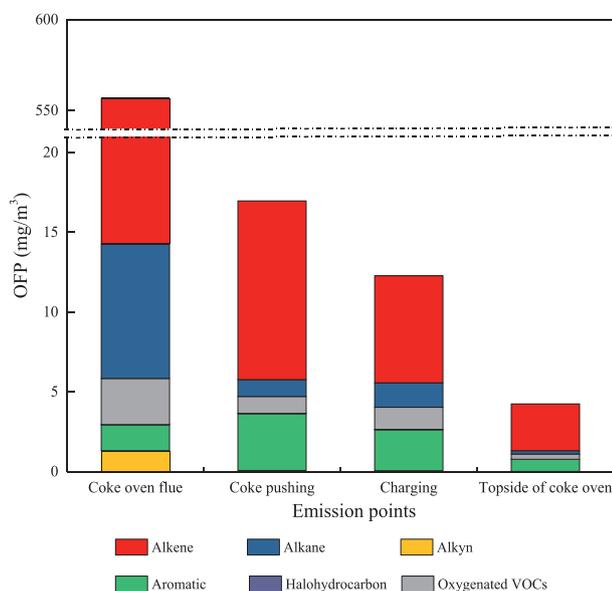


Fig. 5 – Ozone formation potential (OFP) during the coking process.

ethane and propane at each stage of the coking process, we conducted an exploratory analysis of characteristic species ratios. We found that the ratios of ethane: propane: ethylene (the ratios of the three mass concentrations) in the VOCs emissions at different stages of the coking process were significantly different. The characteristic ratio of ethane: propane: ethylene in the VOCs emission of the coke oven chimney was 9:1:19, coke pushing 4:3:5, coal charging 1:1:2, and coke oven top, 2:1:3.

2.3. Chemical reactivity evaluation

VOCs reactivity refers to the potential of an organic substance to form a product or generate O_3 through reaction. The VOCs compositions emitted at different stages of the coking production process are different, and the chemical reactivity is quite different (Derwent et al., 1998). For VOCs species with low-reactivity, even if its atmospheric concentration is high, it is not necessarily an important precursor of O_3 . Conversely, even if the concentration of VOCs species with high-reactivity is low, it may have an important contribution to O_3 production (Tang et al., 2006). At present, there are several evaluation indicators for VOCs reactivity, and different scholars use different methods according to actual conditions (Chen et al., 2017; Zhang et al., 2012; Zeinali et al., 2011; Martien, 2003; Carter, 2010, 1996). Therefore, to evaluate the environmental effects of VOCs emitted from the coke production in different stages, we used the VOCs MIR method, as this is used in the California state regulations and administrative rules (California air resources board, 2017).

The OFP characteristics of VOCs emission from the coke production in different stages is coke oven chimney > coke pushing > coal loading > coke oven top, which agrees well with the $\rho(\text{VOCs})$ of different emission processes (Fig. 5). The reason is that, in daily management, in addition to strengthening the total emission reduction of VOCs, we must also pay attention to the control of species with higher O_3 production potential. From the analysis results, the coke oven chimney is the key process of VOCs emission reduction in coking plants. Alkenes are the key emission reduction species, especially ethylene, propylene, butene and 1,3-butadiene. In addi-

tion, acetaldehyde, benzene, and toluene, also require close attention.

3. Conclusions

(1) VOCs emitted by a wet quenching coking plant include alkanes, alkenes, alkynes, aromatic hydrocarbons, halogenated hydrocarbons and oxygenated VOCs, constituting more than 90 species. The $\rho(\text{VOCs})$ emissions from the coke production processes in different stages are significantly different. Among them, $\rho(\text{VOCs})$ emissions of coke oven chimney are the highest (87.1 mg/m^3), followed by coke pushing (4.0 mg/m^3), coal charging (3.3 mg/m^3) and coke oven top (1.1 mg/m^3).

(2) VOCs species emitted from the coke production processes were dominated by alkanes and alkenes, but the composition proportions were different at the different stages. Alkenes were the most abundant emission species in flue gases of the coke oven chimney accounting for up to 66% of the total VOCs, while the VOCs emissions from coke pushing and coal charging were dominated by alkanes (36% and 42%, respectively), and the alkanes and alkenes emitted from coke oven top were similar (31% and 29%, respectively). Based on the results of the emission characteristics and the maximum incremental reactivities of VOCs emissions at different stages, reduction of VOCs emissions from coke oven chimney flue gases is suggested to be an effective control measure for VOCs emission from coke production, especially for alkenes, including ethylene, propylene, butene and 1,3-butadiene. Additionally, acetaldehyde, benzene, and toluene cannot be neglected.

(3) The B/T of coke oven chimney, coke pushing, coal charging and coke oven top are 8.10, 1.63, 2.10, 5.33, respectively, which is considerably higher than that of vehicle emissions. Furthermore, the characteristics of ethane: propane: ethylene in VOCs emitted from different coke production stages are significantly different. The characteristic ratio of ethane: propane: ethylene in VOCs of coke oven chimney is 9:1:19, coal pushing 4:3:5, coal charging 1:1:2, and on the coke oven top it is 2:1:3. These results are of great significance for the accurate traceability of VOCs.

Declaration of competing interest

This manuscript “Characteristics and Ozone Formation Potential of Volatile Organic Compounds in Emissions from a Typical Chinese Coking Plant” has no conflict of Interest.

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