

Volatile organic compound constituents from an integrated iron and steel facility

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Received 16 November 2007; received in revised form 8 January 2008; accepted 8 January 2008

Available online 16 January 2008

Abstract

This study measured the volatile organic compound (VOC) constituents of four processes in an integrated iron and steel industry; cokemaking, sintering, hot forming, and cold forming. Toluene, 1,2,4-trimethylbenzene, isopentane, *m,p*-xylene, 1-butene, ethylbenzene, and benzene were the predominant VOC species in these processes. However, some of the chlorinated compounds were high (hundreds ppbv), i.e., trichloroethylene in all four processes, carbon tetrachloride in the hot forming process, chlorobenzene in the cold forming process, and bromomethane in the sintering process. In the sintering process, the emission factors of toluene, benzene, xylene, isopentane, 1,2,4-trimethylbenzene, and ethylbenzene were over 9 g/tonne-product. In the vicinity of the manufacturing plant, toluene, isopentane, 1,2,4-trimethylbenzene, xylene and ethylbenzene were high. Toluene, 1,2,4-trimethylbenzene, xylene, 1-butene and isopentane were the major ozone formation species. Aromatic compounds were the predominant VOC groups, constituting 45–70% of the VOC concentration and contributing >70% to the high ozone formation potential in the stack exhaust and workplace air. The sequence of VOC concentration and ozone formation potential was as follows: cold forming > sintering > hot forming > cokemaking. For the workplace air, cokemaking was the highest producer, which was attributed to the fugitive emissions of the coke oven and working process release.

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Keywords: Volatile organic compound (VOC); Steel industry; Emission factor; Ozone formation potential

1. Introduction

Steel is mainly produced at integrated facilities using a series of closely linked processes which include a coke oven, sintering, a blast furnace (BF), basic oxygen steelmaking (BOS), casting and rolling. In general, the sintering process, cokemaking, the heating furnace and the BF are the major air pollution sources.

Pulverized coal is unprocessed coke, which is carbon-rich and used as a carbon source and fuel to heat and melt iron ore in ironmaking. Coke oven gas (COG) is a product of coal thermal cracking gas which includes coal tar, CO, CO₂, particles, hydrocarbons (i.e., methane, benzene, toluene, etc.), ammonia,

NO_x, and SO_x as the main by-products of this process [1]. The sintering process includes iron ore fines, pollution-controlled dusts, coke breeze, water treatment plant sludge, recycled iron-rich materials (i.e., mill scale and processed slag) and flux which forms a porous mass for charging a BF. Molten iron from the BF, flux, alloy materials and scrap are put into the basic oxygen furnace (BOF), melted, and refined by injecting high-purity oxygen. The impurities are removed and reacted with the fluxes and oxygen to form slag. The molten steel is typically cast into slabs, beams or billets. Therefore, high energy and material consumption are typical in the iron and steel industry that also causes serious environmental pollution, especially air pollution.

In Europe, coke ovens and metal ore roasting or sintering installations for the production of pig iron or steel are important sources of non-methane VOCs [2]. Most of the literature

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Table 1
Baseline information and operating conditions of four processes in the integrated iron and steel plant

Processes	Operating parameters			Baseline information of stack exhaust gas			
	Raw materials (t/h) ^a	Fuel (gas: N m ^{3(b)} /h)	Temperature (°C) and product (t/h)	Gas flow rate (N m ³ /min)	O ₂ (%)	H ₂ O (%)	HC (ppm)
Cokemaking	Coal: 29.4–192	BFG ^c /COG ^d : 19100–62000	1230–1260 °C, coke: 23.6–150 t/h	2110–3480	9.2–11.1	8.5–9.6	26–75
Sintering	Flux: 26–36; return fine: 139–170; blended ore: 478.5–585	COG: 1200–1320; coke: 28.2–33.5 t/h	1050–1150 °C; sintering ore: 435–500 t/h	9760–16,670	12.8–16.3	6.7–7.4	95–230
Cold forming	Cold-rolled coil: 140–175	COG: 7000–8500	830–850 °C; cold-rolled coil: 140–175 t/h	1140–1430	10.8–12.5	8.2–9.5	210–286
Hot forming	Plate and billet: 165–260	COG: 9270–12000	1150–1270 °C, 144–257 t/h	1260–1720	8.1–12.3	6.9–13.5	23–68

Only the sintering process is installed with an air pollution control device (APCD), which includes electrostatic precipitation and denitrification; the other processes are not equipped with APCD.

^a t/h: ton/hr.

^b Gas condition at 1 atm and 0 °C.

^c Blast furnace gas.

^d Coke oven gas.

mentions particulate emissions and its compositions (i.e., mass concentration, chemical constituents including metals [3], polycyclic aromatic hydrocarbons [4,5], dioxins and furans [6,7]), and criteria gas pollutants (i.e., CO, NO_x and SO_x) in the iron and steel processes. Quaß et al. [6] estimated that sinter plants could represent the highest industrial source of PCDD/Fs in Europe. The chlorinated volatile organic compounds (VOCs) in the exhaust could be the precursors of dioxins in the iron and steel processes, especially in a sintering plant. Some studies noted the cokemaking process [8]. The organic compounds emitted from air pollution sources (i.e., meat charbroiling, medium duty diesel trucks, gasoline-powered motor vehicles, and fireplace combustion of wood, etc.) were investigated by Schauer et al. [9–12]. Few studies have focused on the constituents of VOCs in the stack exhaust and workplace air of iron and steel industries. Parts of the VOCs are harmful to humans and cause eye and skin irritation, and are harmful to the bronchus. Even more serious is that some of them, including benzene and trichloroethylene, are carcinogenic [13,14]. In addition, VOCs are one of the causes of photochemical smog and ozone formation in the atmosphere [15,16]. Individual compounds of non-methane hydrocarbon (NMHC) have different effects on ozone formation due to their reaction rates and reaction pathways [17,18]. Therefore, it is important to identify the VOC profiles in emission sources to enable control measures to be incorporated in the state implementation plan.

According to the Taiwan Emission Data System, sintering, cokemaking, blast furnaces, and heating processes contribute over 90% of the pollution emissions from an integrated iron and steel plant [19]. Therefore, the objectives of this study were to sample and measure the airborne VOCs emitted from these processes. VOC concentration, emission factors and ozone formation potential were measured to create a profile from various processes in an integrated iron and steel plant.

2. Experimental

The integrated iron and steel plant was built in 1971. The important facilities include four sets blast furnaces, sintering, and cokemaking equipment to produce casting steel as well as two sets of hot forming and cold forming facilities to fabricate steel products.

Exhaust gas and workplace air were sampled from an integrated iron and steel plant located in southern Taiwan. The operating conditions of four processes (cokemaking, sintering, hot forming, and cold forming) are shown in Table 1.

Coal is used as raw material in the cokemaking process. The sintering plant collects the ash from the BF and BOF, returns fines from the sintering plant, and blends these with ore, serpentine, limestone and coke breeze to manufacture sinter. In the cold forming process, the hot-rolled bands are pickled by acid and then cold-rolled at room temperature to form thinner coils. Slab (rectangular type) steel is rolled, milled and heated to 1200 °C, then rolled, leveled, and cooled in the hot forming procedures. Finally, the slab steel is manufactured to form hot-rolled coils.

2.1. Stack VOCs

VOC samples were taken on the days when the plant operation capacity was more than 85% of the rated capacity, to obtain representative samples. Exhaust gases were sampled from the stacks and analyzed by the US EPA Method 18 integrated bag method [20]. Each Tedlar bag (SKC Tedlar 232 Series) was placed inside a rigid air-tight container (SKC-Vac-U-Chamber). Three consecutive samples were collected at each stack at 0.5 L min⁻¹ (Gilian Personal Air Sampler) for 20 min to yield average concentrations over 1 h. Sampling was conducted for the four processes. Five samples were taken for analysis to obtain the representative samples. Fifteen stack exhaust samples were measured in each process.

Table 2
Volatile organic compounds constituent (ppbv) in the stack exhaust of various processes

Groups	Compounds	Cokemaking	Sintering	Hot forming	Cold forming
Paraffins	<i>n</i> -Butane	60 ± 63	876 ± 280	ND	152 ± 64
	Isopentane	319 ± 401	2271 ± 980	37 ± 52	2138 ± 1276
	<i>n</i> -Pentane	131 ± 142	1019 ± 489	66 ± 4.5	782 ± 187
	2,2-Dimethylbutane	26 ± 37	149 ± 85	ND	162 ± 59
	Cyclopentane	36 ± 44	256 ± 122	ND	282 ± 87
	2,3-Dimethylbutane	82 ± 76	353 ± 247	31 ± 44	251 ± 236
	2-Methylpentane	124 ± 143	700 ± 332	23 ± 32	609 ± 436
	3-Methylpentane	116 ± 93	505 ± 238	102 ± 32	530 ± 105
	<i>n</i> -Hexane	141 ± 93	351 ± 164	116 ± 8.9	267 ± 90
	Methylcyclopentane	50 ± 40	137 ± 142	ND	14 ± 19
	2,4-Dimethylpentane	14 ± 19	14 ± 20	ND	22 ± 8.7
	Cyclohexane	31 ± 13	116 ± 29	23 ± 21	75 ± 45
	2-Methylhexane	60 ± 40	257 ± 170	86 ± 14	349 ± 52
	2,3-Dimethylpentane	18 ± 17	69 ± 33	20 ± 28	96 ± 27
	3-Methylhexane	102 ± 57	345 ± 186	71 ± 100	431 ± 254
	2,2,4-Trimethylpentane	35 ± 4.8	72 ± 3.5	14 ± 20	72 ± 24
	<i>n</i> -Heptane	100 ± 50	380 ± 198	135 ± 34	405 ± 50
	Methylcyclohexane	42 ± 22	159 ± 78	42 ± 29	137 ± 13
	2,3,4-Trimethylpentane	56 ± 24	60 ± 34	16 ± 23	21 ± 4.5
	2-Methylheptane	54 ± 26	172 ± 84	94 ± 0.7	149 ± 6.9
	3-Methylheptane	72 ± 31	179 ± 113	101 ± 27	198 ± 44
	<i>n</i> -Octane	78 ± 34	287 ± 160	142 ± 0.04	217 ± 57
<i>n</i> -Nonane	18 ± 0.7	134 ± 62	61 ± 15	92 ± 4.9	
<i>n</i> -Decane	23 ± 33	32 ± 46	ND	21 ± 26	
Olefins	1-Butene	231 ± 168	1534 ± 885	376 ± 278	875 ± 433
	<i>trans</i> -2-Butene	14 ± 20	208 ± 122	ND	138 ± 45
	<i>cis</i> -2-Butene	11 ± 16	208 ± 112	10 ± 14	104 ± 75
	1-Pentene	13 ± 18	169 ± 65	8.5 ± 12	54 ± 72
	Isoprene	24 ± 13	112 ± 131	13 ± 1.5	143 ± 26
	<i>trans</i> -2-Pentene	19 ± 27	176 ± 113	3.8 ± 5.3	109 ± 124
	<i>cis</i> -2-Pentene	16 ± 15	199 ± 203	3.4 ± 4.8	74 ± 90
	1-Hexene	36 ± 18	242 ± 65	24 ± 33	80 ± 57
Aromatics	Benzene	178 ± 26	1986 ± 1901	435 ± 358	2230 ± 1876
	Toluene	1305 ± 338	8044 ± 8343	891 ± 4.0	7661 ± 768
	Ethylbenzene	196 ± 83	1070 ± 806	335 ± 1.5	1272 ± 154
	<i>m,p</i> -Xylene (0.57 + 0.57)	257 ± 102	1462 ± 993	488 ± 7.1	1617 ± 189
	Styrene	121 ± 43	372 ± 137	234 ± 8.0	1210 ± 87
	<i>o</i> -Xylene	99 ± 31	758 ± 420	200 ± 12	2042 ± 90
	Isopropylbenzene	14 ± 3.4	87 ± 27	57 ± 11	848 ± 59
	<i>n</i> -Propylbenzene	14 ± 9.4	108 ± 50	39 ± 2.4	97 ± 10
	<i>m</i> -Ethyltoluene	51 ± 21	319 ± 74	140 ± 11	290 ± 46
	<i>p</i> -Ethyltoluene	42 ± 17	434 ± 311	128 ± 12	395 ± 24
	1,3,5-Trimethylbenzene	56 ± 23	262 ± 167	118 ± 4.0	207 ± 19
	<i>o</i> -Ethyltoluene	4.1 ± 1.9	192 ± 149	34 ± 2.1	165 ± 4.9
	1,2,4-Trimethylbenzene	519 ± 515	989 ± 742	454 ± 12	620 ± 78
	1,2,3-Trimethylbenzene	44 ± 18	170 ± 58	99 ± 6.0	187 ± 5.4
	<i>m</i> -Diethylbenzene	53 ± 24	125 ± 27	105 ± 8.9	144 ± 3.2
<i>p</i> -Diethylbenzene	59 ± 26	139 ± 30	122 ± 3.8	161 ± 8.9	
Halogenated	Bromomethane	ND	12 ± 17	ND	ND
	<i>cis</i> -1,2-Dichloroethylene	24 ± 34	ND	ND	52 ± 68
	Chloroform	24 ± 3.0	60 ± 30	ND	11 ± 3.5
	1,1,1-Trichloroethane	18 ± 11	13 ± 7.1	19 ± 0.7	40 ± 3.6
	Carbon tetrachloride	ND	ND	2698 ± 3816	ND
	Trichloroethylene	164 ± 84	187 ± 16	104 ± 13	427 ± 24
	1,1,2-Trichloroethane	ND	10 ± 14	ND	ND
	Tetrachloroethylene	2.0 ± 2.8	ND	ND	369 ± 130
	Chlorobenzene	32 ± 21	12 ± 16	10 ± 14	716 ± 799
	(1,3 + 1,4)-Dichlorobenzene	35 ± 10	111 ± 32	110 ± 1.8	70 ± 3.6
1,2-Dichlorobenzene	ND	7.0 ± 9.9	ND	ND	

Note: 1,2-dichloropropane, *cis*-1,2-dichloropropene, *trans*-1,2-dichloropropene, and 1,2-dibromoethane were not detected in this study.

Table 3
Concentration profiles (ppbv) of volatile organic compound at the workplace in the vicinity of various processes

Groups	Compounds	Cokemaking	Sintering	Hot forming	Cold forming	Workplace air standard (ppmv) [23]
Paraffins	<i>n</i> -Butane	352 ± 160	19 ± 36	32 ± 35	27 ± 3.4	800
	Isopentane	1440 ± 1424	39 ± 42	70 ± 90	58 ± 9.6	
	<i>n</i> -Pentane	675 ± 399	32 ± 33	30 ± 40	23 ± 4.2	600
	2,2-Dimethylbutane	102 ± 120	3.6 ± 8.8	9.9 ± 13	6.4 ± 1.2	
	Cyclopentane	172 ± 205	4.8 ± 8.0	12 ± 18	9.8 ± 1.9	600
	2,3-Dimethylbutane	124 ± 143	29 ± 31	35 ± 41	28 ± 3.9	
	2-Methylpentane	372 ± 377	25 ± 25	30 ± 35	24 ± 3.4	
	3-Methylpentane	295 ± 334	39 ± 40	42 ± 45	40 ± 4.6	
	<i>n</i> -Hexane	191 ± 134	41 ± 42	39 ± 41	38 ± 4.3	50
	Methylcyclopentane	24 ± 3.4	17 ± 18	0.21 ± 0.24	0.27 ± 0.03	
	2,4-Dimethylpentane	23 ± 22	9.3 ± 13	ND	ND	
	Cyclohexane	43 ± 60	13 ± 14	13 ± 19	16 ± 2.0	300
	2-Methylhexane	156 ± 183	24 ± 25	23 ± 15	15 ± 3.1	
	2,3-Dimethylpentane	45 ± 51	5.6 ± 7.1	10 ± 12	13 ± 1.5	
	3-Methylhexane	187 ± 217	44 ± 46	38 ± 51	26 ± 5.1	
	2,2,4-Trimethylpentane	44 ± 45	23 ± 24	6.4 ± 17	0.33 ± 0.04	
	<i>n</i> -Heptane	165 ± 169	49 ± 51	57 ± 61	55 ± 6.5	400
	Methylcyclohexane	55 ± 48	19 ± 20	15 ± 20	19 ± 2.1	400
	2,3,4-Trimethylpentane	36 ± 30	28 ± 29	14 ± 26	14 ± 2.7	
	2-Methylheptane	46 ± 43	27 ± 28	21 ± 29	14 ± 2.8	
3-Methylheptane	62 ± 60	35 ± 37	38 ± 40	37 ± 4.2		
<i>n</i> -Octane	63 ± 52	42 ± 43	44 ± 47	44 ± 4.9	300	
<i>n</i> -Nonane	18 ± 8.9	21 ± 22	26 ± 28	26 ± 2.9	200	
<i>n</i> -Decane	ND	17 ± 31	14 ± 26	14 ± 2.9		
Olefins	1-Butene	342 ± 435	40 ± 43	51 ± 65	51 ± 7.0	
	<i>trans</i> -2-Butene	69 ± 72	0.18 ± 0.27	1.3 ± 2.4	1.3 ± 0.2	
	<i>cis</i> -2-Butene	68 ± 65	0.24 ± 0.34	0.08 ± 0.11	0.11 ± 0.01	
	1-Pentene	42 ± 59	9.0 ± 25	0.08 ± 0.16	0.10 ± 0.02	
	Isoprene	158 ± 212	9.8 ± 14	5.3 ± 9.2	5.4 ± 1.0	
	<i>trans</i> -2-Pentene	82 ± 108	9.1 ± 10	5.6 ± 7.6	3.6 ± 0.7	
	<i>cis</i> -2-Pentene	50 ± 64	9.5 ± 11	5.8 ± 8.2	3.2 ± 0.6	
	1-Hexene	51 ± 71	30 ± 58	32 ± 44	22 ± 4.3	
Aromatics	Benzene	866 ± 1164	34 ± 37	61 ± 79	54 ± 8.4	5
	Toluene	2893 ± 3893	314 ± 328	787 ± 1001	707 ± 107	100
	Ethylbenzene	144 ± 139	113 ± 119	183 ± 216	177 ± 23	
	<i>m,p</i> -Xylene (0.57 + 0.57)	208 ± 209	156 ± 164	291 ± 353	276 ± 38	100
	Styrene	77 ± 86	66 ± 70	215 ± 274	216 ± 30	50
	<i>o</i> -Xylene	96 ± 113	78 ± 82	340 ± 506	332 ± 55	100
	Isopropylbenzene	9.7 ± 10	16 ± 17	117 ± 189	119 ± 20	50
	<i>n</i> -Propylbenzene	11 ± 11	12 ± 13	32 ± 42	30 ± 4.6	
	<i>m</i> -Ethyltoluene	42 ± 45	47 ± 49	118 ± 155	112 ± 17	
	<i>p</i> -Ethyltoluene	38 ± 42	44 ± 47	111 ± 164	115 ± 18	
	1,3,5-Trimethyl-benzene	39 ± 37	37 ± 38	64 ± 75	61 ± 8.0	25
	<i>o</i> -Ethyltoluene	6.4 ± 8.6	14 ± 14	48 ± 69	45 ± 7.6	
	1,2,4-Trimethylbenzene	150 ± 136	140 ± 144	237 ± 284	230 ± 30	25
	1,2,3-Trimethylbenzene	33 ± 30	26 ± 34	65 ± 81	63 ± 8.8	25
	<i>m</i> -Diethylbenzene	31 ± 26	25 ± 34	51 ± 60	50 ± 6.4	
	<i>p</i> -Diethylbenzene	39 ± 34	28 ± 38	57 ± 67	56 ± 7.2	
Halogenated	<i>cis</i> -1,2-Dichloroethylene	20 ± 29	ND	6.8 ± 19	14 ± 2.7	200
	Chloroform	13 ± 3.2	7.2 ± 13	7.2 ± 13	7.2 ± 1.4	10
	1,1,1-Trichloroethane	10 ± 9.4	5.6 ± 5.8	8.9 ± 10	9.0 ± 1.1	350
	Carbon tetrachloride	ND	ND	109 ± 307	217 ± 143	2
	Trichloroethylene	85 ± 114	47 ± 50	81 ± 111	82 ± 12	50
	<i>cis</i> -1,2-Dichloropropene	ND	ND	4.9 ± 14	ND	
	1,1,2-Trichloroethane	ND	0.04 ± 0.10	ND	ND	10
	Tetrachloroethylene	ND	ND	65 ± 121	65 ± 13	50
	Chlorobenzene	12 ± 18	ND	137 ± 239	143 ± 25	75
	(1,3 + 1,4)-Dichlorobenzene	22 ± 31	16 ± 29	34 ± 36	33 ± 3.8	50–75

Note: bromomethane, *trans*-1,2-Dichloropropene, 1,2-Dibromoethane, 1,2-Dibromoethane and 1,2-Dichlorobenzene were not detected in the workplace.

2.2. Workplace VOCs

Workplace air samples were collected for C3–C11 hydrocarbon analysis using the stainless steel canister sampling method. Six-liter stainless steel-polished canisters were cleaned in the laboratory, pressurized with humidified zero air at $\sim 100^\circ\text{C}$ prior to sampling, and certified as described by U.S. EPA Method TO-14 [21].

VOC species were pre-concentrated in a purge and trap system (Entech 7100 instrument) and subsequently analyzed in a GC/MS (HP-6890 Gas Chromatograph and HP 5973N Mass Spectrometer). The GC was equipped with a fused silica capillary column (non-polar RTx-1, $105\text{ m} \times 0.25\text{ mm i.d.} \times 1.0\ \mu\text{m}$ film thickness). Calibration standards were prepared by diluting a certified standard gas (56 Enviro-Mat Ozone Precursor, Matheson, USA) with ultra high purity nitrogen (99.995%) in dilution bottles. VOCs analysis included the analysis of halogenated VOCs and the standard gases prepared by Matheson Gas Products, GA, USA.

In total, 63 VOC species were analyzed in this study including 24 paraffins, 8 olefins, 16 aromatics, and 15 halogenated species (as shown in Table 2). The performance of the GC/MS was evaluated with perfluorotributylamine for quality control. The relative standard deviation for all VOCs was $<15\%$, the accuracy ranged from $87 \pm 7\%$ (propane) to $104 \pm 12\%$ (*p*-ethyltoluene) and the method detection limit varied from 0.02 (*n*-decane) ppb to 0.14 (*n*-butane) ppb.

3. Results and discussion

Table 1 shows the operation conditions, which included the feed rate, temperature, product, gas flow rate, and air pollution control devices for the four iron and steel plant emission processes. The mixing and crushing coking coals are charged into the coke oven. Dry distillation in the oven produces hot coke and crude COG. Blast furnace gas (BFG) and COG are used as the fuel in the coke-making process. In general, the content of the COG includes CO (21%), CO₂ (21%), H₂ (3.2%) and N₂ (55%).

3.1. Criteria pollutants and operation conditions

Table 1 shows the operation conditions (temperature, flow rate), raw materials, water vapor content, SO_x, NO_x, HC (hydrocarbon), CO₂, CO, and O₂ concentrations of the four processes. HC concentration was higher in the cold forming process than in the other processes. This is caused by the oil addition; the oil is volatilized by heating, and HC is produced by the incomplete combustion of COG. In addition, the sintering process provided a higher SO_x concentration than the other processes, which might be supplied by the BF and BOF recycle ash and ore, especially the BOF de-sulfur ash. The concentrations of SO_x and NO_x were low in the cokemaking process, which may be attributed to the reduced condition of the manufacturing process.

3.2. VOC constituents of stack exhaust

Table 2 shows the VOC concentrations of stack exhaust from the four different processes. Toluene, 1,2,4-trimethylbenzene,

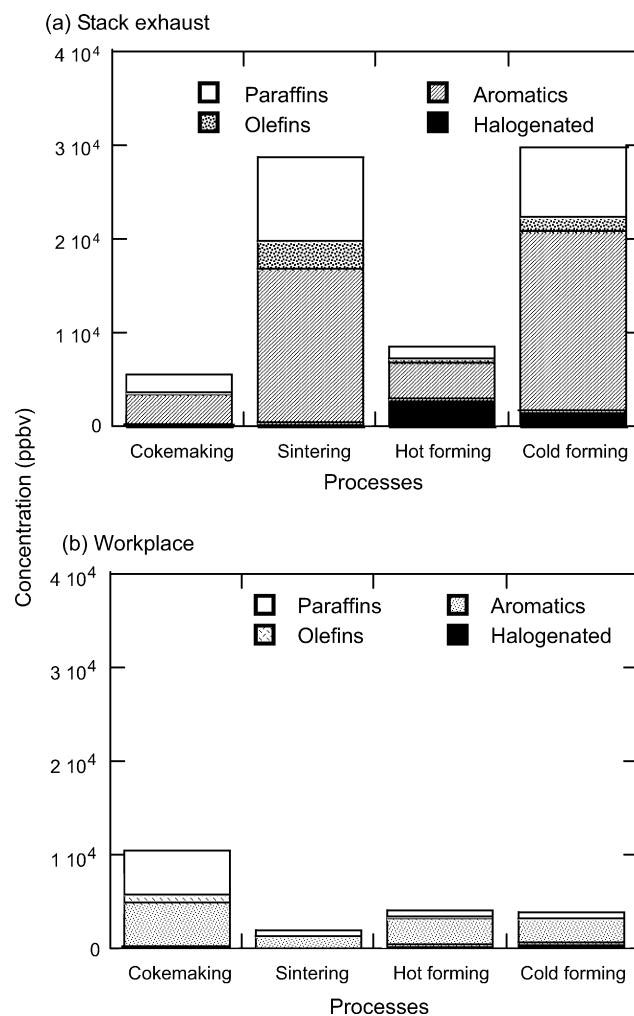


Fig. 1. (a and b) VOC groups concentration in different processes.

isopentane, *m,p*-xylene, 1-butene, ethylbenzene, benzene, trichloroethylene, *n*-hexane and *n*-pentane were the major VOC species of the cokemaking exhaust. Most of them are aromatic compounds; toluene was about 1305 ppbv, 1,2,4-trimethylbenzene, *m,p*-xylene, and ethylbenzene were 196–519 ppbv, paraffin and olefin species were 11–319 ppbv and the concentration of trichloroethylene was 164 ppbv. Generally, cokemaking is a reduction condition, and the coke is an aromatic structure that can cause a high portion of aromatic compounds in the cokemaking exhaust. Some halogenated species, including *cis*-1,2-dichloroethylene, chloroform, 1,1,1-trichloroethane, tetrachloroethylene, chlorobenzene, (1,3 + 1,4)-dichlorobenzene and trichloroethylene, were detectable. Most of them were 2–35 ppbv, except trichloroethylene (164 ppbv). Generally, propene, acetylene, propane, and butane were the major components in the cokemaking process (the concentration was from hundreds to thousands ppmv) except for methane, ethane and ethene (% level concentration) [22].

In the sintering process, the major VOC species in the exhaust included toluene, isopentane, benzene, 1-butene, *m,p*-xylene, ethylbenzene, *n*-pentane, 1,2,4-trimethylbenzene, *n*-butane, and 2-methylpentane; their concentrations were

Table 4
Emission factor (g/tonne-product) of volatile organic compounds from stack exhaust of various processes

Groups	Compounds	Cokemaking	Sintering	Hot forming	Cold forming
Paraffins	<i>n</i> -Butane	0.30 ± 0.11	3.98 ± 2.27	ND	0.19 ± 0.03
	Isopentane	1.65 ± 1.48	13.0 ± 8.67	0.06 ± 0.09	3.37 ± 2.35
	<i>n</i> -Pentane	0.79 ± 0.35	5.86 ± 4.16	0.10 ± 0.01	1.23 ± 0.25
	2,2-Dimethylbutane	0.14 ± 0.02	1.04 ± 0.81	ND	0.31 ± 0.25
	Cyclopentane	0.19 ± 0.14	1.43 ± 1.01	ND	0.43 ± 0.45
	2,3-Dimethylbutane	0.66 ± 0.09	2.50 ± 2.22	0.06 ± 0.09	0.47 ± 0.52
	2-Methylpentane	0.83 ± 0.52	4.81 ± 3.38	0.05 ± 0.07	1.15 ± 1.43
	3-Methylpentane	1.01 ± 0.05	3.47 ± 2.44	0.19 ± 0.09	1.00 ± 0.46
	<i>n</i> -Hexane	1.33 ± 0.32	2.41 ± 1.68	0.21 ± 0.02	0.50 ± 0.08
	Methylcyclopentane	0.43 ± 0.03	0.98 ± 1.13	ND	0.03 ± 0.05
	2,4-Dimethylpentane	0.08 ± 0.12	0.13 ± 0.18	ND	0.05 ± 0.04
	Cyclohexane	0.32 ± 0.16	0.75 ± 0.39	0.04 ± 0.04	0.14 ± 0.03
	2-Methylhexane	0.64 ± 0.15	2.06 ± 1.77	0.17 ± 0.00	0.75 ± 0.14
	2,3-Dimethylpentane	0.16 ± 0.04	0.55 ± 0.39	0.05 ± 0.07	0.21 ± 0.08
	3-Methylhexane	1.18 ± 0.42	2.78 ± 2.11	0.17 ± 0.23	0.94 ± 0.67
	2,2,4-Trimethylpentane	0.56 ± 0.42	0.61 ± 0.20	0.04 ± 0.05	0.18 ± 0.05
	<i>n</i> -Heptane	1.20 ± 0.50	3.05 ± 2.27	0.29 ± 0.12	0.89 ± 0.23
	Methylcyclohexane	0.49 ± 0.20	1.25 ± 0.90	0.09 ± 0.08	0.29 ± 0.12
	2,3,4-Trimethylpentane	0.78 ± 0.38	0.56 ± 0.43	0.03 ± 0.05	0.05 ± 0.04
	2-Methylheptane	0.75 ± 0.33	1.57 ± 1.13	0.22 ± 0.04	0.37 ± 0.09
3-Methylheptane	1.01 ± 0.50	1.66 ± 1.39	0.23 ± 0.02	0.49 ± 0.25	
<i>n</i> -Octane	1.10 ± 0.53	2.64 ± 2.04	0.34 ± 0.06	0.54 ± 0.10	
<i>n</i> -Nonane	0.35 ± 0.30	1.37 ± 0.95	0.16 ± 0.07	0.26 ± 0.30	
<i>n</i> -Decane	0.79 ± 1.12	0.41 ± 0.58	ND	0.07 ± 0.12	
Olefins	1-Butene	1.36 ± 0.20	6.95 ± 5.49	0.41 ± 0.24	1.07 ± 0.23
	<i>trans</i> -2-Butene	0.05 ± 0.07	0.94 ± 0.75	ND	0.17 ± 0.05
	<i>cis</i> -2-Butene	0.04 ± 0.05	0.94 ± 0.71	0.01 ± 0.01	0.13 ± 0.04
	1-Pentene	0.06 ± 0.08	0.93 ± 0.59	0.01 ± 0.02	0.08 ± 0.10
	Isoprene	0.19 ± 0.07	0.66 ± 0.82	0.02 ± 0.00	0.21 ± 0.03
	<i>trans</i> -2-Pentene	0.08 ± 0.12	1.01 ± 0.85	0.01 ± 0.01	0.17 ± 0.06
	<i>cis</i> -2-Pentene	0.10 ± 0.02	1.19 ± 1.35	0.01 ± 0.01	0.11 ± 0.14
	1-Hexene	0.36 ± 0.15	1.58 ± 0.83	0.05 ± 0.07	0.15 ± 0.09
Aromatics	Benzene	1.97 ± 1.45	13.1 ± 14.3	0.65 ± 0.45	3.81 ± 0.32
	Ethylbenzene	2.58 ± 1.28	9.37 ± 8.74	0.74 ± 0.14	2.95 ± 0.25
	Toluene	16.2 ± 10.4	63.4 ± 72.8	1.70 ± 0.31	15.4 ± 2.35
	<i>m,p</i> -Xylene (0.57 + 0.57)	3.43 ± 1.80	12.7 ± 11.1	1.07 ± 0.18	3.75 ± 0.36
	Styrene	1.62 ± 0.90	3.05 ± 1.87	0.50 ± 0.08	2.75 ± 0.13
	<i>o</i> -Xylene	1.38 ± 0.83	6.48 ± 4.99	0.44 ± 0.11	4.74 ± 0.45
	Isopropylbenzene	0.22 ± 0.14	0.81 ± 0.46	0.14 ± 0.00	2.23 ± 0.11
	<i>n</i> -Propylbenzene	0.18 ± 0.04	1.03 ± 0.72	0.10 ± 0.02	0.26 ± 0.13
	<i>m</i> -Ethyltoluene	0.78 ± 0.40	2.99 ± 1.47	0.35 ± 0.09	0.77 ± 0.24
	<i>p</i> -Ethyltoluene	0.65 ± 0.34	4.33 ± 3.91	0.32 ± 0.09	1.05 ± 0.08
	1,3,5-Trimethylbenzene	0.83 ± 0.42	2.56 ± 2.15	0.29 ± 0.06	0.54 ± 0.11
	<i>o</i> -Ethyltoluene	0.06 ± 0.03	1.93 ± 1.83	0.09 ± 0.02	0.44 ± 0.06
	1,2,4-Trimethylbenzene	5.52 ± 1.48	9.81 ± 9.13	1.13 ± 0.24	1.63 ± 0.12
	1,2,3-Trimethylbenzene	0.66 ± 0.34	1.60 ± 0.94	0.25 ± 0.06	0.49 ± 0.08
	<i>m</i> -Diethylbenzene	0.86 ± 0.39	1.29 ± 0.62	0.29 ± 0.08	0.42 ± 0.12
<i>p</i> -Diethylbenzene	0.97 ± 0.46	1.44 ± 0.69	0.34 ± 0.07	0.47 ± 0.13	
Halogenated	Bromomethane	ND	0.07 ± 0.10	ND	ND
	<i>cis</i> -1,2-Dichloroethylene	0.15 ± 0.21	ND	ND	0.11 ± 0.13
	Chloroform	0.41 ± 0.31	0.57 ± 0.41	ND	0.03 ± 0.05
	1,1,1-Trichloroethane	0.27 ± 0.08	0.14 ± 0.11	0.05 ± 0.01	0.12 ± 0.02
	Carbon Tetrachloride	ND	ND	7.45 ± 10.54	ND
	Trichloroethylene	2.56 ± 1.05	1.86 ± 0.67	0.28 ± 0.09	1.23 ± 0.13
	1,1,2-Trichloroethane	ND	0.12 ± 0.17	ND	ND
	Tetrachloroethylene	0.08 ± 0.11	ND	ND	1.34 ± 0.46
	Chlorobenzene	0.40 ± 0.10	0.12 ± 0.16	0.03 ± 0.04	1.76 ± 0.32
	(1,3 + 1,4)-Dichlorobenzene	0.86 ± 0.87	1.26 ± 0.68	0.33 ± 0.06	0.23 ± 0.03
	1,2-Dichlorobenzene	ND	0.06 ± 0.09	ND	ND
	Mass amounted	62	213	20	63

from 700–8044 ppbv. The detectable halogenated species included bromomethane, chloroform, 1,1,1-trimethylethane, trichloroethylene, 1,1,2-trimethylethane, chlorobenzene, (1,3+1,4)-dichlorobenzene and 1,2-dichlorobenzene; their concentrations were 10–187 ppbv. The concentration of trichloroethylene, and (1,3+1,4)-dichlorobenzene were over 110 ppbv.

A special constituent in the hot forming process, carbon tetrachloride, was the highest VOC; this may be attributed to the HCl that was used to clean the surface of the cold-rolled coil. Toluene, *m,p*-xylene, 1,2,4-trimethylbenzene, benzene, 1-butene, ethylbenzene, styrene, *o*-xylene, and octane were the major VOCs in the hot forming process, and their concentrations were 142–891 ppbv. Most of the halogenated VOC species were less than 100 ppbv.

In the cold forming processes, toluene, benzene, isopentane, *o*-xylene, *m,p*-xylene, ethylbenzene, styrene, 1-butene, isopropylbenzene and *n*-pentane were the major VOC species. Their concentrations were from 782 to 7661 ppbv. The concentrations of chlorobenzene, tetrachloroethylene, and trichloroethylene were higher than 369 ppbv.

Fig. 1(a) shows the VOC group profiles of the four processes from stack exhaust. Results indicated that the aromatics accounted for the highest portion of the four processes with percentages of 46–64%. The halogenated VOC portion in the cokemaking, sintering, and cold forming was low (<6%), but it reached 35% in the hot forming process, which may be attributed to the fact that the steel was polished and rust was removed by hydrogen chloride.

3.3. Workplace VOC concentration

Table 3 shows the workplace VOC concentrations in the vicinity of the manufacturing equipment. Toluene, isopentane, benzene, *n*-pentane, 2-methylpentane, *n*-butane, 1-butene, 3-methylpentane, *m,p*-xylene, and 3-methylhexane were the main species in the cokemaking process. Most of the species were paraffin, and their concentrations were 187–2893 ppbv. The concentration of the halogenated VOC species was less than 100 ppbv.

In the sintering process, toluene, *m,p*-xylene, 1,2,4-trimethylbenzene, and ethylbenzene were the predominant VOCs, and the concentrations were 113–314 ppbv. Chloroform, trichloroethylene, 1,1,2-trichloroethane and dichlorobenzene were detectable in the sintering process.

In the hot forming process workplace, toluene, *o*-xylene, *m,p*-xylene, 1,2,4-trimethylbenzene, styrene, ethylbenzene, chlorobenzene, *m*-ethyltoluene, isopropylbenzene, and *p*-ethyltoluene were the principal species, with concentrations from 111–787 ppbv. *cis*-1,2-Dichloroethylene, chloroform, 1,1,1-trichloroethane, carbon tetrachloride, trichloroethylene, *cis*-1,2-dichloropropene, tetrachloroethylene, and chlorobenzene were detectable in the hot forming workplace. In addition, the concentrations of chlorobenzene, carbon tetrachloride, trichloroethylene, and tetrachloroethylene were higher than 50 ppbv.

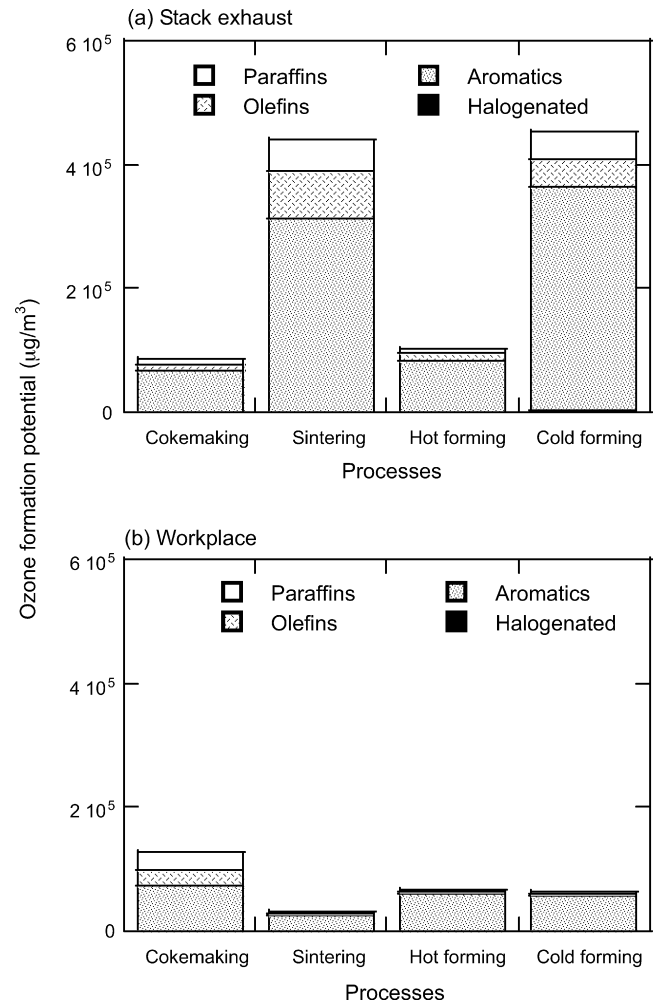


Fig. 2. (a and b) Ozone formation potential ($\mu\text{g}/\text{m}^3$) of VOC groups in different processes.

In the cold forming process workplace, toluene, *o*-xylene, *m,p*-xylene, 1,2,4-trimethylbenzene, carbon tetrachloride, styrene, ethylbenzene, chlorobenzene, isopropylbenzene, and 1,3,5-trimethylbenzene were the dominant VOC species, with concentrations over 100 ppbv. The detectable halogenated VOC species in the cold forming process workplace were similar to those associated with the hot forming process.

Fig. 1(b) shows the VOC groups profile in the workplace. Results indicated that the aromatics were 45–70%, paraffins were 14–45%, olefins were 2–8%, and the halogenated group was 2–15%. The high halogenated VOCs found in the hot forming and cold forming process workplaces may be affected by the HCl that was used for the removal of steel rust. Therefore, the high-chlorinated species were measured in both steel-forming workplaces.

The concentrations of workplace air pollutants from all four processes were lower than the hazardous air pollutants standards for workplace air [23]. However, there were about 30 pollutants included in the workplace air standards, so laborers should utilize personal protective equipment to reduce the health risk.

Table 5
Ozone formation potential ($\mu\text{g}/\text{m}^3$) of main VOC species in stack exhaust of various processes

Compounds	Cokemaking	Sintering	Hot forming	Cold forming
Toluene	20,850	12,8537	14,242	122,405
1,2,4-Trimethylbenzene	19,318	36,802	16,911	23,059
<i>m,p</i> -Xylene	12,301	70,106	23,380	77,518
1-Butene	5774	38,397	9402	21,910
<i>o</i> -Xylene	3393	25,897	6821	69,801
1,3,5-Trimethyl-benzene	3220	15,124	6822	11,985
Ethylbenzene	2576	14,073	4409	16,737
1,2,3-Trimethylbenzene	2534	9829	5714	10,781
Isopentane	1758	12,531	202	11,796
Styrene	1118	3441	2165	11,185
3-Methylpentane	954	4147	835	4357
2-Methylpentane	881	4986	164	4336
<i>n</i> -Hexane	850	2116	701	1611
Isoprene	784	3592	409	4567
1-Hexene	748	5077	493	1687
3-Methylhexane	693	2349	482	2934
<i>n</i> -Pentane	686	5322	347	4082
<i>n</i> -Heptane	610	2116	821	2458
Trichloroethylene	592	672	373	1537
<i>trans</i> -2-Pentene	592	5496	118	3396
20 species	80,232	39,0610	94,811	408,142
Percentage of the 20 species per the 54 species	92	89	93	90

3.4. VOCs emission factor

Table 4 shows the emission factor of VOCs for the four different manufacturing processes. Toluene, 1,2,4-trimethylbenzene, *m,p*-xylene, ethylbenzene, trichloroethylene, benzene, isopentane, styrene, 1-butene and *o*-xylene were the dominant VOC species emitted from the cokemaking stack. Their emission factors were from 1.36 to 16.2 g/tonne-coke. Most emission factors of detectable halogenated VOCs were less than 0.3 g/tonne-coke, except for trichloroethylene (2.6 g/tonne-coke). Based on AP-42 [22], the VOC emission factors (methane, ethane and acetone were not included) totaled 47 g/tonne, which is lower than in this study [22]. Generally, the VOC species (i.e., benzene, toluene, ethylbenzene, xylene, etc.) concentration was also lower than in this study. This may be attributed to having no APCD (air pollution control device) to reduce air pollutant emissions.

In the sintering process, the emission factors of toluene, benzene, isopentane, *m,p*-xylene, 1,2,4-trimethylbenzene, ethylbenzene, 1-butene, *o*-xylene, *n*-pentane and 2-methylpentane were in the range of 4.81–63.4 g/tonne-sintering ore. The emission factor of halogenated VOCs was less than 1.9 g/tonne-sintering ore.

In the hot forming process, the emission factor of carbon tetrachloride was 7.4 g/tonne-steel. Emission factors of toluene, 1,2,4-trimethylbenzene, and *m,p*-xylene were 1.1–1.7 g/tonne-steel, and the others were less than 1.0 g/tonne-steel. Most halogenated species were less than 0.33 g/tonne-steel.

For the cold forming process, the high emission factor (g/tonne-steel) species included toluene (15.4), *o*-xylene (4.7), benzene (3.8), *m,p*-xylene (3.8), isopentane (3.4), ethylbenzene (3.0), styrene (2.8), isopropylbenzene (2.2), chlorobenzene (1.8) and 1,2,4-methylbenzene (1.6). Emission factors of

trichloroethylene, tetrachloroethylene, and chlorobenzene were over 1.2 g/tonne-steel.

In this study, the VOC emission factors were 62 g/tonne for cokemaking, 213 g/tonne for sintering, 20 g/tonne for hot forming, and 62 g/tonne for cold forming. The US EPA reported that the VOC emission factor was 68–566 g/tonne for the sintering process of the steel industry [24,25]. The VOC emission of the sintering process was in the range of the literature. Based on the emission inventory of a heat-treating furnace in the steel industry, the VOC emission factor was 64–545 g/tonne-feedstock-processed. The emission factor of our study was low compared to this study [24,25].

3.5. Ozone formation potential of VOCs

3.5.1. Stack exhaust

The OH radical reactivity method, the incremental reactivity, and the photochemical ozone creation potential have been widely used to measure photochemical reactions [26–28]. Generally, the maximum incremental reactivity (MIR) is popular in the assessment of the ozone formation potential from various VOC compounds. The equation is as follows [29]:

$$\text{MIR} = \max \left[\frac{\partial(\text{O}_3)_p}{\partial E_i} \right] \text{ for all VOCs/NO}_x \quad (1)$$

where $(\text{O}_3)_p$ is maximum ozone concentration, and E_i is an increment of VOC concentration.

Table 5 shows the ozone formation potential of the VOC species. Toluene, *m,p*-xylene, 1,2,4-trimethylbenzene, 1-butene, *o*-xylene, 1,3,5-trimethylbenzene, ethylbenzene, 1,2,3-trimethylbenzene, isopentane and styrene were the major ozone formation species that were emitted from the stacks of the four processes. Trichloroethylene was the highest ozone formation

Table 6
Ozone formation potential ($\mu\text{g}/\text{m}^3$) of main VOC species at the workplace of various processes

Compounds	Cokemaking	Sintering	Hot forming	Cold forming
Toluene	46,232	5010	12,572	11,290
<i>m,p</i> -Xylene	9962	7498	13,948	13,221
1-Butene	8570	1011	1287	1271
Isopentane	7947	217	388	322
1,2,4-Trimethylbenzene	5601	5203	8823	8573
Isoprene	5038	315	170	173
<i>n</i> -Pentane	3527	217	156	119
<i>o</i> -Xylene	3264	2666	11,618	11,338
2-Methylpentane	2651	178	349	327
<i>trans</i> -2-Pentene	2545	284	176	114
Benzene	2518	99	177	156
3-Methylpentane	2421	316	349	327
<i>trans</i> -2-Butene	2311	6.0	43	43
1,3,5-Trimethyl-benzene	2278	2116	3679	3521
<i>cis</i> -2-Butene	2165	8	2	4
1,2,3-Trimethylbenzene	1922	1516	3754	3628
Ethylbenzene	1896	1487	2413	2327
<i>cis</i> -2-Pentene	1558	297	180	101
Cyclopentane	1309	36	95	74
3-Methylhexane	1270	300	259	180
20 species	114,985	28,780	60,438	57,109
Percentage of the 20 species per the 54 species	91	87	90	90

potential halogenated species. The sequence of VOC ozone formation potential was as follows: cold forming \approx sintering > hot forming > cokemaking. The ozone formation potential of the cold forming and sintering process exhaust gas was about 4 and 5 times that of the hot forming and cokemaking processes, respectively.

Fig. 2(a) shows the ozone formation potential of the different groups and processes. The VOC group ozone formation potential sequence was aromatics > paraffins > olefins > halogenated. Generally, the ozone formation potential was less than 1%; that was attributed to the halogenated VOCs. Aromatics were highly concentrated in the stack, which was one of the reasons for the high ozone formation potential of the exhaust.

3.5.2. Workplace

Table 6 shows that *m,p*-xylene, toluene, 1,2,4-trimethylbenzene, 1-butene, *o*-xylene, 1,3,5-trimethylbenzene, 1,2,3-trimethylbenzene, ethylbenzene, and styrene were the main ozone formation species in the workplace atmosphere. Trichloroethylene was still the highest ozone formation species among the halogenated VOCs. The VOC cokemaking ozone formation potential was about 4 times that of sintering, twice that of hot forming, and twice that of cold forming. The fugitive emission of cokemaking was more serious than the others, causing the high ozone formation potential in the workplace. In addition, the ozone formation potential of paraffins and olefins, including isopentane, *trans* and *cis*-2-butene, *n*-pentane, isoprene, *trans* and *cis*-2-pentene, 2 methylpentane and 3-methylpentane, was high in the cokemaking process.

In the four processes, the VOCs portion of the ozone formation potential was aromatics > paraffins > olefins > halogenated VOCs (Fig. 2(b)). Generally, the portion of aromatics was over

75%, and the portion of olefins was less than 10% in sintering, cold forming and hot forming. But the percentages of aromatics, paraffins and olefins were about 59, 22, and 19%, respectively. The ozone formation potential of halogenated VOCs was in the vicinity of 1% for the four different processes.

Furthermore, the cokemaking process VOC ozone formation potential in the workplace was 50% higher than the stack exhaust. For other processes, the ozone formation potential of the stack exhaust was higher than in the workplace. When the door of the coke oven was open and the coke car was pulled out, high VOCs were emitted into the workplace atmosphere, causing high ozone formation potential. Therefore, the ozone formation potential of the workplace air was about twice that of the hot and cold forming processes and 4 times that of the sintering process.

4. Conclusions

Toluene, 1,2,4-trimethylbenzene, isopentane, *m,p*-xylene, 1-butene, ethylbenzene, and benzene were the predominant VOC species in four processes of the integrated iron and steel industry. However, some of the chlorinated compounds were high (in the hundreds ppbv level), i.e., trichloroethylene in all four processes, carbon tetrachloride in the hot forming process, chlorobenzene in the cold forming process, and bromomethane in the sintering process. Generally, toluene was high in all four processes except the hot forming process, where carbon tetrachloride was the highest. In the sintering process, the emission factors of toluene, benzene, xylene, isopentane, 1,2,4-trimethylbenzene, and ethylbenzene were over 9 g/tonne-product. In the vicinity of the manufacturing process, toluene, isopentane, 1,2,4-trimethylbenzene, xylene and ethyl-

benzene were high. Toluene, 1,2,4-trimethylbenzene, xylene, 1-butene and isopentane were the major ozone formation species. Aromatic compounds were the predominant VOC groups, constituting 45–70% of the VOCs concentration and contributing >70% to the high ozone formation potential in the stack exhaust and workplace air. In addition, future study should address the relationship between source emissions and workplace air.

Acknowledgement

The authors express their sincere thanks to the National Science Council, Taiwan, ROC (Contract NSC 91-2211-EPA-Z-242-002 and 92-2211-EPA-Z-242-001) for funding this study.

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