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Development of a continuous UAV-mounted air sampler and application to the quantification of CO_2 and CH_4 emissions from a major coking plant

Tianran Han et al.

Correspondence to: Shao-Meng Li (shaomeng.li@pku.edu.cn)

Section SI-1. Evaluation of CO_2 emissions through carbon material balance

Figure S1 illustrates the coking process flow and the structure of a coking oven. Coking is a process in which coking coal is heated in an oxygen-free environment to produce coke, a high-carbon metallurgical coke used in steel production. The process takes place in a coke oven, where coking coal is heated at temperatures exceeding 1000 °C, driving off all volatile components of the coal and leaving behind coke. Coke oven gas (COG), the byproduct of coking, is mainly composed of the components listed in Table S1 (Razzaq et al., 2013). This gas is recovered and mostly reused as fuel in firing the coke oven to maintain the high temperatures needed for coking (Zhang, 2019), reducing/eliminating the need for external fuel sources. However, burning COG generates CO_2, which is the primary waste gas emitted.

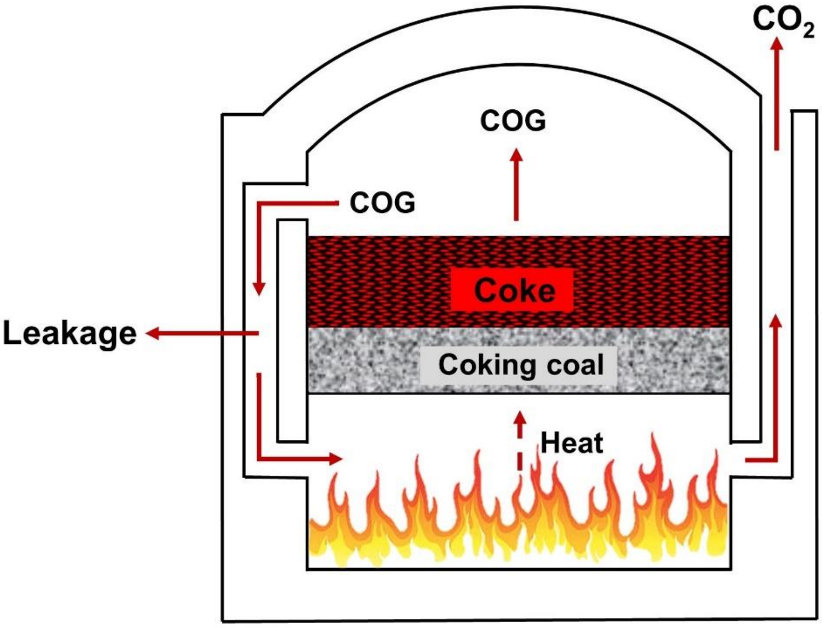

Figure S1. The conceptual coking process flow and the structure of the coking oven

Table S1. Main carbon constitutes and their corresponding compositions (vol%) in coke oven gas

Component	Content
CH_4	23~27%
CO_2	1.5~3%
CO	5~8%
C_2H_4	2~4%

The main products of coking are coke, COG, and slag. In Chinese coking plants (Zhang, 2019), typically half of the produced COG is used as fuel in firing the coke oven, while a small portion is recycled for producing chemical products, and the rest is either leaked (5 %) (Hein, 2012) or an unknown fraction is directly released into the atmosphere. The Shagang coking plant has implemented a process for recycling slag. This process involves reusing the slag, which is generated during the coking process, as part of the fuel for the coking oven. As a result, the carbon in the slag is similarly oxidized into CO_2 and subsequently released into the atmosphere as well. Therefore, the CO_2 emissions (E_{co_2}) mainly come from the combustion of COG ($E_{\mathrm{combustion-COG}}$), the combustion of slag ($E_{\mathrm{combustion-slag}}$), and the direct release of COG (E_{release}):

$$E_{co_2} = E_{\mathrm{combustion-COG}} + E_{\mathrm{combustion-slag}} + E_{\mathrm{release}} \tag{1}$$

Based on the carbon material balance, the amount of carbon in COG combusted in the coking oven ($C_{combustion-COG}$) during the coking process can be derived from material balance:

$$C_{combustion-COG} = \alpha(C_{coal} - C_{coke} - C_{slag}) \tag{2}$$

where C_{coal} is the amount of carbon in coal, C_{coke} the amount in coke, and C_{slag} the amount in slag. α is the fraction of COG used in firing the coking oven and is 0.5 based on operation data at the Shagang coking plant. The measured coking plant consists of two coke oven batteries, each with its own stack. According to the faculty at the coking plant, each coking oven battery produced 127.8 t coke hr^{-1}, thus totalling 255.6 t coke hr^{-1} (p_{coke}) between the two batteries during the UAV measurement period with a coke yield of 78.5 %. The coking batteries are in continuous operation and the coking time (the time from charging the coal to pushing of coke out of the oven) is 26 hours. Thus a 30-minute flight is a suitable length of time for measurement and material balance analysis. The carbon content of coking coal typically ranges from 80 % to 87 % (Dai et al., 2022). Assuming an average value of 83.5 %, the total amount of carbon in the coking coal used by the coking plant per hour can be calculated as:

$$C_{coal} = \frac{p_{coke}}{78.5\%} \times 83.5\% = 272\ t\ C\ hr^{-1} \tag{3}$$

according to the US EPA, metallurgical coke has a carbon content of 82 % to 87 % (U.S. Environmental Protection Agency, 2008). If an average value of 84.5 % is taken, the produced carbon in the coke during the coking process can be calculated as:

$$C_{coke} = p_{coke} \times 84.5\% = 216\ t\ C\ hr^{-1} \tag{4}$$

Generally speaking, the yield of slag is 0.05 % to 0.07 % of the coal charged for coking process (an average value of 0.06 % is taken here), and that the carbon content of slag is around 80 % (Li, 2022). Thus, the total amount of carbon in the produced slag can be calculated as:

$$C_{slag} = \frac{p_{coke}}{78.5\%} \times 0.06\% \times 80\% = 0.16\ t\ C\ hr^{-1} \tag{5}$$

by substituting Eq. (3), (4) and (5) into Eq. (2), the mass of carbon in the combusted COG ($C_{combustion-COG}$) during the coking process is calculated to be 27.9 t hr^{-1}. Thus, $E_{\mathrm{combustion-COG}}$ and $E_{\mathrm{combustion-slag}}$ can be calculated respectively:

$$E_{\mathrm{combustion-COG}} = C_{combustion-COG} \times \frac{M_{CO_2}}{M_C} = 102.3\ t\ CO_2\ hr^{-1} \tag{6}$$

$$E_{\mathrm{combustion-slag}} = C_{slag} \times \frac{M_{CO_2}}{M_C} = 0.59\ t\ CO_2\ hr^{-1} \tag{7}$$

where M_{CO_2} and M_C is the molar mass of CO_2 and the atomic mass of carbon, respectively.

As certain amount of CO_2 is directly released into the atmosphere along with COG, the carbon mass in the released and measured CO_2 ($C_{release}$) can be derived as:

$$C_{release} = \beta\left(C_{coal} - C_{coke} - C_{slag}\right) \times \frac{\varphi_{CO_2}}{\varphi_{CO_2} + \varphi_{CH_4} + \varphi_{CO} + 2\varphi_{C_2H_4}} = 0.16\ t\ hr^{-1} \tag{8}$$

where β is fraction of COG that is directly released into the atmosphere, taken to be 0.05 as described above, φ_{CO_2}, φ_{CH_4}, φ_{CO}, and $\varphi_{C_2H_4}$ are the volume fractions for the main constituents in COG (Table S2). Thus, the corresponding CO_2 emissions from the direct release of COG (E_{release}) cen be derived as:

$$E_{\mathrm{release}} = C_{release} \times \frac{M_{CO_2}}{M_C} = 0.59\ t\ CO_2\ hr^{-1} \tag{9}$$

by substituting Eq. (6), (7) and (9) into Eq. (1), the total CO_2 emissions (E_{co_2}) from the full coking process is calculated to be 103 t CO_2 hr^{-1}.

Taking into account the variation in carbon content found in both coking coal and coke, the variation in the fraction of COG used as fuel (assuming a range of 0.4 to 0.6), the uncertainty of slag yield, as well as the range in the volume fraction of the main components of COG, the total uncertainty range of CO_2 released into the atmosphere during the coking process can be estimated to be 31 % by the equation below:

$$\delta^2 = \delta^2_{C_{coal}} + \delta^2_{C_{coke}} + \delta^2_{COG\ as\ fuel} + \delta^2_{slag\ yield} + \delta^2_{volume\ fraction} \tag{10}$$

Thus, the total amount of CO_2 released into the atmosphere during the full coking process estimated from the coke production data is 103 ± 32 t CO_2 hr^{-1}, which is consistent with the CO_2 emission results (110 ± 18 t CO_2 hr^{-1}, see main text) from the current UAV-measurements, as shown in Figure S2.

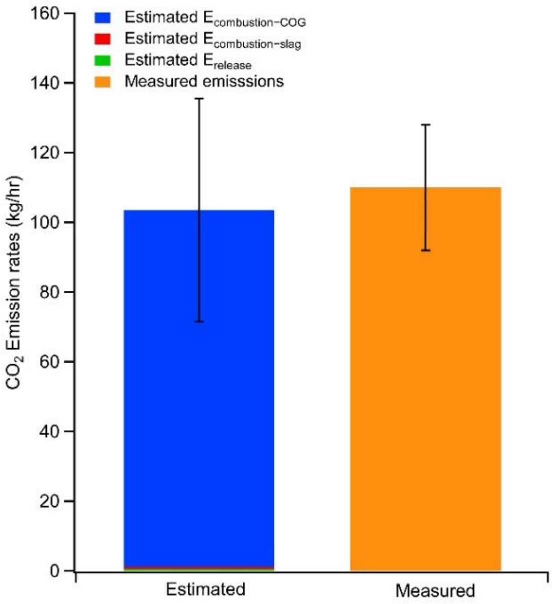

Figure S2. Comparion between the measured and estimated CO_2 emission rates from material balance

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