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Modeling of Off-Gas Emissions from Wood Pellets During Marine Transportation

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After a fatal accident during the discharge of wood pellets at Helsingborg, emissions from pellets during marine transportation became a concern for the safe handling and storage of wood pellets. In this paper, a two-compartment model has been developed for the first time to predict the concentrations of CO, CO_2, CH_4, and O_2 inside the cargo ship and the time and rate of forced ventilation required before the safe entry into the stairway adjacent to the storage hatch. The hatch and stairway are treated as two perfectly mixed tanks. The gas exchange rate between these two rooms and the gas exchange rate with the atmosphere are fitted to satisfy a measured tracer final concentration of 33 p.p.m.v. in the stairway and an average final hatch to stairway CO, CO_2, and CH_4 concentration ratio of 1.62 based on measurement from five other hatch and stairway systems. The reaction kinetics obtained from a laboratory unit using a different batch of pellets, however, need to be scaled in order to bring the prediction to close agreement with onboard measured emission data at the end of voyage. Using the adjusted kinetic data, the model was able to predict the general trend of data recorded in the first 12.5 days of the voyage. Further validation, however, requires the data recorded over the whole journey. The model was applied to predict the effect of ocean temperature on the off-gas emissions and the buildup of concentrations in the hatch and stairway. For safe entry to the cargo ship, the current model predicted that a minimal ventilation rate of 4.4 hr^{-1} is required for the stairway's CO concentration to lower to a safe concentration of 25 p.p.m.v. At 4.4 hr^{-1}, 10 min of ventilation time is required for the safe entry into the stairway studied.

Keywords: confined spaces; gas emissions; marine transport; modeling; storage; ventilation; wood pellets

INTRODUCTION

On 16 November 2006, a fatal accident happened in the port of Helsingborg when a bulk vessel was discharging its load of wood pellets. A sailor and a stevedore entered the stairway adjacent to the cargo hatch and both collapsed. The sailor did not survive and the stevedore was severely injured. This accident was not the first of its kind as in 2002 a similar accident happened in the Port of Rotterdam, although that occurrence was not investigated thoroughly. After the 2006 accident, projects were carried out to investigate the Helsingborg accident. Collected data indicated that the stairway environment had an abnormally low O_2 concentration of ~15% which would cause extreme fatigue and emotional instability (Hong Kong Special Administrative Region Marine Department, Marine Accident Investigation Section, 2007). On top of O_2 deficiency, CO concentration in the stairway exceeded the hygiene limit by at least 10 times (Swedish Maritime Safety Inspectorate, 2007). The toxic effects of CO result from the formation of carboxyhemoglobin in the blood stream with a normal level of 1–3%. While a level of >25% is considered severe poisoning (Piantadosi, 2002), the stevedore had a carboxyhemoglobin content of 43.8% when admitted to the hospital (Svedberg *et al.*, 2008). CO_2 concentration in the stairway was also >50 times higher than the

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15-min exposure limit (Swedish Maritime Safety Inspectorate, 2007).

Deaths and injuries caused by entry of enclosed spaces during marine transportation operations are common. According to the Marine Accident Investigator's International Forum, from 1991 to 2008, the recorded fatalities and injuries related to enclosed spaces from 18 administrations are 123 and 125, respectively (Meyer, 2008). Although not all of the incidents were caused by emissions originating from organic-based cargoes, the figures demonstrate that the issues of oxygen deficiency and exposure to toxic chemicals are valid threats. Cargoes that are considered potentially oxygen depleting according to International Maritime Organization's Code of Safe Practice for Solid Bulk Cargoes (BC Code) include, but are not limited to, grains, oilseeds, forest products, such as lumbers, chips, pellets, and sawdust, fishmeal, sulphidic ores, coal products, and metal wastes (Transport Canada—Marine Safety, 1991; Svedberg *et al.*, 2009). Even when one focuses only on incidents involving forest-based cargoes, five deaths on top of several injuries have been recorded since 2005 according to the Maritime Environment Section of the Swedish Transport Agency, as pointed out by Svedberg *et al.* (2009).

The emissions from various biomass have been previously studied. These include methane emissions from organic household waste or landfills (Bogner *et al.*, 1997; Beck-Friis *et al.*, 2000) and emissions from the degradation of forest products in landfills (Micales and Skog, 1997; Ximenes *et al.*, 2008). The existence of these studies signifies a general awareness of carbon compound off-gassing from organic materials. Narrowing the subject of study to forest products during storage or application, the emissions of volatile organic compounds (VOCs), such as terpenes, are also reported (Rupar and Sanati, 2005; Roffael, 2006). The off-gassing phenomenon has also been investigated from the perspective of climate change where the study focuses on greenhouse gas emissions, namely N_2O and methane, of wood residues during storage (Wihersaari, 2005). Specifically for wood pellets, some studies on VOCs and CO emissions during storage (Svedberg *et al.*, 2004; Arshadi and Gref, 2005) have also been reported. It was found that the emission is temperature dependent, with CO and CO_2 emission being most likely caused by autooxidative degradation of fats and fatty acids (Svedberg *et al.*, 2004). Gas concentrations in various wood pellet cargo systems (Melin *et al.*, 2008; Svedberg *et al.*, 2008) have also been monitored during ocean transportation. Most recently, off-gas emission kinetics at the temperature range of 20–55°C were reported by Kuang *et al.* (2008).

As previously stated, wood pellets are not the only type of cargoes emitting toxins and creating an oxygen-deficient environment. Svedberg *et al.* (2009) recently published their work on oxygen depletion and toxic gas presence in the marine vessel's stairway adjacent to cargo hatches containing logs and wood chips after voyage. Comparing results from this study to previous studies on wood (Svedberg *et al.*, 2008), it was found that the CO emission from wood pellets cargo was much higher than cargoes carrying wood logs and chips. It was proposed that the dominating mechanism for wood pellet off-gassing may be auto-oxidative degradation while the dominating mechanism for non-thermally processed forest products such as logs and chips is microbiological activities (Madsen *et al.*, 2004; Svedberg *et al.*, 2009).

Owing to their carbon-neutral and renewable characteristics, the demand for wood pellets has increased greatly in the past 5 years. The rate of increase in Canadian overseas pellet export is more rapid than in domestic usage. There is thus a need to develop the capability of predicting off-gas emissions during marine transportation in order to avoid similar tragedies from occurring. Furthermore, being able to predict off-gas concentrations and understand the factors controlling the emission rates will allow the industry to devise ways to minimize emissions or to manage the safe handling, storage, and unloading of wood pellets during marine transportation operations.

In this paper, we attempted for the first time to develop a two-compartment model based on cargo configurations and experimental phenomena obtained from onboard monitoring systems (Melin *et al.*, 2008; Svedberg *et al.*, 2008). Model parameters were estimated based on the recently reported kinetic data of Kuang *et al.* (2008), measured SF_6 tracer concentration (Melin *et al.*, 2008), and the measured concentration ratios for three sets of cargo hatch and stairway system on a vessel traveling from British Columbia, BC, to the Port of Helsingborg (Svedberg *et al.*, 2008). The predicted concentrations at the end of the ocean journey were then compared with the measured final concentrations of CO, CO_2, CH_4, and O_2 in the stairway of the storage system (Melin *et al.*, 2008). The model was then applied to examine the effect of ocean temperature on the off-gas emission and concentration buildup at the end of the ocean journey. The model was further applied to estimate the required forced ventilation rate and ventilation time to lower the CO concentration to a safe level to prevent potential accidents during unloading. Finally,

recommendations were made on what needs to be measured onboard the cargo ship in order to further validate and improve the current model.

MODELING

System of study

The system being monitored is a cargo hatch and its adjacent stairway of a pellet-loaded ocean vessel. The off-gas concentrations within the system right before pellet discharge and during the voyage from Vancouver to Helsingborg were measured (Melin *et al.*, 2008; Svedberg *et al.*, 2008). The model in this paper is constructed based on the system studied (Melin *et al.*, 2008) and end of voyage data for other vessels traveling the same route (Svedberg *et al.*, 2008) are also utilized for the fitting of model parameters, as described later.

In the study, the hatch contained 4111 tonnes of wood pellets. The ship departed Vancouver on 26 January 2007, and the voyage took ~7 weeks (Melin *et al.*, 2008). Gas samples were collected from the stairway only at Helsingborg right before pellet discharge. These samples were analyzed by Fourier transform infrared spectroscopy to determine the final CO, CO_2, and CH_4 stairway concentrations. Detailed descriptions of the system and the instrument setup can be found in Melin *et al.* (2008) and Svedberg *et al.* (2008).

The multigas analyzers recorded the concentrations, in parts per million by volume, of CO and CO_2 at four locations at varying heights in the cargo hatch during the voyage and the same was done for the staircase. Unfortunately, the analyzers failed a few days into the journey due to unexpectedly high concentrations of CO and CO_2. Thus, only the concentrations for the first 12.5 days are usable. However, the concentration data for O_2 are reliable and complete. The recorded data showed that there was no obvious concentration gradient in the vertical direction. For this project, the gas mixture is assumed to be perfectly mixed vertically and horizontally in the hatch and the stairway.

Fifteen thermometers were distributed in the cargo space. There were signs of a vertical temperature gradient but the variation was moderate so the system is assumed to have no temperature gradient in the model simulation.

Tracer gas was used to examine the air exchange rate within the environment. A 17.24 kg of sulfur hexafluoride, SF_6, was injected into the bottom portion of the hatch right after the pellets were loaded. Upon arrival at Helsingborg, SF_6 concentration in the stairway was measured before pellet discharge and the value obtained was 33 p.p.m.v.

Derivation of a 2-continuously stirred tank reactor model

There are various approaches that can be taken to model the emissions of an enclosed system. These models can be divided into simple bulk-mixing models, diffusion-based models, and complex computational fluid dynamic (CFD) models (Hellweg *et al.*, 2009). For the bulk-mixing models, the concentration within each zone or box does not vary spatially, only temporally. On the other hand, diffusion models such as eddy-diffusion models and Gaussian plume dispersion models, which take into account directional airflows, are capable of predicting how the concentrations at each point in the system varies with time. However, this type of model requires information such as eddy diffusivity and property of flows. Moreover, difficulties are further amplified in our system due to the presence of porous media, such as wood pellets. The CFD involves a nonlinear set of equations describing mass, energy, and momentum balances. Provided that the emission kinetics are known, this model is capable of yielding results with high accuracy. However, the amount of information required for this type of modeling is extensive and the procedures are also extremely time-consuming. Given that the off-gas emission kinetics are not entirely understood at this point, CFD is not a desirable model for this case study.

It appears that a simple bulk-mixing model consisting of two continuously stirred tank reactors (CSTRs), one representing the cargo hatch and the other for the stairway, would be the appropriate first approximation for this study. This decision is supported by the data recorded (Melin *et al.*, 2008; Svedberg *et al.*, 2008) as little vertical concentration gradient was noted in the stairway and the hatch while there was significant difference in the gas compositions between the hatch and the stairway over time. The model is shown schematically in Fig. 1, with internal exchange of gases (Q_3 and Q_4) between the hatch and the stairway. Although there was likely gas exchange between the environment and both the hatch and the stairway, it is assumed that gas exchange only occurs between the stairway space and the environment since experimental data showed that the concentration in the cargo hatch was always higher than in the stairway, as shown by the hatch-to-stair concentration ratio in Table 1.

Mass balances for CO, CO_2, and CH_4 are established for the hatch space by equation (1) and for the stairway section by equation (2). Note that

Table 1. Final gas concentrations from different marine vessels' wood pellet storage systems (Svedberg *et al.*, 2008).

	Vessel A			Vessel B								
	Hatch	Stair	Ratio	Hatch 2	Stair 2	Ratio	Hatch 4	Stair 4	Ratio	Hatch 6	Stair 6	Ratio
CO (p.p.m.v.)	14 650	10 960	1.34	11 950	7710	1.55	7240	1460	4.96	8860	5300	1.67
CO_2 (p.p.m.v.)	7070	5450	1.30	21 570	12 360	1.75	17 430	2960	5.89	18 820	8690	2.17
CH_4 (p.p.m.v.)	632	468	1.35	956	589	1.62	388	79.9	4.86	454	246	1.85
O_2 (%)	NA	NA		0.8	8.4		7.6	16.9		5.7	10.9	
CO/CO_2	2.07	2.01		0.55	0.62		0.42	0.49		0.47	0.61	

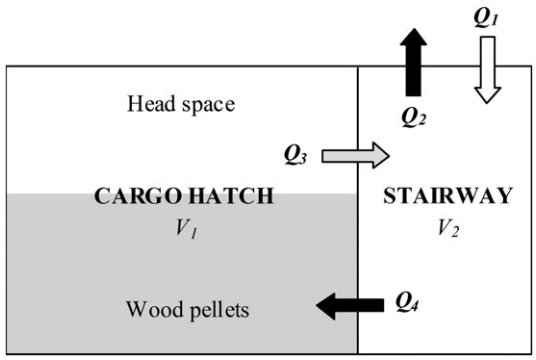

Fig. 1. Schematic diagram of the 2-CSTR model.

subscript 1 refers to the cargo hatch and subscript 2 refers to the stairway. Subscript i represents any of CO, CO_2, or CH_4. Q represents volumetric flow of gas in the unit of cubic meter per day. $R_{i,G}$ represents the generation of species i in the hatch space from stored wood pellets and is time dependent. For the direction and location of each flow please refer to Fig. 1.

$$\frac{dC_{i,1}}{dt} = R_{i,G} + \frac{Q_4 C_{i,2}}{V_1} - \frac{Q_3 C_{i,1}}{V_1}, \quad (1)$$

$$\frac{dC_{i,2}}{dt} = \frac{Q_1 C_{i,A}}{V_2} - \frac{Q_2 C_{i,2}}{V_2} + \frac{Q_3 C_{i,1}}{V_2} - \frac{Q_4 C_{i,2}}{V_2}, \quad (2)$$

C_i is the concentration of i in the cargo hatch or the stairway. $C_{i,A}$ is the concentration of i in the surrounding atmosphere. V_1 is the total gas volume in the hatch, which is 2825 m^3, while V_2 is the estimated gas volume in the staircase section, which is 230 m^3. The rates of gas exchange to and from the stairway and the environment are Q_1 and Q_2, respectively. Under steady state, $Q_1 = Q_2$ and $Q_3 = Q_4$.

The mass balances for O_2 are based on the consumption of O_2 for the production of CO and CO_2 and are given by equations (3) and (4) for the hatch and stairway, respectively. The mass balance equations of the inert tracer SF_6 are represented by equations (5) and (6) for the hatch and stairway, respectively.

$$\frac{dC_{O_2,1}}{dt} = -0.5R_{CO,G} - R_{CO_2,G} + \frac{Q_4 C_{O_2,2}}{V_1} - \frac{Q_3 C_{O_2,1}}{V_1}, \quad (3)$$

$$\frac{dC_{O_2,2}}{dt} = \frac{Q_1 C_{O_2,A}}{V_2} - \frac{Q_2 C_{O_2,1}}{V_2} + \frac{Q_3 C_{O_2,1}}{V_2} - \frac{Q_4 C_{O_2,2}}{V_2}, \quad (4)$$

$$\frac{dC_{SF_6,1}}{dt} = \frac{Q_4 C_{SF_6,2}}{V_1} - \frac{Q_3 C_{SF_6,1}}{V_1}, \quad (5)$$

$$\frac{dC_{SF_6,2}}{dt} = \frac{Q_1 C_{SF_6,A}}{V_2} - \frac{Q_2 C_{SF_6,1}}{V_2} + \frac{Q_3 C_{SF_6,1}}{V_2} - \frac{Q_4 C_{SF_6,2}}{V_2}. \quad (6)$$

Estimations of model parameters

Kuang *et al.* (2008) measured CO, CO_2, and CH_4 concentrations inside a 45-l reactor containing BC wood pellets operating at 20, 30, 40, 50, and 55°C and developed first order reaction kinetics. Emission characteristics were reported in the form of emission factor, f_i, with a unit of g of gas i emitted per kilogram of pellets. The form of f_i is described by

$$f_i(t) = f_{i,\infty}\left[1 - \exp(-k_i t)\right], \quad (7)$$

where $f_{i,\infty}$ is the peak (plateau) emission factor and k_i is the reaction rate constant. Based on the experimental values of $f_{i,\infty}$ and k_i provided by Kuang *et al.* (2008), equations (8) to (10) are obtained for CO, CO_2, and CH_4, respectively:

$$f_{CO}(t) = (1.184 \times 10^{-4} T - 2.144 \times 10^{-2}) \times \left\{1 - \exp\left[-3.492 \times 10^{11} \exp\left(-\frac{71332}{8.314T}\right) t\right]\right\}, \quad (8)$$

$$f_{CO_2}(t) = (2.237 \times 10^{-3}T - 6.294 \times 10^{-1}) \times \left\{1 - \exp\left[-2.332 \times 10^{9}\exp\left(-\frac{59835}{8.314T}\right)t\right]\right\}, \quad (9)$$

$$f_{CH_4}(t) = \left(4.317 \times 10^{-5}T - 1.230 \times 10^{-2}\right) \times \left\{1 - \exp\left[-8.707 \times 10^{10}\exp\left(-\frac{70847}{8.314T}\right)t\right]\right\}. \quad (10)$$

The units of temperature and time are in Kelvin and day, respectively. The emission rate for species i is obtained by the differentiation of the emission factor f_i.

$$f_i^{'} = \frac{df_i}{dt} = k_i f_{i,\infty} \exp(-k_i t). \quad (11)$$

By assuming ideal gases, the rate of generation of species i due to chemical reactions, denoted as $R_{i,G}$ in the unit of the ratio of gas volume emitted per day to the total gas volume in the hatch studied, can be described by equation (12). In equation (12), M_p is the total mass of pellets in kilogram and Mw_i is the molecular weight of species i in kilograms per kilomole and V_1 is the gas volume in the hatch in m^3.

$$\frac{dC_{i,G}}{dt} = \frac{f_i^{'} RT M_p}{P V_1 Mw_i} = R_{i,G}. \quad (12)$$

The values of Q_1 and Q_3 are fitted to satisfy two measured parameters, namely the final stairway SF_6 tracer concentration of 33 p.p.m.v. and the average final gas concentration ratio between the hatch and the stairway based on various sets of measured onboard data (Svedberg *et al.*, 2008) (see Table 1). It appears that Hatch and Stairway 4 in vessel B were not as well sealed as the other systems so it is treated as an outlier and not included in the working data set. The average ratio of hatch to stairway final concentration is then calculated to be 1.62.

The initial guess value for Q_1 is obtained by treating the hatch and the stairway as a single well-mixed chamber. From SF_6 mass balance with an initial concentration of 880 p.p.m.v. calculated from the injected amount of SF_6 into a total volume of 3055 m^3, final concentration of 33 p.p.m.v., 0 p.p.m.v. SF_6 in the atmosphere, and a voyage time of 50 days, a Q_1 value is calculated to be 201 $m^3 day^{-1}$. This value is then assigned as the first estimate for both Q_1 and Q_3.

With the input of the first estimate for Q_1 and Q_3, the 2-CSTR model is run in MATLAB with the initial SF_6 concentration set to 954 p.p.m.v. in the hatch, based on the initial injected amount of SF_6 into the hatch, and 0 p.p.m.v. in the stairway to compute the two measured parameters that the model must satisfy by trial and error. The Q_1 and Q_3 values are changed until the model yields both a final SF_6 stairway concentration of 33 p.p.m.v. and an average ratio of hatch to stairway final concentrations of 1.62 for CO, CO_2, and CH_4. The flow rates that satisfy the fitting requirements are found to be 277 $m^3 day^{-1}$ and 407 $m^3 day^{-1}$ for Q_1 and Q_3, respectively.

RESULTS AND DISCUSSION

Model evaluation and validation

2-CSTR model. The model is constructed using MATLAB and solved using ODE45, a Runge–Kutta method. Temperatures in the hatch and stairway are taken as the medians of the readings from the 14 temperature sensors (one of the 15 sensors was lost during discharge). The time span being evaluated is from Day 0 to Day 50, corresponding to the length of the voyage. Table 2 shows the predicted and measured gas concentrations at the end of the voyage.

Comparing the predicted final stairway concentrations to the measured concentrations in Table 2, one can see that the current model severely underestimated the concentrations of CO, CO_2, and CH_4. On the other hand, the final O_2 level estimated by the model by assuming that all O_2 is transformed

Table 2. Predicted final gas concentrations in stairway and hatch space in parts per million by volume.

Gas species	Hatch to stairway concentration ratio	Hatch space	Stairway		Scaling factor
		Predicted	Predicted	Measured	
CO	1.67	2012	1205	11 498	9.56
CO_2	1.54	2474	1607	5752	4.21
CH_4	1.66	78.9	47.6	184	3.85
O_2	0.99	20.6	20.8	7	—
SF_6	1.65	54.5	33.0	33	1

into CO and CO_2 is substantially higher than the measured value. This indicates that a large amount of O_2 may have been bonded into different forms of oxygenated intermediates and thus were not accounted for in the model. Another possibility may have been the adsorption of O_2 onto wood pellets. Such a trend in uncounted O_2 disappearance was also observed by Svedberg *et al.* (2008), who further suggested that oxygen might be consumed in the auto-oxidation of residual lipophilic extractives in the pellets. More studies need to be carried out in order to address the low O_2 levels in the pellet storage space.

As air infiltration rate was estimated from measured SF_6 tracer concentration, it is speculated that the main reason for the deviations in the predicted CO, CO_2, and CH_4 concentrations may be from the uncertainty of the chosen reaction kinetics.

2-CSTR model with adjusted kinetics The pellets used in the kinetic study of Kuang *et al.* (2008) were obtained from one single pellet mill in BC, which might not represent the average properties of the large quantity of pellets in the cargo hatch reported by Svedberg *et al.* (2008). In view of the low O_2 concentrations of ~7% recorded at the end of different voyages (Svedberg *et al.*, 2008), it is highly possible that O_2 may become a limiting reactant in an enclosed environment such as the sealed laboratory units. Having limited O_2 would cap the maximum emission of CO and CO_2 thus affecting the $f_{i,\infty}$ values obtained from the experiments. Since the activation energy for biomass degradation of wood and wood pellets has been reported in the literature in a range similar to Kuang *et al*'s (2008), an attempt is carried out to adjust the reaction kinetics by scaling the $f_{i,\infty}$ values to match the measured gas concentrations at the end of the voyage. The scaling factors are found by trial and error and are presented in the last column of Table 2. With the scaling factors, the predicted final CO, CO_2, and CH_4 stairway concentrations are close to the measured values but the predicted O_2 concentration is still at 19.8%, much higher than measured. The vast difference between the predicted and actual O_2 final concentration, even after scaling the $f_{i,\infty}$ values, confirms that a large amount of O_2 was indeed not transformed into CO and CO_2. It should be noted that this observation, however, should not have affected the results of the CO and CO_2 concentration predictions as they were based on their kinetic parameters obtained from sealed containers similar to the sealed hatch and stairway in the ocean vessel.

The scaling factors range from 4 to 10 and the scaling factor for CO is approximately double those of CO_2 and CH_4. This ratio may be dependent on pellet properties as the experimental data in Table 1 shows that for two different cargoes of wood pellets (A and B) both originating from British Columbia, the CO to CO_2 ratio for cargo A is much higher than cargo B, suggesting that the CO to CO_2 ratio depends heavily on the types of pellets and the relative contribution from biological and thermochemical reactions that take place in the system.

Figure 2 illustrates the evolution of the gas compounds in the cargo with original and scaled models as well as the data gathered from the onboard multigas analyzer during the first few days of the voyage before instrument malfunctioning occurred (Melin *et al.*, 2008).

The model predicts that both CO and CO_2 reached their peaks at around Days 25 and 35 due to the balance between tapering off-gas emission rate and the continual removal of pollutants from the vessel via air infiltration. This can be explained by the fact that CO is an intermediate product from hydrocarbon oxidation, which is in equilibrium with CO_2. For both CO and CO_2, the stairway readings in the first 12 days are fairly well captured by the 2-CSTR model. On the other hand, the hatch readings more closely resemble the scaled 2-CSTR model for CO_2. The modeled tracer profiles (not shown here) suggest that the tracer first diffused from hatch to stairway via internal exchange and part of the tracer is removed from the stairway via ventilation. Since SF_6 was only measured in the stairway at the end of voyage, future work should monitor SF_6 concentration inside the hatch too. Since only the data over the first few days are available, it is hard to conclude whether the model gives good agreement with the actual concentration profiles until a full set of data covering the whole voyage becomes available in the future. This model is merely a first attempt to demonstrate how to model the off-gas emissions and concentration buildup inside containers transporting woody biomass materials over long ocean journeys.

Simulation using 2-CSTR model

Even accounting for uncertainties in the reaction kinetics, it has been demonstrated in this study that the cargo hatch and stairway system needs to be treated as two CSTRs with gas exchanges in order to predict the off-gas emission buildup in the wood pellets cargo ship. In this section, the model is applied to explore the impact of temperature during the voyage on the buildup of pollutant concentrations in the cargo ship as well as the forced ventilation requirement at the end of voyage in order to lower the

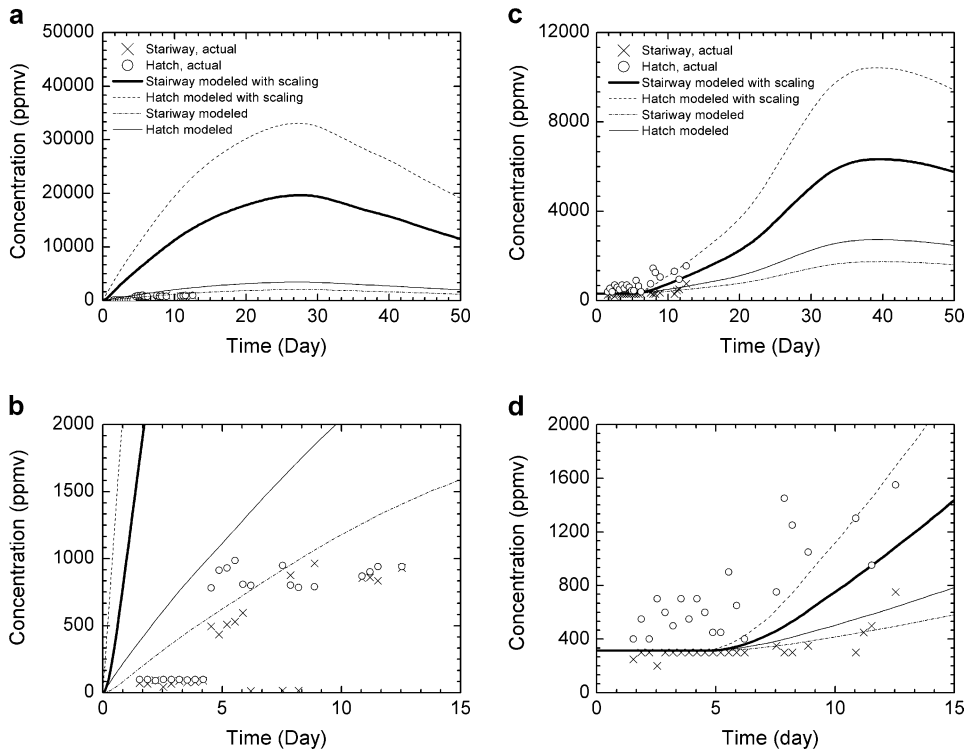

Fig. 2. Measured and predicted concentration profiles from 2-CSTR models (a) for CO during the entire voyage, (b) a close-up of CO profiles during the first 2 weeks of the voyage, (c) for CO_2 during the entire voyage, and (d) a close-up of CO_2 profiles during the first 2 weeks of the voyage.

pollutant concentration to below the acceptable level to ensure safe entry into the stairway.

Temperature effect. Since temperature directly impacts off-gassing reaction kinetics, it is expected that the pollutant concentration buildup will be impacted by ocean temperature and surrounding atmosphere temperature during the voyage. By assuming a constant temperature throughout the voyage ranging from 5 to 30°C (presented in Kelvin in the figures below), simulations are carried out for the same cargo ship and the simulated concentrations at the end of voyage are plotted in Fig. 3 for CO, CO_2, and CH_4. CO concentration at the end of voyage in the cargo ship is seen to increase with increasing temperature initially and then decrease after reaching a peak value at around 15°C, while CO_2 and CH_4 concentrations increase monotonically with increasing temperature.

Forced ventilation rate and required time before safe entry to the stairway. The main motive of this study is to understand off-gassing in order to prevent accidents from happening in the future during storage and unloading of wood pellets. The American Conference of Governmental Industrial Hygienists has set the threshold limit values (TLV) based on time-weighted average for CO and CO_2 to be 25 and 5000 p.p.m.v., respectively (Canadian Center for Occupational Health and Safety, 2006). From concentrations listed in Table 1, it is clear that CO concentration needs to drop by 100 times to reach the TLV level while CO_2 just needs to drop <10 times to reach TLV level and O_2 needs to increase by just <10 times to reach the acceptable level. Therefore, CO will be the limiting compound to be monitored in the forced ventilation process.

To calculate the required time and rate of forced ventilation, the final CO concentration predicted from the scaled 2-CSTR model is used as the starting value before forced ventilation is commenced. The rate of forced ventilation is described here as the 'air exchange rate' (ACH) with a unit of 1/hour, which is defined as the number of times the system's total gas volume is replaced by ventilation air within an hour. The ventilation time required for safe stairway entry at a given ACH can be read from Fig. 4 by finding the intersection of the concentration profile line at the specific ACH curve and the 25 p.p.m.v. TLV line. Note that the ACH curves in Fig. 4 are total ACH, which is the combined effect of a natural ventilation of 3.78×10^{-3} hr^{-1} and forced ventilation.

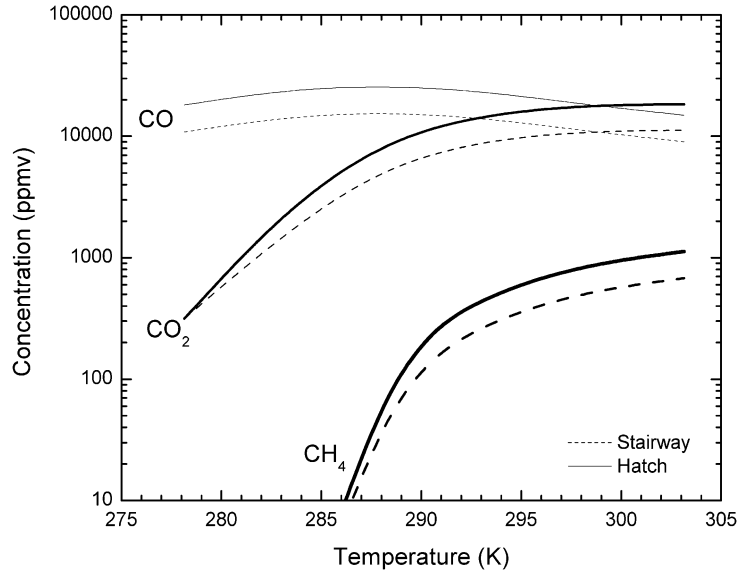

Fig. 3. Effect of temperature on predicted final concentration using scaled 2-CSTR model for CO, CO_2, and CH_4. Solid lines for hatch and dashed lines for stairway.

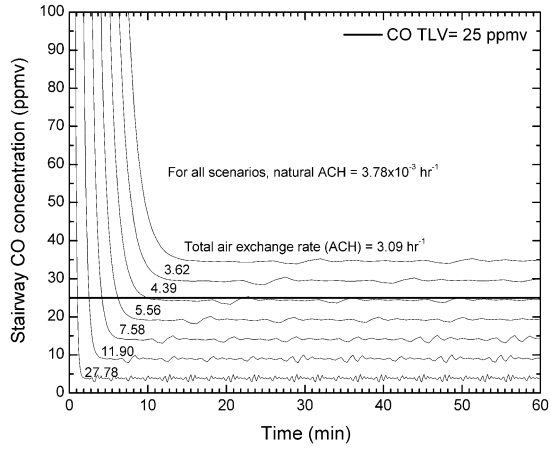

Fig. 4. Predicted CO concentration profiles in stairway with forced ventilation at different air exchange rate.

Due to the continuous release of off-gases from wood pellets, it is seen in Fig. 4 that there exists a minimum ventilation rate, $\sim$4.4 hr^{-1}, below which the CO concentration in the stairway can never be lowered to the TLV level.

Future improvements of the model

To improve the off-gassing reaction kinetics of wood pellets, kinetic data at lower temperatures ($<$25°C) and in well-ventilated environments should be obtained to extend the kinetic equations to the low temperature region and to evaluate the effect of convective mass transfer and O_2 level on the off-gas concentration buildup in wood pellet storage spaces. To validate the current CSTR model, multigas meters should be installed in several locations of the hatch and stairway to monitor the spatial distribution of gas concentrations during the ocean voyage. Furthermore, to avoid the inconsistency of the kinetics data and the monitored off-gas emission data measured onboard the vessel, the reaction kinetics of the same type of wood pellets loaded onto the ship should be determined using a small reactor preferably installed in the stairway area of the ship.

The current isothermal CSTR reactor model can be further improved in the future by coupling an energy balance equation accounting for the heat exchange between the storage space and surrounding environment. The heat sinks and sources may include infiltration air, ocean water, and the release of reaction heat from the off-gassing reactions. Lastly, if the prediction of oxygen level in the storage system is desired, better kinetics models need to be developed to account for oxygen consumption, which would require improved understanding of the reaction mechanisms and pathways responsible for biomass degradation, both biologically and thermochemically.

CONCLUSIONS

By modeling the hatch and stairway system in a marine cargo vessel as two well-mixed compartments with kinetic parameters obtained from laboratory experiments performed by Kuang *et al.* (2008), it was found that the parameters need to be scaled in

order to reproduce the magnitude of pollutant concentrations observed onboard. This may be due to the oxygen-limiting environment in the laboratory experiment and the fact that different batches of pellets were used in the laboratory experiment and onboard. Using the model with adjusted kinetic parameters, the general trend of data recorded in the first 12.5 days of the voyage could be predicted. Further validation, however, requires the data recorded over the whole journey. It was also noted that in both the unscaled and the scaled models, the predicted oxygen levels were much higher than the measured values. This result indicates that most of the oxygen may have been converted into various oxygenated intermediates instead of CO and CO_2 or simply adsorbed onto wood pellets. The reaction kinetics model needs to be improved by incorporating the effect of oxygen concentration into the kinetic equations.

A sensitivity analysis on the storage temperature showed that the final CO concentration increased with increasing storage temperature initially and then decreased after reaching a peak value when the environmental temperature is constant at $\sim$15°C throughout the entire trip. Both CO_2 and CH_4 final concentrations increased monotonically with temperature.

Assuming that the kinetic parameters applied were correct, the natural ventilation for the system studied was found to be $3.78 \times 10^{-3}\ hr^{-1}$. Based on the same assumption, different combinations of the total ventilation rate and time required prior to a safe entry into the stairway were estimated. The modeled results suggested a minimum forced ventilation rate of $\sim$4.4 hr^{-1}, below which the CO concentration in the stairway can never be lowered to the TLV level. At 4.4 hr^{-1}, it takes $\sim$10 min for the CO concentration in the stairway to reach a safe concentration of 25 p.p.m.v.

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