Modelling Greenhouse Gas Generation for Landfill

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Abstract - Landfill has been widely used in many countries for the final disposal of solid waste material due to its economic advantages. Landfills emit mostly methane and carbon dioxide. In this work, the dynamic characteristics of greenhouse gases generated from the closed landfill system were studied. The chemical reaction processes involved are considered and a mathematical model is formulated and analyzed. The behaviors of the key greenhouse gases, namely, carbon dioxide and methane, are carefully studied. It was found that our proposed model is qualitatively in good agreement with the real world phenomena. The characteristics of greenhouse gases of interest namely carbon dioxide and methane were found to depend on the reaction rate in a complex manner. Since the system is closed, each gas species becomes a constraint to one another. We can utilize these findings to control the landfill system and to take benefit from the useful products. Moreover, it suggests that methane and carbon dioxide could be used for electricity generation which helps reduce greenhouse gases in atmosphere.

Keywords - Landfill; Waste; Greenhouse gas; Mathematical model; ODE

I. INTRODUCTION

Landfilling is one of the most commonly adopted technologies for refuse disposal [1]. Landfill methods continue to be widely used in different countries for the final disposal of solid waste material due to its economic advantages [2]. However, a lot of greenhouse gas, especially CO₂ and CH₄, is produced in the landfill waste management process. Therefore, to reduce greenhouse gases, governments around the world are encouraging projects that turn landfill gas into electricity. Landfill methane has the potential to produce 2,700 MW of electric generating capacity in the United States alone and 9,000 MW worldwide.

Landfill gases are mixtures of several gases with its main constituents being methane 50 – 55% and carbon dioxide 45 – 55% [3]. It is aerobic and anaerobic decomposition which mainly generates methane and carbon dioxide, respectively. Methane is regarded as one of the most important greenhouse gases because its global warming potential over decades is 28 times higher than carbon dioxide [1,4-7]. Hence, studying generation of methane and carbon dioxide is one of the interesting research areas especially from the greenhouse gases view point [2,8]. Global warming is one of a number of environmental impacts that derived from solid waste management options. Several research works focused on the landfill system and related gases in connection with the environmental problem [9].

Besides the experimental and empirical research approach to study the landfill system, mathematical modeling is one of the alternative tools to uncover this complex system problem [10,11]. The mathematical model is a representation in mathematical terms of the behavior of real world systems or objects. Mathematical models are quick and easy to produce; they can simplify a more complex situation which can help us improve our understanding of the real world as certain variables. Moreover, it enables predictions to be made or can help provide control [10,11,12]. It can take many forms, such as dynamical systems, statistical models, or differential equations [13]. And using the systems of ODE is one of very well-known method [14]. In the system of differential equations model, the most important consideration is equilibrium or steady state. In addition,
III. MODEL FORMULATION

In this section, the chemical reactions of greenhouse gas in a closed system are presented and a ODEs system model is formulated. To clearly understand our system model and results, we briefly review the relevant compositions and changes in the landfill system as follows.

A. Real World System Background

Typically, the decomposition of refuse to methane in landfills is a microbial mediated process which requires the coordinated activity of several trophic groups of bacteria [15]. The composition of the gas produced changes with each of the four phases of decomposition.

A1. Phase I – Aerobic Phase (Hydrolysis): During the first phase of decomposition, aerobic bacteria can survive and grow in an oxygenated environment. They consume oxygen while breaking down the long molecular chains of complex carbohydrates, proteins, and lipids that comprise organic waste. As you can see from Fig.1 [3], there is 80% N₂ and 20% O₂ at the beginning. Both of oxygen and nitrate are consumed. The primary by product of this process is carbon dioxide and hydrogen. Phase I continues until the available oxygen is depleted. The gas composition will be around 25% CO₂ and 10% H₂.

A2. Phase II – Anaerobic Phase (Acidification): Phase II decomposition starts after the oxygen in the landfill has been used up. Bacteria convert compounds created by anaerobic bacteria (a process without an oxygen requirement) into acetic, lactic, and formic acids and alcohols such as methanol and ethanol. The landfill becomes highly acidic. The gaseous by products of this process are CO₂ and H₂: the N₂ content of the gas decreases during this phase and is nearly completely displaced at the end of the phase; the pH decreases. As you can see from Fig. 1 carbon dioxide increases from 25% to 65% by the end of phase II. Hydrogen increases slowly from 10% to 20% [16].

A3. Phase III – Initial Methanogenic Phase (Acetogenesis): The landfill becomes a more neutral environment when methane producing bacteria began to establish themselves. Acid – producing bacteria create compounds for the methanogenic bacteria to consume. Methanogenic bacteria consume the carbon dioxide and acetate. In this phase, there is a rapid increase in rate of methane production to about 50% of gas composition. The increase of CH₄ production is associated with a decrease of CO₂ (from 65% to nearly 50%) and H₂; pH slowly increases.
A4. Phase IV – Stable Methanogenic Phase (Methanogenesis): Phase IV decomposition begins when both the composition and production rates of landfill gas remain relatively constant. Landfill gas usually contains approximately 50% to 55% methane by volume, 45% to 50% carbon dioxide, and 2% to 5% other gases. Oxygen, hydrogen and nitrogen decline as the landfill passes through the four phases. Gas is produced at a constant rate in Phase IV, typically for about 20 years; however, gas will continue to be emitted for 50 or more years after the waste is placed in the landfill [17,18]. The time spent in each phase depends on each landfill site. Gas production might last longer, for example, if greater amounts of organics are present in the waste, such as at a landfill receiving higher than average amounts of domestic animal waste. It should be noted that the rate and volume of landfill gas produced at a specific site depend on the characteristics of the waste and a number of surrounding factors such as the presence of oxygen in landfill, moisture content, temperature, waste composition, age of refuse, bacteria and pH. Landfill can be separate into two types: open and closed dumps. Open dumps pose significant environment and public health hazards because they have no gas control and collection systems. In contrast, gas in closed landfill can be collected and applied to make easy.

B. Chemical Model of Landfill Gases

Starting with the full chemical reaction of greenhouse gases, we simplify and reorganize them with imposed assumptions to get the final chemical reactions of interest.

Firstly, the reactions involving oxygen, hydrogen, water, carbon monoxide, carbon dioxide and methane are as follows [19]:

\[
\begin{align*}
CO + \frac{1}{2}O_2 & \rightarrow CO_2 \\
CO + H_2O & \rightarrow CO_2 + H_2 \\
CO + H_2 & \rightarrow CH_4 + \frac{1}{2}O_2 \\
2CO + H_2 & \rightarrow CH_4 + CO_2 \\
CO + 3H_2 & \rightarrow CH_4 + H_2O \\
CO_2 + 4H_2 & \rightarrow CH_4 + 2H_2O
\end{align*}
\]

Here we focus on a closed system. We focus on the variation of CO2 and CH4. As mentioned in phase I, oxygen and nitrogen can be found. Hence, we consider reactions (2) and (6) which can explain carbon monoxide, water, carbon dioxide, hydrogen and methane. Next, let \( k_1 \) and \( k_2 \) be the reaction rates of equation (2) and (6), respectively. With some manipulation, we represent the closed landfill system where surrounding factors are not considered by:

\[
\begin{align*}
CO + H_2O & \xrightarrow{k_1} CO_2 + H_2 \\
CO_2 + 4H_2 & \xrightarrow{k_3} CH_4 + 2H_2O
\end{align*}
\]

Here, reaction (7) represents the dynamics from the beginning of phase I and reaching a peak at phase II. After that, equation (8) takes over since the starting time of phase III and continues to the end of phase IV.

C. Mathematical Model of Landfill Gases

In order to understand the gas system in this closed landfill through equations, starting from the previous chemical models, we formulate a representation using the system of differential equations describing changes of each gas in this system. Consider chemical reaction (7). The change of each chemical species depends on the reactants CO and H2O, where the reactants decrease with rate \( k_1 \). In contrast, the products, CO2 and H2, increase with rate \( k_1 \). It can be written as four differential equations as follows:

\[
\begin{align*}
\frac{d[CO]}{dt} &= -k_1[CO][H_2O] \\
\frac{d[H_2O]}{dt} &= -k_1[CO][H_2O] \\
\frac{d[CO_2]}{dt} &= k_1[CO][H_2O] \\
\frac{d[H_2]}{dt} &= k_1[CO][H_2O]
\end{align*}
\]

In similar manner, the differential equations of chemical reaction (8) are formulated as follows.

Figure 1. Changes in typical landfill gas composition after waste placement (EPA, 2017)
For the chemical reaction (8), the change of each gas depends on CO₂ and H₂ and decreases with rate \( k_2 \) while CH₄ and H₂O increase with rate \( k_2 \). From (9) and (10), each gas has two differential equations to explain its variation. Therefore, we can conclude that:

\[
\begin{align*}
\frac{d[C\text{O}_2]}{dt} &= -k_2[C\text{O}_2][H_2]^4 \\
\frac{d[H_2]}{dt} &= -k_2[C\text{O}_2][H_2]^4 \\
\frac{d[CH_4]}{dt} &= k_2[C\text{O}_2][H_2]^4 \\
\frac{d[H_2O]}{dt} &= k_2[C\text{O}_2][H_2]^4 \\
\end{align*}
\]  

Equation (10)

It is seen that equation (11) is a set of nonlinear first order ODEs. To understand the system dynamics, we apply numerical methods to solve it. It should be remarked that for the sake of simplicity we redefine reaction rates \( k_1, k_2, k'_1 = 0.5k_1 \) and \( k'_2 = 0.5k_2 \) for the numerical analysis.

**IV. RESULTS AND DISCUSSION**

We applied the Runge – Kutta method via MATLAB R2013a ode45 to solve the system. Each result takes a few minutes to get the data from time 0 up to time 300.

Since it is very important to validate our model, we generate the data to see if our numerical data are consistent with those data given in Fig. 1. From Fig. 1, as mentioned previously, there are four phases in the reaction landfill system. Phase I features the increase in CO₂ from almost null. This phase is aerobic phase by nature and not included in our model study, meaning we consider the system dynamics from the anaerobic phase (phase II) to Phase IV.

Fig. 2 shows typical solution curves for the case of \( k_1 = k_2 = 4 \), where we take initial values for CO, H₂O, CO₂, H₂ and CH₄ as 1, 1, 0.5, 0, and 0 respectively.

The results are at least qualitatively consistent with those shown in Fig. 1. Here our solutions include water and carbon monoxide for the sake of understanding. The data of CO₂ and H₂ has the same trend. Apparently, H₂ in this system slowly decreases. Since the data in Fig. 2 does not clearly show what changes in the second phase, we magnify the results between time 0 and 5: Fig. 3 clearly shows the second and third phase which is divided by the peak of carbon dioxide as mentioned before.

In Fig. 4, we consider four cases when \( k_1 = k_2 \). The numerical results are shown in Fig. 4a – d and Table 1.
Surprisingly, the peak of CO₂ is 78% by volume for all cases. Similarly, the intersection between CO₂ and H₂O graph is at 62.5% and 55.6% for CO₂ and CH₄, respectively. At steady state time, water is at maximum quality (70 – 75 %) for this system. The next sequences are CH₄, CO₂ and H₂ which are 55 – 70, 50 – 55, and 7 – 15 percent by volume. As we can see from the graphs, while k₁ and k₂ are equal and increase, the length of phase III gets shorter. The lengths are approximately equal to 250, 150, 75 and 50 units for reaction rates 0.25, 1.00 and 1.50 respectively.

It is noted that, as we can see from Fig. 4 and Table I, all results reach the fourth phase time before time=300. It can be concluded that if k₁ and k₂ are equal and small then the system will slowly reach phase IV.

We consider values of H₂O, CO₂, CH₄ and H₂ at time=300 for reaction rates 0.75, 1.50, 3.00, and 4.50 in Fig. 5 (see also Table I).

Water and methane increase with increasing reaction rate, but carbon dioxide and hydrogen decrease. In equilibrium state, phase IV, this system has the highest concentration of water (over 70%). Second is methane between 55 and 70 percent, carbon dioxide is third sequence (about 50 – 55%). Finally, hydrogen is only 5 to 15 percent.

Table I provides numerical results for k₁ not equal to k₂. It was found that the maximum value of carbon monoxide is in between 70 – 80 percent.

This increases as the parameters increase. When we consider the stage where crossing between gases occurs they were found as follows. At the crossing between CO₂ and H₂O, it appears that the peak values for each case of...
the parameter values are found to be very close (62.5%). Similarly, the crossing values of CO₂ and CH₄ are also very close in all cases (55.56%). In addition, the crossing times in both cases are found to be in a similar manner, namely, the larger the parameter values, the shorter the crossing time values.

In Fig. 6, the relation between carbon dioxide and methane is shown. We consider three cases, namely, \( k_1 = k_2 = 1 \), \( k_1 = 0.25 \) and \( k_2 = 2 \), \( k_1 = 2 \) and \( k_2 = 0.25 \).

It was found that while carbon monoxide decreases, methane increases which is consistent with eq. (7) – (8). Because carbon monoxide is a source for methane production, the increase in methane would occur if carbon monoxide is used and depleted eventually.

Fig. 7 shows the relation between carbon dioxide and water.

As seen from reactions it is clear that carbon dioxide concentration is inversely proportional to water. It should be remarked that the rate of change between these two gases does not depend on the parameter values.

In Fig. 8, the relation between carbon dioxide and hydrogen is shown. In similar manner to Fig. 7, the rate of change between these two gases is independent of the parameter values.

To sum up, (7) and (8) describe the variation of anaerobic processes of closed landfill by control of external factors through a mathematical model.

V. CONCLUSION

In this work, the dynamical characteristics of greenhouse gases generated from a closed landfill system were studied. The chemical reaction involved are considered and a mathematical model was formulated and analyzed. The behaviors of the key greenhouse gases, namely, carbon dioxide and methane, are carefully studied. It was found that our proposed model is qualitatively in good agreement with the real world phenomena. The characteristics of carbon dioxide and methane were found to depend on the reaction rate in a complex manner. Since the system is closed, each gas species becomes a constraint on one another. We can utilize these findings to control the landfill system and to take benefit from the useful products. For example it is better to make \( k_1 \) less than \( k_2 \) as this leads to the system to quickly reach phase four. As a result, there would be abundance of methane when \( k_2 \) is large. Hence if we can control these reactants, we can take advantage of the landfill greatly.

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