Simulation of ozonolysis of volatile organic compounds: Effect on flue gas composition

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Abstract. This study shows that the reaction of ozone with various volatile organic compounds (VOC) yields different flue gas composition in terms of the carbon dioxide, oxygen and moisture contents. Steam production and thermal output requirements from a combustion system (i.e., a boiler) may dictate the range of operating conditions, such as the air to fuel mass flow rates. To improve the combustion efficiency in these operating conditions, low temperature plasmas have been used to ionize air and generate ozone as an oxidant for ozonolysis with the VOC. Therefore, this study simulates the reaction mechanism of the ozonolysis of VOC and the effect on the flue gas composition, which affects the combustion efficiency. Simulation results show that residual oxygen in the flue gas reduces, reducing the excess air. Thus, the corresponding efficiency loss through dry flue gas would be reduced. Literature data shows that emissions of alkanes, alkynes and alkenes per unit mass of solid fuel is evident for both coal and biomass, and thus ozonolysis of these VOC would reduce the excess air, improving the combustion efficiency.

1. Introduction

Current power generation technologies rely on the combustion of solid fuels such as coal and biomass. The combustion of both coals and biomass emits volatile organic compounds (VOC) which include alkanes, alkenes, alkynes and aromatics. The composition profiles of VOC differ for different fuels, and the concentration is related to the fuel volatile matter content.

Emission factors of VOCs for coal and biomass range from 0.04 to 4.5 g/kg and 0.06 to 19.69 g/kg [1, 2]. The variation in the emission factors is due to the type of fuel and combustion system. Open burning of crops emits higher amounts of VOCs (10 g/kg) compared to residential stoves burning wood (1.92 g/kg) and biomass boilers with wood pellets as fuel (0.15 g/kg) [1, 2]. The amount and reaction of the VOCs with the oxidant determines the flue gas composition. Of particular concern is the residual oxygen and carbon dioxide (CO₂) content in the flue gas, which determine the excess air and the dry flue gas losses, and hence the combustion efficiency. The higher the residual oxygen content, the higher is the excess air, which results in a higher dry flue gas loss and lower combustion efficiency.

Steam production and thermal output requirements from a combustion system (i.e., a boiler) demands a certain amount of airflow rate, resulting in a smaller window of operating conditions for optimum
excess air and low dry flue gas loss. Various studies used low temperature plasmas to generate ozone as the oxidant for reaction with the VOC (i.e. ozonolysis of VOC) to improve the combustion performance [3, 4]. Ehn et al. [3] reported that addition of low concentrations of O₃ into low-swirl methane (CH₄)-air flame at lean conditions increased formaldehyde (CH₂O), determined from Planar Laser Induced Fluorescence (PLIF) imaging of hydroxyl (OH) and CH₂O. The increase in CH₂O was well predicted by Large Eddy Simulations (LES) with CH₄-air-O₃ reaction mechanisms. The sub-mechanism for O₃ included its presence in the flame and its interaction with all other species. Simulation results also showed that the addition of O₃ increased the laminar flame speed, allowing the flame to burn under more turbulent conditions [3].

Similar results are shown in the work by Gao et. al.[5], who investigated the effect of ozone addition on laminar flame speeds of alkenes and alkanes. Ozonolysis of alkanes (CH₄ and C₂H₆) have shown to increase the flame speed over lean to rich equivalence ratios, whereas for alkenes, the flame speed was reduced [5]. A photocatalytic and ozone oxidation (UV/TiO₂+O₃) system was combined to decompose VOCs from the fumes of cooking stoves. Fiberglass filter (FGF) was coated with TiO₂, and a continuous-flow reactor combined photocatalysis with ozone oxidation. The VOCs in the simulated cooking fume decomposed by 64 %, with ozonolysis only contributing 34 % [6].

Ozonolysis of VOCs was also performed to understand the effects of a precursor hydrocarbon on the formation of secondary organic aerosols (SOA), and to predict the SOA formation potential [7]. A model was developed to predict the VOC (mainly alkenes) conversion rates by O₃, OH, and NO₃ in residential spaces [8].

The above studies did not present the final flue gas composition as a result of the ozonolysis of the VOC. The flue gas composition, specifically, the carbon dioxide (CO₂), residual oxygen (O₂) and moisture content (H₂O), are often used to determine combustion efficiencies. The carbon dioxide and residual oxygen content are used to calculate efficiency losses due to dry flue gas exiting the stack, and the moisture content determines the wet flue gas losses. Thus, this study investigates the reaction mechanisms of the ozonolysis of VOCs and the effect on the flue gas composition by thermodynamic equilibrium simulations.

2. Methodology

2.1. Volatile Organic Compound Composition of Biomass and Coal

Coal and biomass have a volatile matter (VM) content of approximately 40% to 60% and 80% respectively [9, 10]. Table 1 shows the properties of coal and wood that were obtained using a CHNS analyzer (LECO, model 628) for ultimate analysis and a thermogravimetric analyzer (LECO) for proximate analysis. Under optimal boiler conditions, flaming combustion is dominant, and the residual pyrolysis products are emitted as VOCs. For the purpose of the simulation, 0.5 kg and 0.8 kg of volatile matter are estimated to be emitted from 1 kg of coal and biomass [11]. The corresponding VOC compositions can be found in [11]. For alkenes/alkynes, the amount is 0.35 and 0.41 kg/kg of coal and biomass; for alkanes, the content is 0.030 and 0.14 kg per kg of coal and biomass; for aromatics, the content is 0.08 and 0.064 to 0.312 kg/kg of coal and biomass respectively.

2.2. Simulation of ozonolysis of volatile organic compounds

The simulation was performed with FactSage 7.2, a commercially available software that calculates Gibbs free energy to simulate various chemical reactions. For the sake of brevity, the methodology is simplified, and readers are referred to the FactSage website for more details about the equations involved to simulate the reactions [12]. Ozone reacts with alkane, alkene, and alkyne in 10 kg of air at 600 °C according to the following reaction:

\[ aO_3 + bC_nH_{2n} + cN_2 + dO_2 \]  \hspace{1cm} (1)
In this simulation, C\textsubscript{x} based hydrocarbons are simulated, therefore x is 2, and y corresponds respectively for ethyne, ethene and ethane. The amount of ozone produced from the low temperature reactor, a is 0.01 and 0.02 kg. This amount is subtracted from the mass of oxygen, b is thus (2.1 – a) kg. The amount of mass for nitrogen, c is 7.9 kg. The amount of VOC, b is estimated at 0.2 kg. More details of the simulation are found in [11].

3. Results and Discussion

3.1. Effect of ozonolysis of volatile organic compounds on the O\textsubscript{2} and CO\textsubscript{2} contents

For flue gas from C\textsubscript{2} hydrocarbons, Table 1 shows that the O\textsubscript{2} and CO\textsubscript{2} are the lowest for C\textsubscript{2}H\textsubscript{6} with no ozonolysis. With increasing O\textsubscript{3} to 20 g, the residual O\textsubscript{2} decreases by 0.002 %. Similar results are observed for C\textsubscript{2}H\textsubscript{2} and C\textsubscript{2}H\textsubscript{4}.

| Mass of O\textsubscript{3} (g) | CH\textsubscript{4} | C\textsubscript{2}H\textsubscript{2} | C\textsubscript{2}H\textsubscript{4} | C\textsubscript{2}H\textsubscript{6} |
|--------------------------------|----------------|-----------------|-----------------|----------------|
| 0  | 11.203 | 3.4615 | 13.104 | 4.3700 | 12.379 | 4.0188 | 11.754 | 3.7195 |
| 10 | 11.202 | 3.4615 | 13.103 | 4.3703 | 12.378 | 4.0188 | 11.753 | 3.7195 |
| 20 | 11.201 | 3.4615 | 13.102 | 4.3703 | 12.377 | 4.0187 | 11.752 | 3.7195 |

Based on literature, the aromatic emissions from biomass are higher on average than coal [11]. Aromatics were not included in the simulation work, since the least complex form of aromatics has six carbons (C\textsubscript{6}H\textsubscript{6}), and the ozonolysis of a C\textsubscript{6} hydrocarbon would yield a higher amount of CO\textsubscript{2} compared to C\textsubscript{2} hydrocarbons. The ozonolysis of CH\textsubscript{4} and C\textsubscript{2}H\textsubscript{6} show a significant difference in the CO\textsubscript{2} emissions (3.4615 % and 3.7195 % respectively).

3.2. Effect of ozonolysis of volatile organic compounds on H\textsubscript{2}O, NO and OH contents and temperature

The other main constituents of the flue gas from ozonolysis of C\textsubscript{2}H\textsubscript{6} by 20 g of O\textsubscript{3} are N\textsubscript{2} (78.7700 %), H\textsubscript{2}O (5.5726 %), NO (0.1704 %), and intermediates such as OH (0.0137), O and HO\textsubscript{2} (<0.001 %). The residual O\textsubscript{3} is less than 1 ppm. Table 2 shows the composition of H\textsubscript{2}O, NO and OH in the flue gas after ozonolysis of the VOC. With increase in O\textsubscript{3}, the OH concentration increases for the ozonolysis of C\textsubscript{2}H\textsubscript{2} by 5.2 %; C\textsubscript{2}H\textsubscript{4} by 4.3 %; and C\textsubscript{2}H\textsubscript{6} by 3.3 %. The increase in OH concentration is an increase in O\textsubscript{3} concentration [13]:

\begin{align*}
O\textsubscript{3} & \rightarrow O_{2} + O \quad (2) \\
O + CH\textsubscript{4} & \rightarrow CH\textsubscript{3} + OH \\
H + O\textsubscript{2} & \rightarrow OH + O \\
H + O\textsubscript{3} & \rightarrow OH + O_{2} \quad (5)
\end{align*}

The chain termination reaction of OH + H\textsubscript{2} → H\textsubscript{2}O [13] suggests that an increase in OH should increase H\textsubscript{2}O or moisture content in the flue gas. Instead, an increase in OH corresponds with a decrease of H\textsubscript{2}O, by 0.0092 % for the ozonolysis of C\textsubscript{2}H\textsubscript{2}; 0.0049 % for C\textsubscript{2}H\textsubscript{4}; and 0.0036 % for C\textsubscript{2}H\textsubscript{6}. This is because the increase in O\textsubscript{3} increases the reaction temperature as shown in Figure 1, and the increase in temperature reduces the amount of H\textsubscript{2}O in the flue gas, more so for C\textsubscript{2}H\textsubscript{2} (alkynes), followed by C\textsubscript{2}H\textsubscript{4} (alkenes) and C\textsubscript{2}H\textsubscript{6} (alkanes).
Figure 1. Variation of reaction temperature with ozonolysis of volatile organic compounds

Table 2. Composition of H₂O, NO and OH after ozonolysis of respective volatile organic compounds

| Mass of O₃ (g) | CH₄ | C₂H₂ | C₂H₄ | C₂H₆ |
|---------------|-----|------|------|------|
|               | H₂O (%) | NO (%) | OH (%) | H₂O (%) | NO (%) | OH (%) | H₂O (%) | NO (%) | OH (%) |
| 0             | 6.9144   | 0.1837 | 0.01813 | 2.1800   | 0.2012 | 0.01065 |
| 10            | 6.9143   | 0.1853 | 0.01843 | 2.1799   | 0.2036 | 0.01083 |
| 20            | 6.9141   | 0.1870 | 0.01873 | 2.1798   | 0.2056 | 0.01121 |
|               | 4.0131   | 0.1744 | 0.0116 | 5.5728   | 0.1671 | 0.01324 |
| 10            | 4.0143   | 0.1761 | 0.0118 | 5.5727   | 0.1687 | 0.01346 |
| 20            | 4.0129   | 0.1778 | 0.0121 | 5.5726   | 0.1704 | 0.01370 |

4. Conclusions
This study shows that the reaction of ozone with volatile organic compounds reduces efficiency losses associated with excess air in combustion systems. Increasing the amount of ozone decreases the amount of residual O₂ from by 0.002 %. The effect of ozonolysis on the dry flue gas loss is more pronounced for alkanes (0.0019 %), followed by alkynes (0.0016 %) and alkenes (0.0009 %). The increase in ozone
increases the reaction temperature, and the increase in temperature reduces the amount of moisture in the flue gas, more so for alkynes, followed by alkenes and alkanes. An increase in ozonolysis of the VOC increases the OH concentration and decreases the moisture content in the flue gas. The moisture content decreases because the increase in O$_3$ increases the reaction temperature, and the increase in temperature reduces the amount of moisture in the flue gas. Overall, the simulation suggests that reaction of ozone with volatile organic compounds increases the efficiency of combustion. The simulation suggests that the residual oxygen and moisture content in the flue gas decreases, increasing the reaction temperature. The experimental investigation of the effect of the ozone addition on the combustion efficiency is presented in an upcoming article.

Acknowledgments
Tenaga Nasional Berhad funded this work (TNBR/ SF195/2015 & TNBR/ SF240/2016).

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