Full Length Article

Carbon monoxide release mechanism in cellulose combustion using reactive forcefield

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GRAPHICAL ABSTRACT

ABSTRACT

The generation of carbon monoxide, that can cause loss of human life, is unavoidable during combustion of wood related biomass fuels. A correct understanding of reactions associated with carbon monoxide formation during cellulose combustion is critical for the safe application of biomass fuels. Although bench-scale experiments have been applied to quantify products generated during cellulose combustion, the details of reactions are still very hard to be figured out. In this work, a fundamental approach using molecular dynamics simulations equipped with reactive forcefield has been adopted to study reactions in the oxidation process of a major pyrolyzed product of cellulose called cellobiose. The effect of temperature on the reaction mechanism has also been studied. By tracking the reaction details during cellobiose oxidation, the predicted reaction pathway is in good agreement with experimental results. The initiation stage of oxidation involves the decomposition of cellobiose with the formation of formyl and carboxyl groups, and the formation of carbon monoxide is highly dependent on the concentration of these groups. Subsequently, the formed carbon monoxide is oxidized into carbon dioxide, where reaction steps for the formation and decomposition of carboxyl group are involved. A higher temperature promotes the decomposition of cellobiose with the formation of more formyl and carboxyl groups causing more
1. Introduction

As recent global scenarios represent an increase in energy demand, biomass fuels have regained popularity in modern society as a valuable replacement for fossil fuels with lower overall carbon dioxide (CO₂) emissions [1–3]. All types of wood wastes including forestry residues, mill residues, agricultural residues, urban wood and yard wastes and dedicated biomass crops make excellent biomass fuels and can be used in a wide variety of biomass technologies. In particular, wood and charcoal are major cooking and heating fuels in poor countries and regions. However, wood smoke generated during wood burning contains harmful pollutants such as carbon monoxide (CO), and safety issues of wood, especially wood used in daily life, are critical. Hundreds of people or more die annually from CO poisoning related to the use of home heating appliances [4,5]. The ability to predict chemical reactions, especially those related to CO releases from wood combustion, has become increasingly important for safety engineering.

Wood fuels consist of three major structural biopolymers, namely cellulose, hemicellulose, and lignin, with percentages of these components varying in different biomass materials [6,7]. Cellulose as the chief component in wood fuels is a long-chain polymer of cellulose consists of β-D-glucopyranosyl groups linearly linked together through positions 1 and 4 of adjacent glucose units. Aggregation of the linear chains of the cellulose macromolecules within the microfibrils provides a crystalline structure that is inert and inaccessible to chemical reagents [8–10]. Moreover, as cellulose can provide outstanding mechanical properties, thermal degradation of cellulose-based materials is manifested by random scissions in the glycosidic linkages (the C-O bonds connecting the adjacent atoms based on atomic valence rules (For example, a stiff coordinated atoms). The potential can be divided into bond-order dependent and non-bond order dependent contributions. 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Experimental results predicted by ReaxFF provide an unbiased representation of the pre- and post-ignition oxidation chemistry. ReaxFF has been successfully utilized in analysis of hydrocarbon oxidation, decomposition, and reaction of energetic materials, thermal decomposition of epoxy resin, etc [19–22].

In this work, the reactions of cellobiose oxidation at different temperatures are studied using MD simulations equipped with ReaxFF. The reaction pathways are predicted to figure out the CO emission mechanism. As all the parameters of ReaxFF are obtained from the QM calculation, the results correlated to the covalent properties of glucose molecules are predicted by ReaxFF and fitted to the results from density functional theory (DFT). Simulations of cellobiose oxidation at different temperatures are performed. The reaction pathways predicted by ReaxFF are compared with experimental results for validation. The intermediates, free radicals, CO and CO₂ of cellobiose oxidation under different temperatures are identified and quantified. Such a thorough understanding of the reactions during cellobiose oxidation contributes to improving the understanding upon the combustion of cellulose-based materials and enables the development of effective control upon carbon monoxide formation. A comprehensive understanding of the reaction mechanism at atomic scale provides a new perspective for the development of eco-friendly materials while further enriching the theory of material design. For example, the formation of CO can be slowed by reducing the concentration of critical free radicals that dominate the reaction steps associated with carbon monoxide formation. Furthermore, the approach using MD simulations equipped with ReaxFF adopted in this work is valuable for predicting the combustion behavior of various polymers, extending the understanding of chemistry occurring during the combustion process.

2. Computational details

2.1. ReaxFF

ReaxFF applies a bond-order formalism in conjunction with a polarizable charge description to describe both reactive and nonreactive interactions between atoms, allowing accurate modeling of both covalent and electrostatic interactions for various materials. The energy of a system is the sum of several partial energy contributions defined as [23]:

\[
E = E_{\text{bond}} + E_{\text{over}} + E_{\text{under}} + E_{\text{vol}} + E_{\text{ele}} + E_{\text{conj}} + E_{\text{id}} + E_{\text{Coul}}
\]  

(1)

where \(E_{\text{bond}}\) is the bond energy associated with forming bonds between atoms and is a function of interatomic distance; \(E_{\text{over}}\) and \(E_{\text{under}}\) are energy penalties imposed for over-coordinated atoms and under-coordinated atoms based on atomic valence rules (For example, a stiff energy penalty is applied if a carbon atom forms more than four bonds.); \(E_{\text{vol}}\) and \(E_{\text{ele}}\) are the energy of valence angles and energy related to torsion angles; \(E_{\text{conj}}\) is the contribution of conjugation effects to the molecular energy; \(E_{\text{id}}\) is energy of the van der Waals force and \(E_{\text{Coul}}\) is the energy of Coulomb force. The units of these parameters are kcal/mol. The potential can be divided into bond-order dependent and non-bond order dependent contributions. The bond order (BO) between atoms \(i\) and \(j\) is calculated directly from the interatomic distance \(r_{ij}\) as following [20,24]:

\[
BO_{ij} = BO_{ij}^{\text{mix}} + BO_{ij}^{\text{polar}} + BO_{ij}^{\text{polar}} = \exp[p_{\text{bo,1}}(\frac{r_{ij}}{a})^{1.5}] + \exp[p_{\text{bo,3}}(\frac{r_{ij}}{a})^{1.5}] + \exp[p_{\text{bo,5}}(\frac{r_{ij}}{a})^{1.5}]
\]

(2)

\[
+ \exp[p_{\text{bo,7}}(\frac{r_{ij}}{a})^{1.5}]
\]
where \( r_0^\sigma, r_0^\pi \) and \( r_0^{\pi\pi} \) are the equilibrated distances of the sigma bond (\( \sigma \)), the first pi bond (\( \pi \)) and the second pi bond (\( 2\pi \)) respectively with units of Å. \( P_{bo,1}, P_{bo,2}, P_{bo,3}, P_{bo,4}, P_{bo,5}, \) and \( P_{bo,6} \) are unitless empirical parameters. All covalent interactions such as \( E_{bond}, E_{val} \) and \( E_{int} \) are expressed in terms of these bond orders so that all terms dissociate properly as any bond is broken ensuring that all partial energy contributions related to valence interactions disappear smoothly with bond dissociation [25]. For the non-bonded interactions, the interactions between every pair of atoms are calculated regardless of whether the connectivity changes. BO is used to obtain a smooth transition from non-bonded to \( \sigma \), \( \pi \) and \( 2\pi \) bond character [26] and it is inversely proportional to bond length. The covalent bond feature necessitates the addition of a bond-order correction to remove spurious bond character between non-bonded neighbors. Terms in the potential dependent on BO are calculated directly from the corrected BO. Since the bond orders are updated at every iteration, the connectivity of the system can change continuously. The ReaxFF formulation uses a geometry-dependent charge calculation scheme electronegativity equalization model (EEM) that accounts for polarization effect and modeling of charge flow leading to a bridge between QM and empirical forcefield [25]. The electronegativity of an atom \( i \) in a N-atom molecule can be expressed by [27,28]

\[
\chi_{eq} = \chi_i^{QM} + \Delta \chi_i \cdot 2 + (\eta_i^{n} + \Delta \eta_i) q_i + \sum_{j \neq i}^{N} \frac{q_j}{r_{ij}}
\]

(3)

where \( \chi_{eq} \) is the electronegativity of the molecule; \( \chi_i \) and \( \eta_i \) are the electronegativity and hardness of the isolated atom \( i \) respectively; and \( \Delta \chi_i \) and \( \Delta \eta_i \) are corrections to the respective isolated atom values due to the incorporation of the atom in a molecule. Both \( \chi \) and \( \eta \) have units of eV. \( q_i \) and \( q_j \) represent the atomic charge on atom \( i \) and atom \( j \) respectively, and \( r_{ij} \) is the interatomic distance between atoms \( i \) and \( j \) with a unit of Å [29]. The sum of \( q_i/r_{ij} \) is the external potential of the atom \( i \) with a unit of eV. Moreover, the individual atomic electronegativities are equal to the molecular electronegativity and the sum of the atomic charges is equal to the total molecular charge; the actual values of atomic charges can be determined by solving a set of linear equations (3) [28]. A fundamental difference between ReaxFF and non-ReaxFF is that ReaxFF does not use fixed connectivity assignments for the chemical bonds and the connectivity in ReaxFF is determined by bond order. ReaxFF not only determines equilibrium bond lengths, valence angles, and so forth from the chemical environment of the system but can also handle connectivity changes associated with reactions.

The ReaxFF description of each element is transferable across different phases including gas, liquid and solid phases and environments [30,31]. For example, an oxygen atom is treated with the same in Eq. (2) whether that oxygen is in the gas phase as \( O_2 \), or in the liquid phase within an \( H_2O \) molecule, or incorporated in a solid oxide [26]. The potential parameters for oxygen are transferable to a wide variety of oxygen systems including oxygen molecule, oxygen ion, oxygen atom in various crystal and amorphous structures, surfaces, clusters, and interface. Such transferability allows the developed ReaxFF parameters of hydrocarbon oxidation [19] used to predict the combustion of cellobiose molecule. All the parameters of ReaxFF for hydrocarbons are generated from QM calculation describing single, double and triple bond dissociation in systems including atoms of carbon, oxygen and hydrogen [32,33]. These parameters are then optimized by minimizing the following sum of squares [17,30,34]:

\[
Error = \sum_{i}^{N} \left[ \frac{(\chi_i^{QM} - \chi_i^{ReaxFF})}{\sigma_i} \right]^2
\]

(4)

where \( \chi_i^{QM} \) is the DFT result; \( \chi_i^{ReaxFF} \) is the result predicted by ReaxFF; and \( i \) is the number of DFT results for one type of properties (such as bond, valency angle, torsion angle and heat of formation). The unit of \( \times x \) depends on the type of properties. For example, when \( \times x \) represents the bond property, it has a unit of Å. When \( \times x \) represents the heat of formation, it has a unit of kal/mol. \( \sigma_i \) is the accuracy specified. Once the error for one type of properties is defined, a deviation between the QM calculated and the ReaxFF predicted data of more than this acceptance criterion can have a relatively large influence on the sum of squares [34]. The atomic relaxations during the ReaxFF fitting procedure have been carried out with a conjugate gradient minimizer until convergence less than a specific value.

Fig. 1 shows the details of the workflow for ReaxFF. The uses of the relationship between bond-order and bond-distance that are intimately coupled with dynamic charges shown in Eqs. (2) and (3) enable ReaxFF to determine the charge state of an atom or ion accurately and autonomously. Specifically, from the atomic positions in each frame of the trajectory, the atomic connectivity (bond order) is determined as a function of interatomic distance and can be calculated based on Eq. (2). The covalent terms that are dependent on bond order such as bond energy, angle energy, and torsion angle energy can be calculated. Various contributions are totalized to obtain the net force on each atom for a given timestep. After position updates, the bond order is updated, and the charge is redistributed based on Eq. (3). The bond order of each atom among consecutive frames is then compared to detect any change of covalent bonds. A single change of bond order includes information about dissociation, association or isomerization reactions. Multiple
connectivity changes between the same frames are considered as parts of the same reaction [35]. All the changes of bond order in consecutive frames are assembled, and the corresponding reaction equations are formulated to generate the reaction pathway of combustion.

2.2. Simulation details

The QM calculation is performed using the B3LYP hybrid DFT functional. The Mulliken populations have been used to calculate the charges. Mulliken charges can accurately describe the local electronegativity and provide a self-consistent scheme for obtaining charges for the ReaxFF training set. The MD simulations are performed in LAMMPS [36] in isothermal and isochoric ensembles (namely VNT ensemble) where the temperature is controlled by a thermostat. The decomposition of a system with one glucose molecule and a system with an oxygen molecule is performed in MD simulations to fit the QM results. The simulation procedure starts with the minimization of systems at a low temperature of 300 K.

Crystalline cellulose Iβ, which is predominant in wood, is chosen as the representative cellulose model. The structure of cellulose fibrils at different scales is shown in Fig. 2. The cellulose has a monoclinic unit cell with dimensions of a = 7.8 Å, b = 8.2 Å, c = 10.4 Å and an angle γ = 96.5° at the ab plane [37–39]. There are two parallel chains in the unit cell where one chain (the origin chain) is positioned at the corner of the unit cell parallel to the c axis direction, and the second chain (the center chain) passes through the center of the ab plane. Each chain in the unit cell is composed of two glucose residues linked by the β (1–4) glycosidic linkage [37]. As the study of cellulose combustion is focused on cellobiose oxidation, a series of systems with one cellobiose molecule and 50 oxygen molecules are constructed in Materials Studio software from Accelrys [38] as shown in Fig. 3(a); each system has the same number of atoms but different configurations. A periodic boundary condition is applied to three directions of the system. The geometry optimization and energy minimization by the conjugate gradient method are performed on the modeled structure at 300 K. The modeled systems are equilibrated for 1 ns in NVT ensemble. The temperature of the equilibrated systems is increased to 2000 K, 2500 K and 3000 K respectively. The systems are then equilibrated at different high temperatures in NVT ensemble for reactions. The total simulation time for the systems is determined by the extent of oxidation for the cellobiose molecule and the simulations are terminated when no further oxidation is observed, namely all the carbon atoms from the cellobiose molecule are in the form of CO2.

The high temperature used in the MD simulations is to ensure that the reactions occur. According to collision theory, where for a reaction to occur it is necessary for the reacting atoms or molecules to collide with one another, and the collision frequency (Z) for a reaction between A and B is defined as [39,40]:

$$Z = \frac{N_A N_B}{V} \frac{8k_B T}{\pi \mu_{AB}^2}$$

(5)

where $N_A$ and $N_B$ are the number of the atom A and the atom B; $V$ is the volume with a unit of $m^3$; $\sigma_{AB}$ is the reaction cross-section simplified as $\sigma_{AB} = \pi (r_A + r_B)^2$ with a unit of $m^2$; $r_A$ and $r_B$ are the radii of the atom A and the atom B with units of m; $k_B$ is Boltzmann’s constant; $T$ is the temperature with a unit of K; and $\mu_{AB}$ is the reduced mass of the reactants A and B with a unit of kg. As the total number of atoms is less than 200 in the modeled system, the high temperature can increase the probability of effective collision for reaction occurrence, as shown in Fig. 3(b). Because the temperature can significantly affect atom collision, cellobiose oxidation at different temperatures i.e. 2000 K, 2500 K and 3000 K is studied.

3. Results and discussion

3.1. Comparison of covalent properties between DFT calculation and ReaxFF

As the parameters of ReaxFF for glucose molecules are based on the existing literature for carbohydrate [23], the covalent related properties including the dissociation energies of various bonds, the valence angle bend energy and the rotational barriers of the dihedral angle for the monomer of cellobiose namely glucose are first predicted by ReaxFF. These predicted properties are then predicted by DFT calculation, and the ReaxFF predicted values are compared with DFT calculated data for validation. Fig. 4 shows a comparison of bond dissociation curves in oxygen and glucose molecules predicted by ReaxFF and DFT calculation. ReaxFF provides a good representation of the dissociation energies and equilibrium bond distance for the O=O bond in oxygen and C-C, C-

![Fig. 2.](image-url)
O, C-H and O-H bonds in the glucose molecule. For valence angle bend properties, the geometry of glucose is minimized for various fixed values of the angles and the rest of the structure is relaxed during the minimization. Fig. 5 compares the valence angle bend energy curves of C-C-O and C-C-C with the DFT data. Fig. 6 shows a comparison of the rotational barrier for the four types of H-O-C-C dihedral angles between

![Fig. 3](image-url)  
(a) The initial model of reaction with one cellobiose molecule and 50 oxygen molecules; (b) effect of temperature on the collision frequency where the effective collision is increased with the rise of temperature.

![Fig. 4](image-url)  
Fig. 4. Dissociation for different types of bonds in glucose molecule predicted by ReaxFF and calculated by DFT (a) O-O bond in oxygen; (b) H-O bond in glucose; (c) C-O bond in glucose; (d) C-H bond in glucose; (e) C-C bond in glucose. The relative potential energy means the difference of potential energy between non-equilibrated state and equilibrated state.
ReaxFF and DFT calculation. It is found that ReaxFF successfully reproduces the valence angle bending and the dihedral angle for glucose units. These results indicate that it is reliable to use these ReaxFF parameters to predict the covalent related properties of polymers consisting of glucose such as cellobiose.

Fig. 5. Rotational barriers for different torsion angles (a) C-C-C and (b) C-C-O in glucose molecule predicted by ReaxFF and calculated by DFT. The relative potential energy means the difference of potential energy between non-equilibrated state and equilibrated state.

Fig. 6. Energies for distortion of different dihedral angles in glucose molecule predicted by ReaxFF and calculated by DFT (a) H11-O4-C4-C3; (b) H9-O2-C2-C1; (c) H8-O1-C1-C5; (d) H8-O1-C1-C2. The relative potential energy means the difference of potential energy between non-equilibrated state and equilibrated state.
3.2. Oxidation of the cellobiose molecule

The simulations of oxidation between cellobiose and oxygen molecules at different temperatures are performed with parameterized ReaxFF. As mentioned above, the system is first equilibrated at 300 K, and then it is gradually raised to 2000 K, 2500 K and 3000 K respectively. No reaction between cellobiose and oxygen is observed in such a stage. As the oxygen is sufficient during the simulation, the cellobiose is finally oxidized into CO2 and H2O. The cellobiose starts to decompose at approximately 16 ps when the oxidation occurs at 2000 K and the oxidation reaction as shown below is completed after about 4.5 ns.

\[ \text{C}_{12}\text{H}_{22}\text{O}_{11} + 12\text{O} \rightarrow 12\text{CO}_2 + 11\text{H}_2\text{O} \]  

With the increment in temperature to 3000 K, the oxidation reaction is completed within approximately 2.7 ns at 3000 K. It is found that the cellobiose molecule is initially decomposed. Various intermediate products, free radicals, CO and CO2 are generated in this stage. Specifically, the main intermediate products formed include glycolaldehyde (C3H6O3), acrylic acid (C3H4O2), methyl formate (C2H4O2), acetaldehyde (C2H4O), acetylene (C2H2), glyoxal (C2H2O2), formic acid (CH2O2), formaldehyde (CH2O), hydrogen (H2) and water (H2O). The occurrence of these products has also been found in experiments on wood combustion and pyrolysis of glucose and cellobiose [41–45], indicating that the reaction pathway predicted by ReaxFF is reliable.

Fig. 7 shows the reaction pathway of cellobiose at 2500 K and 3000 K. As the reactions at 2000 K are much closer to those at 2500 K, the details of cellobiose oxidation at 2000 K are not represented. When oxidation occurs at 2500 K, the glycosidic bond of cellobiose molecules is initially broken with the formation of one glucose molecule (C6H12O6) and one levoglucosan molecule (C6H10O5). C6H12O6 is decomposed into two C3H6O3 molecules which are converted into C2H2O2 through different reaction routes as shown in Fig. 7(a). For example, one C3H6O3 molecule is dehydrated forming C3H4O2 which reacts with hydroxyl (·OH) to form the free radical ·C3H5O3. Such free radical is then decomposed into CH2 and CH2O, C2H2 subsequently reacts with O2 to form C2H2O2. For another C3H6O3 molecule, it is directly decomposed into free radicals ·C2H2O2 and ·CH3O, and then, the free radical ·C2H2O2 reacts with the free radical ·HO2 to form C3H6O4. C6H12O6 is transformed into C2H2O2 with the release of H2O2. The CH2O is oxidized into ·CH3O and then decomposes into CH2O2 and ·OH. In addition, the C6H10O5 is also converted into C6H12O6 and C2H2O2 by a series of decomposition reactions listed in Fig. 7(a) with the release of CO2. Through a series of reaction steps, all intermediate products are converted into two types of free radicals namely carboxyl group (·CHO2) and formyl group (·CHO). The free radicals ·CO2 and ·CHO are converted into CO through the following reactions:

\[ \cdot\text{CHO}_2 \rightarrow \text{CO} + \cdot\text{OH} \]
\[ \cdot\text{CHO} + \cdot\text{OH} \rightarrow \text{CO} + \text{H}_2\text{O} \]  

At the end of the decomposition stage, all the carbon in cellobiose is converted to CO and CO2. Subsequently, all CO molecules are oxidized into CO2 completing the whole oxidation process. It is found that CO formed during cellulose oxidation is from the decomposition of ·CHO2 and ·CHO.

Different from the pyrolysis at 2500 K, the backbone of cellobiose is directly broken with the formation of C4H6O2 and C6H12O6 at the beginning of decomposition occurred at 3000 K as shown in Fig. 7(b). This reaction occurs because less energy is required for the dissociation of glycosidic bonds compared with other bonds in cellobiose and more energy can be provided for bond dissociation at high temperature. The decomposition of C6H12O6 results in the formation of C2H4O2 and H2O2. C10H18O9 is converted into C2H2O2, methacrylic acid (C4H6O2) and C2H4O2. The decomposition of C4H6O2 leads to the production of the free radicals ·C2H2 and ·C2H2O2. The free radical H is observed from the decomposition of ·C2H2 with the formation of C2H2. C2H2 is then oxidized into C2H2O2 and C2H2O is converted into C2H2O2. Similarly, the reaction that occurs at 2500 K, cellobiose is pyrolyzed into C2H2O2, C2H4O2, CH2O2 and CH2O. These molecules are then converted into ·CHO and ·CHO2 which are important species for producing CO.

Through analysis of the reaction pathway for cellobiose oxidation at different temperatures, it is found that this oxidation process can be divided into two stages. The first stage involves the conversion of cellobiose into CO and CO2. The production of CO is dependent on the
decomposition of the free radicals ∙CHO2 and ∙CHO. During this process, a small amount of oxygen also participates in the reaction. Although the temperature has an obvious effect on production of the intermediates, C3H6O3, C2H4O2, C2H2O2, C2H2O, CH2O2 and CH2O are critical intermediate products in the pyrolysis of cellobiose. The majority of free radicals ∙CHO2 and ∙CHO is from the decomposition of the products C2H2O2, C2H4O, CH2O and CH2O. The second stage involves the oxidation of CO into CO2. This reaction occurs when the first step is completed. As MD simulation can give the details of atomic arrangement, the bond breaking, and formation events can be identified. Fig. 8 shows examples of bond breaking and formation for different reactions involved in the oxidation of cellobiose molecule under temperature of 2500 K. The reaction related to the dissociation of glycosidic bonds is shown in Fig. 8(a), and a dehydration reaction is shown in Fig. 8(b). The reaction is determined by detecting the change of bond order among continuous snapshots. The molecular structure can be determined by tracking the atom position in a molecule benefiting to confirm the species of intermediates produced in the oxidation process. This is also one advantage of using the approach of MD simulations with ReaxFF to analyze the reaction pathway.

3.3. Effect of temperature on the production of CO and CO2

Fig. 9 shows the quantity of CO and CO2 formation during the oxidation process of cellobiose at different temperatures. Generally, the quantity of CO first increases and then reduces, whereas the quantity of CO2 continues to increase throughout the whole oxidation process. Such change trends for CO and CO2 are correlated to the two stages of cellobiose oxidation. In the first stage, cellobiose is decomposed into the free radicals ∙CHO2 and ∙CHO through different routes. More ∙CHO2 and ∙CHO are produced, and more CO and CO2 are converted. An increase in both CO and CO2 concentration is observed. The subsequent reduction in CO concentration is because of its oxidation. It is also found that the oxidation of CO does not occur at the first stage. This is because the reaction temperature in simulations is very high compared with the experimental value. The pyrolysis of molecules is an endothermic reaction whereas the oxidation of CO is an exothermic reaction. Such a high temperature in the simulation promotes the endothermic reaction while it has a negative effect on the exothermic reaction. The first stage of cellobiose oxidation at temperatures of 2000 K, 2500 K and 3000 K is finished within 1.9 ns, 0.45 ns and 0.25 ns respectively.

By tracking the change of CO and CO2 at the second stage, it is found that the reduction of CO concentration is behind the increase of the CO2 concentration. This finding indicates that the occurrence of the following reaction is not a first-order reaction:

\[
\text{CO} + \frac{1}{2}\text{O}_2 \rightarrow \text{CO}_2
\]  

CO reacts with ∙OH to form ∙CHO2, and ∙CHO2 is decomposed into CO2 and ∙H. The unstable free radical ∙H subsequently reacts with O2 to form free radical ∙HO2 which is consumed with H2O to produce H3O3. The critical ∙OH is generated by the decomposition of the product H3O3. This observation is consistent with experimental results that ∙OH can be involved in the conversion of CO to CO2 [46]. This detailed understanding on the chemical reaction in equation (8) reveals that the existence of water molecules can affect the reaction pathway of CO oxidation because CO can also be oxidized into CO2 through the following reaction under conditions without water molecules:

\[
\text{CO} + \text{O}_2 \rightarrow \text{CO}_2 + \cdot\text{O}
\]  

The change of potential energy for oxidation at different temperatures is shown in Fig. 10. As the simulated oxidation process is performed under isometric conditions, the change of potential energy can be used to evaluate the change of reaction enthalpy. The activation
energy of each reaction step during cellobiose oxidation can be directly deduced from the profile of the potential energy change. The heat release rate for the first oxidation stage is much higher than that for the second oxidation stage. This profile for the change of potential energy can help to evaluate the heat release in the combustion process compared with experimental and numerical results [47,48].

The bond change during pyrolysis of cellulose has been quantified and compared with the experimental data. New chemical bonds related to C=O bonds such as C=O, C-C=O, and O=C-O are generated, and the proportion of C-C, C-O and O=C-C is significantly reduced during the pyrolysis process. The C=O related bonds are included in all important intermediate products such as C₃H₆O₃ (HO-CH₂-CH₂-COOH) with a carboxyl group, C₂H₂O₂ (H₂C=O) with two formyl groups, CH₂O₂ (HCOOH) with a carboxyl group and CH₂O (H₂C=O) with a formyl group. These intermediate products are decomposed into free radicals ∙CHO₂ and ∙CHO which dominate the formation of CO. The oxidation of CO into CO₂ involves reaction steps correlated with the production and formation of the free radical ∙CHO₂. This result indicates that if the concentrations of the free radicals ∙CHO₂ and ∙CHO are effectively controlled, the release of CO can be slowed. The free radical ∙OH is involved in almost all the key reactions related to the decomposition of the cellobiose molecule into molecules with a low content of carbon. For example, the decomposition of intermediate products C₃H₄O₂ and C₂H₄O, which are formed independently of temperature, requires the participation of free radical ∙OH to convert into ∙CHO and ∙CHO₂. Cellobiose oxidation can be decelerated by decreasing the concentration of ∙OH because higher energy barriers are required to be overcome through other reaction routes. To reduce the concentration of these critical free radicals, molecules with a strong ability to react with these free radicals can be added. Moreover, this study of cellobiose oxidation provides an insight into the oxidation mechanism of char that dominates the combustion of natural cellulose-based materials such as wood during burning. In the experiments, the char composed of carbon, oxygen and hydrogen has been simplified to consist of only carbon. Based on this simplification, different models have been proposed for about the char reaction mechanism, including a one-step model where char reacts with oxygen to form CO₂, a two-step model where char reacts with oxygen to form CO which is then oxidized.

**Fig. 9.** The change in the number of CO and CO₂ at different temperatures (a) 2000 K; (b) 2500 K; (c) 3000 K. The change of the CO concentration is consistent with the two-stages of oxidation process. The increment of the CO concentration is due to the more generation of ∙CHO₂ and ∙CHO during the decomposition of the cellobiose molecule. The reduction of the CO concentration is caused by the oxidation of CO to CO₂.

**Fig. 10.** The potential energy change during the reaction process at different temperatures. The energy release rate is higher at the first stage than that at the second stage. The increment of temperature accelerates the heat release rate.
into CO₂; a char gasification model where char reacts with CO₂ to form CO which is then oxidized to CO₂, and a mixed two-step and gasification mode [50–52]. From the simulation results, it is found that CO is converted into CO₂ through several reaction steps, and the free radical -OH, O₂ and H₂O are involved in this conversion. This finding provides more detailed insight into the char oxidation mechanism and contributes to extending the understanding on the combustion of cellulose-based materials. With a fundamental understanding upon cellulose combustion, a new generation of cellulose-based composites, which can significantly reduce the toxic gas released during burning, becomes feasible, and it is envisioned that such composites can provide a safe and sustainable application for wood waste, leading to an enormous impact and significance to society. Additionally, as the details of water molecules participating in the reactions have been revealed, this work lays a foundation to study the effect of humidity on the combustion reaction of cellulose-based materials.

4. Conclusions

CO is unavoidably generated in the combustion of wood fuels that mainly consist of cellulose. CO can cause the loss of human life when wood is used as a home heating appliance. Although experimental and numerical approaches have been applied to study cellulose-based material combustion, and have proposed to estimate CO generation as a risk factor for human health. However, the details of cellulose combustion remain uncertain. In this work, an approach using MD simulations equipped with ReaxFF has been successfully applied to predict the oxidation behavior of cellulose which is the main pyrolyzed product of cellulose. Cellulose is initially decomposed into smaller molecules such as C₅H₇O₂, C₂H₂O₂, CH₂O, and CH₄O which are the main sources of the important free radicals CHO₂ and CHO. The quantity of CO is highly dependent on the concentration of these two free radicals. In addition, the free radical OH plays a significant role in the decomposition of cellulose. An effective control on the concentration of free radicals CHO₂, CHO and OH enables the reduction of the CO release during cellulose combustion. This work not only clearly clarifies the complex reaction process of cellulose oxidation but also provides a great theoretical guide for the further development of effective strategies in CO control and for the design of eco-friendly materials.

Credit authorship contribution statement

Huali Hao: Conceptualization, Methodology, Investigation, Writing - original draft. Cheuk Lun Chow: Funding acquisition, Project administration, Supervision, Writing - review & editing. Denvid Lau: Funding acquisition, Project administration, Conceptualization, Supervision, Writing - review & editing.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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References


[38] BIOVIA, Accelrys Software Inc. Materials Studio. 2007.


