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Production of Calcium Carbide from Fine Biochars**

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Carbon is the most abundant source of energy and chemicals on the earth. Biomass produced from photon-activated conversion of atmospheric CO_2, and biomass fossils such as coal and petroleum are all carbon-rich sources. In around only one century of heavy industrial use of petroleum, this hydrocarbon source has already depleted to a point of a widespread concern over its scarcity in the decades to follow.[1] Biocarbon, also known as biochar, can be readily produced from a vast sustainable supply of lignocellulosic biomass through pyrolysis.[2] It is often in fine form and characterized by low mechanical strength and high activity in comparison to coal-derived chars. The ability to use biochar for the production of chemicals with high energy efficiency will largely alleviate our dependence on shrinking petroleum feedstock. Herein, we show reaction of fine biochars with fine CaO for the production of CaC_2, an important starting material for production of many commodity chemicals. The process offers the potential to redirect the carbon conversion pathway.

CaC_2 is produced by the reaction $3C + CaO + E^1 \rightarrow CaC_2 + CO$, where E^1 is the energy required for the process, about 445.6 $kJ\,mol^{-1}$ at above 2000 °C.[3] CaC_2 can be readily converted into acetylene by treatment with water: $CaC_2 + 2H_2O \rightarrow C_2H_2 + Ca(OH)_2$. Acetylene is an oxygen-free platform chemical for production of chemicals, for example, polyvinylchloride (PVC), vinyl acetate, and 1,4-butanediol. In this carbon conversion process, the main products CaC_2 and then C_2H_2 are readily separated from other components.

The current CaC_2 production technology dates back to 1892 and has not changed much since then.[4,5] It uses an electric arc furnace, which is limited only to small-scale operations, typically less than 40 kt CaC_2 per year. This process requires granular char and CaO of 5–30 mm in size and with sufficient mechanical strength, such as coal char, to allow unrestricted release of byproduct CO. Because of the low reaction rate resulting from the low surface area and poor contact between the large feed particles, high temperatures (about 2200 °C) and long reaction times (1–2 h) are usually required.[6] These constraints inevitably result in high energy consumption ($4000\,kWh\,t_{CaC_2}{}^{-1}$), high production cost, and high CO_2 emissions in electricity generation.[7]

Autothermal heating by combustion of chars has been studied as an alternative process for CaC_2 preparation.[8–10] However, the use of large feed particles, as with the electric arc process, requires long production times and high reaction temperatures to obtain sufficient yields; therefore, the process is not economically attractive for commercial development.

We report a considerably reduced temperature (by 500 °C), shortened reaction time, and increased thermal efficiency in converting fine biochar into CaC_2. More importantly an autothermal reactor similar to the modern high throughput gasification reactors could be used. Figure 1 shows thermogravimetric/differential thermogravimetric (TG/DTG) data and mass spectra for released CO for the reaction of pine wood char and CaO at a nominal particle size of 0.022 mm with a C/CaO molar ratio of 3.6. The total mass loss at temperatures higher than 1510 °C corresponds to a CaC_2 yield of 99 % based on CaO. XRD analysis (Figure S1 in the Supporting Information) confirms CaC_2 as the main product. Gas chromatograph analysis of the C_2H_2 released from CaC_2 hydrolysis shows a CaC_2 yield of 97 %.

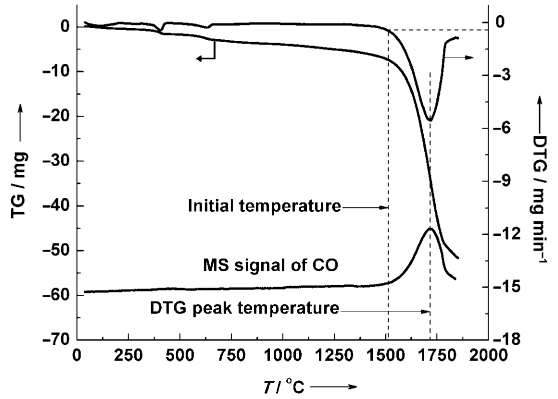

Figure 1. TG/DTG curves and MS signal for release of CO from the reaction of CaO and a pine wood char of size 0.022 mm at a C/CaO molar ratio of 3.6.

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Figure 2 shows initial and DTG peak temperatures of the reaction using chars of different particle sizes derived from pine wood and bamboo. The initial temperature, defined in Figure 1 as the temperature when DTG signal reaches

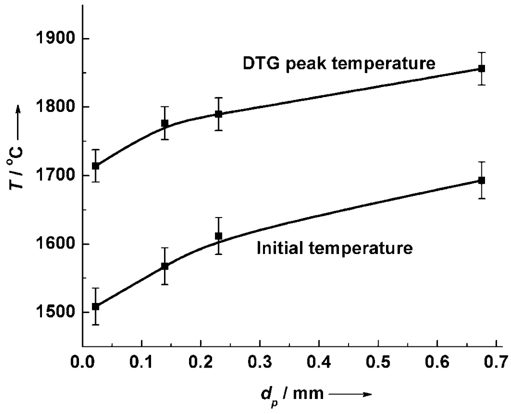

Figure 2. The initial and DTG peak temperatures of CaC_2 formation through CaO and biochars (from pine wood and bamboo) of different particle sizes (d_p).

-0.5 mg min^{-1} (corresponding to a CaO conversion rate of about 1.2 % min^{-1}), decreases from about 1700 °C for a size of 0.675 mm to 1510 °C for a size of 0.022 mm; correspondingly, the peak temperature decreases from about 1850 to 1710 °C.

Figure 3 shows mass-loss rates (DTG) at 1650 °C for reactions of CaO with various biochars as well as other carbon materials. Clearly the biochars have higher d_{002} values (from XRD) and are more active than the coal chars, petroleum coke, and graphite.

The results indicate that CaC_2 can be produced at temperatures much lower than that required by the current electric arc process. The process involves little vaporization of the reactants and CaC_2 except for the release of CO. The high CaC_2 yield indicates constant mass transfer between the chars and CaO at the conditions used. Since the melting points of char and CaO are much higher (3625 °C for graphite and 2580 °C for CaO), the mass transfer may be attributed to nanocrystal migration. The temperatures in Figure 2 are all higher than the Tammann temperature of CaO, one half of its melting point in Kelvin (1154 °C), and above which nanocrystal migration becomes significant.[11] This hypothesis is supported by the experiments shown in Figure 4. Figure 4 a,b shows the appearance of a sample before and after the reaction when a C/CaO mixture with a molar ratio of 3.5 was heated to 2000 °C at a rate of 20 °C min^{-1}. The carbidization between 1510 and 1900 °C yielded a final mixture containing 86.5 % CaC_2 and 13.5 % char (Figure S2 in the Supporting Information). The product (Figure 4 b) is loose with dense particles. When the C/CaO molar ratio (1.8) was below the reaction stoichiometry (Figure 4 c,d), the carbidization temperature was unchanged but additional mass loss after the full conversion of the char at 1828 °C was observed (Figure S3 in the Supporting Information). Figure 4 d indicates the formation of eutectics consisting of CaC_2 and CaO.

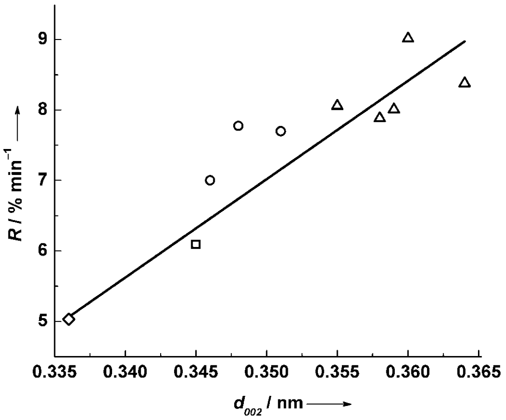

Figure 3. Conversion rates of CaO (R) at 1650 °C for reaction of CaO with chars. The d_{002} values are the interplanar distances from XRD analysis of the chars treated at 1650 °C. △: biochars (from apricot shell, willow wood, bamboo, corncob, and pine wood, in the order of increasing d_{002}); ○: coal chars (from anthracite, bituminous coal, and lignite, in the order of increasing d_{002}); □: petroleum coke; ◇: graphite.

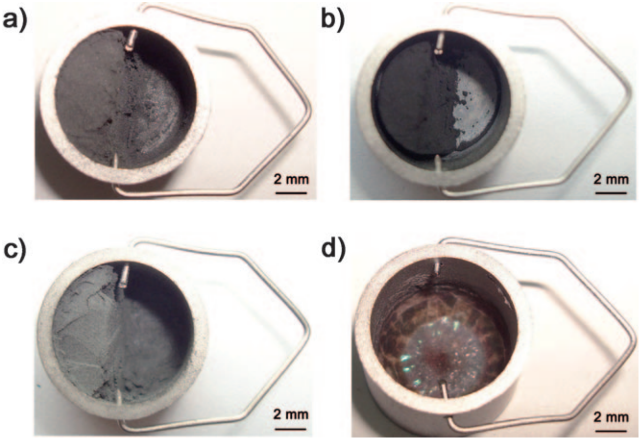

Figure 4. Photos of fine reactants of size 0.022 mm and the products obtained after heating to 2000 °C at 20 °C min^{-1}. Top: at a C/CaO molar ratio of 3.5, a) before and b) after the reaction; bottom: at a C/CaO ratio of 1.8 c) before and d) after the reaction.

When a larger particle size (e.g. 5 mm in diameter) is used (Figure 5), the initial temperature is shifted to 2020 °C and the DTG peak temperature to 2090 °C (Figure S4 in the Supporting Information). The core (char) and shell (CaC_2) structure in the products indicate migration of CaO into the char during the process.

Contacting the core–shell structure (Figure 5 b) with H_2O transformed the CaC_2 shell into loose $Ca(OH)_2$ that peels off from the core, yielding a CaO conversion of 77.8 % to CaC_2 and a mass loss of 4.8 % in addition to the release of CO. The visual spillage on the mouth of the crucible indicates formation of foaming slurry during the experiment and explains the additional weight loss at temperatures higher than 2128 °C (Figure S4 in the Supporting Information). The formation of a eutectic mixture by CaO and CaC_2 under the

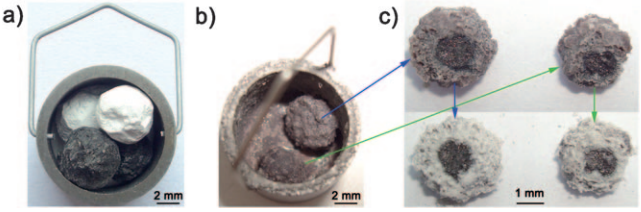

Figure 5. Appearance of the reactants and the product. a) Two CaO and two char granules of size 5 mm at a C/CaO molar ratio of 3.15 in a TG crucible; b) after heating at a rate of 20 °C min^{-1} to 2150 °C in Ar; c) cut product particles (top: black char core and gray CaC_2 shell; bottom: black char core and white $Ca(OH)_2$ shell, upon contact with moisture).

experimental conditions agrees with published results, which record the lowest eutectic temperature of 1650 °C for a CaO/CaC_2 molar ratio of 0.62.[12]

The experimental observations suggest that CaC_2 production at temperatures between 1154 °C (the Tammann temperature of CaO) and 2580 °C (the melting point of CaO) is controlled initially by CaO nanocrystal migration. Eutectic mixtures of different compositions may be formed at the interface of CaO and CaC_2 when temperature is higher than 1650 °C. The eutectic phase accelerates CaO migration towards the char. This mechanism is schematically shown in Figure 6.

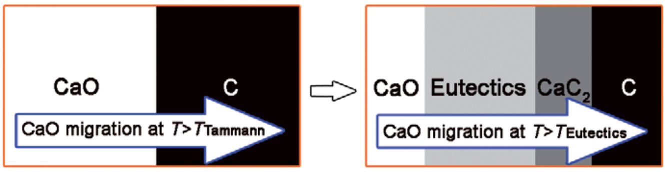

Figure 6. Reaction process of CaO and C for the production of CaC_2.

Clearly CaC_2 production is controlled by mass transfer of CaO toward the char phase. A smaller particle size results in a greater contact surface area and a reduced mass transfer barrier for the reaction; thus, the reaction rate is enhanced even at lower temperature (Figure 7). From the data in Figure 7, a reaction time of 4.6 min for 95 % conversion of CaO at 1750 °C was determined when the particle size was 0.022 mm (assuming a first-order reaction to CaO; see the Supporting Information). The dramatic decrease in temperature and reaction time, compared to 1–2 h at about 2200 °C for the electric arc process, point to a tremendous potential for energy saving. This result also implies that CaC_2 production can be carried out in autothermal mode, since the temperature becomes comparable to many autothermal processes such as pulverized coal gasification (1400–2000 °C) and the BASF process of oxidative dehydrogenation of methane for acetylene production (1540 °C).[6,13,14]

Computer simulation using Aspen Plus (Figure 8) confirms that autothermal CaC_2 production is achievable by oxidizing a fraction of char to CO to meet the energy requirement of the reaction, and the process is of higher thermal efficiency than the electric arc process especially when the reactants are preheated by the high-temperature CO generated from the CaC_2 production (see the Supporting Information).

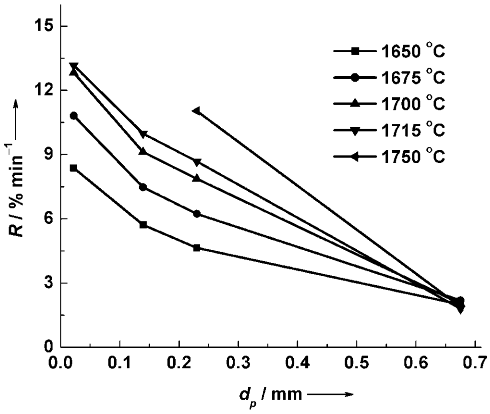

Figure 7. Conversion rate of CaO (R) at different particle sizes (d_p) at a pine wood char/CaO molar ratio of 3.6.

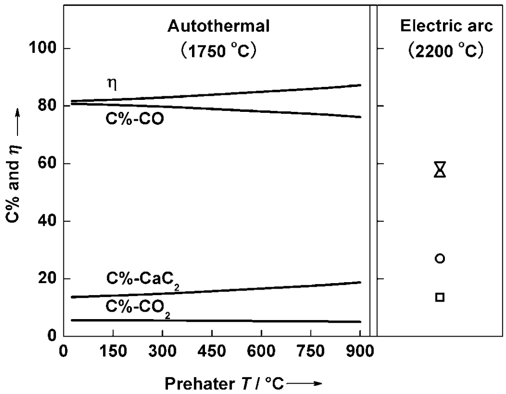

Figure 8. Carbon yields to CaC_2 (C% CaC_2), CO (C% CO), and CO_2 (C% CO_2), and thermal efficiency (η) of autothermal and electric arc processes determined by Aspen Plus simulation. The autothermal process includes preheating by the high-temperature side-product CO. ○: C% CaC_2, □: C% CO, ▽: C% CO_2, △: η.

In summary, fine biochars as feed for CaC_2 production make the autothermal process feasible at a temperature about 500 °C lower than that of the current electric arc process. The reaction time is also reduced from 1–2 h to less than 5 min. The reaction mechanism may involve eutectic mixtures at the CaO/char interphase. Coupling this process with biomass pyrolysis forms a new route for biomass conversion, which is extendable to coal-based processes.

Experimental Section

A thermoanalyzer from Setaram (Setsys Evolution 24) and a mass spectrometer from Balzers (Omnistar 200) were used. CaO had a purity of 98.3 %. The carbon sources include five biochars (derived from apricot shell, willow wood, bamboo, pine wood, and corncob), three coal chars (derived from anthracite, bituminous coal, and lignite), petroleum coke, and graphite. The preparation procedure and conditions of all the chars include pyrolysis in N_2 at 900 °C for 3 h, acid washing with a HF + HCl solution at 60 °C for 24 h, and drying at

120 °C for 5 h. Proximate and ultimate compositions determined for all the carbon sources are shown in Table S1 in the Supporting Information. Blank TG-MS experiments (with empty crucible) were made to account for the effect of buoyancy caused by the temperature rise.

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