Reduction of Carbon Dioxide in Atmosphere to Reverse Climate Change

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Svante Arrhenius (1859-1927) was a Swedish scientist who was the first to claim in 1896 that CO_2 released from burning of fossil fuels and other combustion processes might cause global warming. However, he viewed the Earth's greenhouse effect caused by CO_2 positively and believed the greenhouse effect would prevent the world from entering a new ice age, and also a warmer earth with sufficient CO_2 would bring abundant crops to feed the rapidly increasing population. He estimated that it would take 3000 years to have the atmospheric concentration of CO_2 doubled. Yet the current estimate is about one hundred years. It seems that part of his calculations is not in line with the present situation. From the beginning of the Industrial Revolution (around 1750), the concentration of CO_2 in the atmosphere has risen from 280 ppm to the current 400 ppm, which is among the highest levels in the past 20 million years. The increase was mainly caused by the burning of fossil fuels. There is inexhaustible free oxygen in the air, and the combustion of fossil fuels per kilogram produces some 10^6 times more energy than one kilogram of wind energy obtained at wind velocity of seven meters per second. Thus, other alternative energy sources can hardly compete with fossil fuels. However, burning fossil fuels produces CO_2 to cause the greenhouse effect and climate change, resulting in many wildfires and droughts in recent years. Although some people still say the global warming and climate change caused by CO_2 is a hoax or scam, most scientists think that the correlation between them is real based on various scientific data. Thus, most countries have focused on their efforts to reduce CO_2 concentration in the atmosphere to mitigate climate change in the future.

So far, scientists have many suggestions and ideas on how to reduce CO_2 concentrations in the atmosphere. Bio-energy with carbon capture and storage (BECCS) and Biochar are two most mentioned technologies. BECCS produces negative CO_2 emissions by combining bioenergy (energy from biomass) with geologic carbon capture and storage, i.e. the CO_2 released by burning biomass was captured and injected into deep geological formations. The fusing of these technologies can generate “negative emissions” by taking atmospheric CO_2 temporarily locked in plants and storing them permanently in geological formations. Here energy is the main product and the negative emissions a by-product. The 4th Assessment Report of Intergovernmental Panel on

Climate Change identified BECCS as the key technology for reaching the target of low CO_2 atmospheric concentration. Potential negative emissions via BECCS has been estimated by UK's Royal Society as equivalent to 50-150 ppm decrease in global atmospheric CO_2 concentration. Biochar production involves the heating of biomass in an oxygen-starved environment in a process called pyrolysis or torrefaction. Due to the fact that biomass fixes CO_2, which was once in the atmosphere, the stable and solid carbon in the biochar is a form of negative emissions technology. The pyrolysis process also produces bioliquid and syngas as the energy resource which can be used to substitute fossil fuel sources. The storage of biochar in soils can be used as a soil enhancer or amendment and as decontamination agent by adsorption of toxic heavy metals in soils. Two recent reports (*Nature Communication*, 2010 [1] and *Nature*, 2015[2]) described the potential of sustainable biochar to mitigate global climate change, boost agricultural yields, and control pollution. When biocoal was made from biomass in my lab, about one half or less of the biomass was turned into biocoal, one tenth was turned into syngas that can be burned to generate electricity, and two fifths into a crude but valuable bioliquid or biooil. Tim Flannery, the eminent Australian explorer and naturalist, argues that these properties of biochar "allow us to address three or four critical crises at once: the climate-change crisis, the energy crisis, and the food and water crises", because putting biochar in the soil not only fertilizes the soil, but also helps to retain water. The problem is that many of the suggestions and ideas are not in line with economics or may have unexpected results. For example, storage sites will presumably be designed to confine all injected CO_2 for geological time scales. Nevertheless, experiences with engineered systems suggest a small fraction of operational storage sites may have leakage to release CO_2 to the atmosphere in CCS. The pyrolysis of biomass in an oxygen-starved environment may need a high temperature and a longer time to increase the cost of making biochar so that no private or government has the intention to invest. According to one op-ed in the New York Times in July of this year that less than 1000 tons of biochar is produced globally each year. It illustrates that the production of biochar is indeed a problem on the economic benefits. In order to solve this problem, Academician Frank Shu of Institute of Astronomy and Astrophysics and I believe that traditional pyrolysis using hot flue gas to effect the heat transfer is not in line with economics. We should use hot liquid instead to effect the fast heat transfer to comply with economics and to be adaptable for commercialization in the future. Normally, the volumetric heat capacity of liquid is about 2000 times larger than that of gases so that the heat transfer speed by liquid is at least several hundred times faster than that of gases. An example in case is in sauna. One can stay in a sauna room for a short while even if the temperature of the steam reach 90°C. However, if the temperature of a hot spring is close to 50°C, one could not stand in the hot spring for a few seconds. If the heat transfer speed is fast, the time required for pyrolysis will be shorter. The temperature of pyrolysis does not need to be high. Only the temperature to break down part of the bonds in biopolymers of biomass is needed. In general, flammable heat transfer oil decomposes above 300°C so that we select the inflammable eutectic molten acetate salt, which is relatively stable at 300°C, as the heat transfer medium. We found that pyrolysis of plants in molten salt at 300°C for 10 minutes can give biocoal with the similar quality as the commercial biochar which was claimed to be produced at 1000°C. The advantages of biocoal are: (1) a carbon neutral biofuels, (2) lower weight and transportation cost, (3) higher heat density and combustion efficiency, (4) retention of some of the fibrous structure for easy handling, (5) high stability for long term storage, (6) no emission of greenhouse gases, such as methane and nitrous oxide, as from rotten biomass; (7) possibility of carbon trading in the future. Biocoal prepared from plant such as leucaena in a molten salt at 300°C for 10 minutes gave the molar ratio of hydrogen to carbon at about 1.2, which does not meet the standard of less than 0.7 defined by the International Biochar Association for biochar to be buried in the soil. A higher hydrogen content would lead to a slow release of some organic materials to damage the soil. We found that changing to other kinds of eutectic salt for the pyrolysis of plant at 400-500°C for 10 minutes could provide biochar with molar ratio of hydrogen to carbon less than 0.7 easily.

The biomass used in our pyrolysis process included old plants, fruit peels, used chopsticks and toothpicks, etc. The most commonly used plant is leucaena, which is considered one of the 100 most invasive species, due to its fast-growth, sprouting ability, drought resistance, and pest resistance. It is estimated that 300 million seeds may be produced per hectare per year. A lot of leucaena are available in Penghu Islands, Pingtung and Taitung counties. According to reports, leucaena in Penghu Islands was imported during the Japanese occupation era, and was introduced to Hengchun Peninsula by Taiwanese enterprises about sixty years ago. Since then, it has been widely distributed over more than 5,000 hectares in Taiwan. It is one of the most invasive alien species in Taiwan. It has nitrogen fixation capabilities, but its roots will release mimosa hormone, a toxin to other plants, so that leucaena has clustering features to form dense thickets and can destroy the biodiversity by crowding out the growth of native species. It is estimated that with a capacity of treating 360 tons of leucaena per day, it will take us eight years to finish the existing leucaena in Taiwan. The advantages to use eutectic acetate salts to transfer the heat in pyrolysis are: non-toxic, lower-melting, water-soluble, non-flammable, and no detonation due to the presence of air because the cladding of molten salt around the biomass to isolate from air. Besides, there is no black particulate emission during the pyrolysis. We are able to use our charcoal fines oxidizer to remove tar and charcoal fines. The only drawback is the need to recycle the molten salt. Fortunately, acetates have good water solubility, for example, 100mL of water can dissolve 253g of potassium acetate at 20°C. The acetates coating on biocoal and in its nanopores can be washed out easily after soaking to give the washing solution a salinity down to 0.1% by weight or less. Traditional pyrolysis of plants produced less syngas and bioliquid in unit time so that most of them were burned to provide the heat. The use of molten salt for pyrolysis can produce more syngas and bioliquid in unit time so that we can condense the bioliquid for further separation and purification to collect valuable organics or for further application. As to the aspects of energy, a plant absorbs free solar energy and CO_2 to transform and store them as chemical energy in chemical bonds in a plant. We need to heat the eutectic salt to melt so that the biopolymers in a plant can be partially decomposed to give biocoal and released syngas and bioliquid. Syngas is the energy source to keep the desired temperature of molten salt or to generate electricity for our facilities. Bioliquid such as acetic acid, methanol, and acetone, can be an energy source or to provide valuable chemicals after separation and purification. Biocoal still retains a lot of chemical energy which can be transformed into thermal energy or electricity. Thus, we estimate that the ratio of in and out of thermal energy in our process is about 1/5 to 1/10. Currently, our team has built up a pilot plant (photo below) in National Tsing Hua University, Hsinchu, under the financial support from the Ministry of Science and Technology and Academia Sinica. We hope that we can build up a truly commercial machine to carry out pyrolysis of biomass based on the collected data in the pilot plant.

One criticism sometimes voiced against the widespread use of biomass as a renewable resource is that it appropriates agricultural land. However, based on the results of a study cited by the United Nations Industrial Development Organization, there will be likely 610 exajoules (EJ, $1*10^{18}$ J) bioenergy available from residues and abandoned agricultural land in the world in 2050, in principle, without impacting food production. For reference, the total global primary energy consumption in 2012 was 560 EJ. Since 560 EJ of positive emission leads empirically to a CO_2 increase of 2.2 ppm per year after accounting for all sinks, known and unknown, a 500 EJ carbon-negative emission would then, in principle, remove CO_2 from the atmosphere at the rate of 2 ppm per year. It is estimated that the world could have a stabilized CO_2 concentration at 450 ppm by 2050 with the efforts from all governments in the world. Thus, it would be possible to reduce CO_2 concentration to 350 ppm, a consensus value of the atmospheric CO_2 as hoped by the scientific community, by 2100.

In conclusion, if we want to reduce the concentration of atmospheric CO_2 to mitigate or reverse climate change, we could proceed from biochar which we have considerable advantages especially in the field of fast commercial production of biochar. Taiwan has the leading technology in the world. In addition, Academia Sinica already has been granted patents about the continuous process of pyrolysis of biomass in molten salt from Taiwan (Republic of China), the United States, Canada, Russia, and mainland China.

References:

[1] Woolf, D. *et al.* Sustainable biochar to mitigate global climate change. *Nat. Commun.* 1:56 doi: 10.1038 / ncomms1053 (2010).

[2] Cernansky, R., State-of-the-Art Soil, *Nature*, Vol 517, 258-260 (2015).