Biomimetic Sequestration of CO_2 and Conversion to $CaCO_3$ Using Carbonic Anhydrase

Soon Kwan Jeong, Yeo Il Yoon, Sung Chan Nam
Korea Institute of Energy Research
(jeongsk@kier.re.kr)

Keywords: CO_2 Capture, $CaCO_3$, Carbonic Anhydrase

The contribution of greenhouse gases, especially carbon dioxide, to global warming is well recognized. An energy source option for the humankind energy system has become too numerous, and the thirst for more and more energy targets on usage of fossil fuels in coal-fired power plants, steel industries, and cement contributes to an increasing amount of CO_2 emission. The flue gases from conventional coal-fired power plants in Korea typically contain 12~14% CO_2 with the balance consisting mainly of nitrogen and small quantities of oxygen and impurities. The carbon dioxide concentration of flue gases is insufficient for direct compression to transport and storage of carbon dioxide. In order to get concentrated CO_2 from flue gases, we have to install CO_2 capture process such as amine or ammonia absorption. The amine-based solvents are widely used for the CO_2 capture process. Despite of the good CO_2 absorption capacity and fast absorption rate, they have some drawbacks such as corrosion, loss of solvent, generation of heat stable salts, and high penalty for energy consumption during regeneration. If an alternative solvent system having less energy for regeneration could be developed, it is very attractive option to install CO_2 capture facility. Since recently, emerging ex-vivo applications of carbonic anhydrase for its potential use in CO_2 capture technologies are attracting attentions. The objective of the present study was to investigate the feasibility of using enzymes as a biocatalyst for hydration of CO_2, as well as its precipitation in the form of calcium carbonate.

The hydration rate of carbon dioxide of bovine carbonic anhydrase (BCA) and hemocyte of diseased shell (HDS), measured through the p-NPA reaction, was determined by the UV absorbance. Figure 1 shows the differences in the reaction rates measured by the average slope of p-NPA conversion with respect to the concentrations of BCA and HDS. The reaction rate of BCA was higher than that of HDS. The k_{cat}/K_m rate constant was 230.7 $M^{-1}s^{-1}$ for BCA and 194.1 $M^{-1}s^{-1}$ for HDS. Considering that HDS is a water-soluble, conjugated protein, the k_{cat}/K_m value of HDS may be regarded as near to that of BCA. This means that BCA, which is expensive and difficult to extract, can be replaced by the more economical HDS biocatalyst extracted from oysters. $CaCO_3$ was produced by adding Ca^{2+} ion to the CO_2 hydrated solution containing CO_3^{2-}. The amount of $CaCO_3$ was also measured at different times during the reaction. The initial formation of $CaCO_3$ required about 15 s in the $CaCO_3$ precipitation experiment without the biocatalysts. In contrast, when BCA and HDS were added, $CaCO_3$ formation occurred within 5 seconds, on average, for a 3 times faster reaction rate. The final quantity of the produced $CaCO_3$ was the same since it was dependent on the amount of CO_3^{2-} originally dissolved in the water. $CaCO_3$ particles produced without the biocatalysts were larger than 10 mm in diameter, but were less than 4 mm when BCA and HDS were used. This may be because the biocatalysts enhanced the $CaCO_3$ production, thereby preventing agglomeration of particles. Additional study may be required in this regard. Figure 2 shows the XRD results for the structure of the $CaCO_3$ produced in this study. The $CaCO_3$ structure may also be the calcite structure, as indicated by a calcite

peak with $2\theta=29^{o}$. The calcite structure was apparent with or without biocatalysts, indicating that the use of the biocatalysts did not affect the $CaCO_3$ structure of the reaction product. Calcium carbonate is a common and thermodynamically stable mineral found in rocks worldwide, and is the main component of shell of marine organism, snails and eggs. If the widespread transformation of CO_2 to $CaCO_3$ is possible, it will represent a stable process for long-term CO_2 capture and storage. In addition, the process yields a final product, $CaCO_3$, which can be utilized as road pavement or paper coating materials.

The study presented here is only the beginning for the capture and storage of CO_2 using enzyme, especially HDS. Additional studies on various conditions which include cloning of enzyme, operating conditions, and scale-up factor are underway.

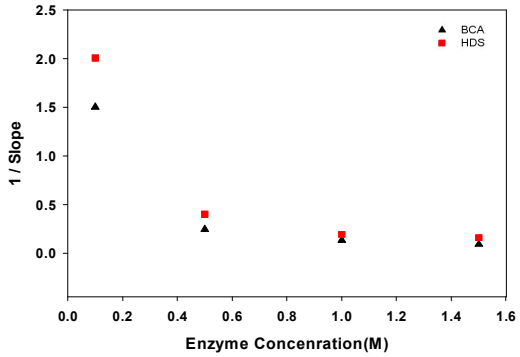

Figure 1. Effect of enzyme concentration on reaction rate.

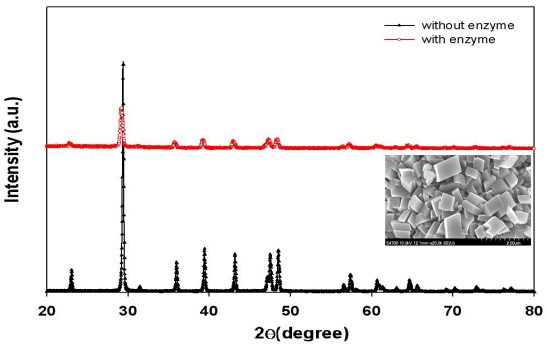

Figure 2. XRD patterns of precipitated $CaCO_3$.