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Mini Review

The Future of Carbon Dioxide

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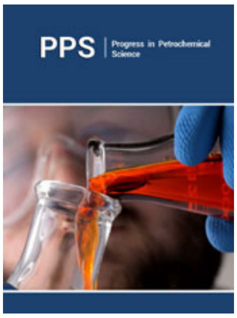

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Introduction

Current research and scientific studies clearly indicate that CO_2 should be treated as a basic or auxiliary raw material that already allows or in the near future will enable the production of a number of goods for further use [1]. Current directions of using carbon dioxide are presented in the figure below Figure 1; [2].

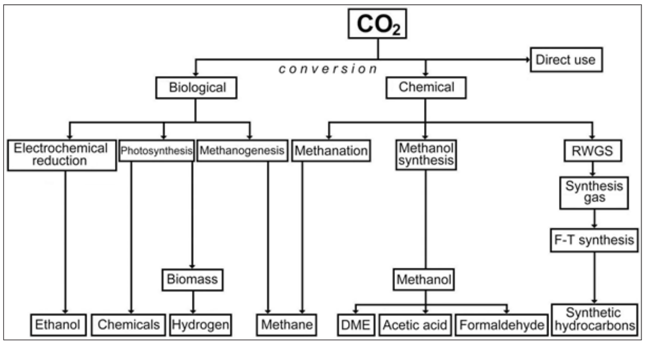

Figure 1: Capture and utilization of CO_2 (CCU) pathways (RWGS - reverse water gas shift; F-T - Fischer-Tropsch; DME - dimethylether) [2].

General Overview

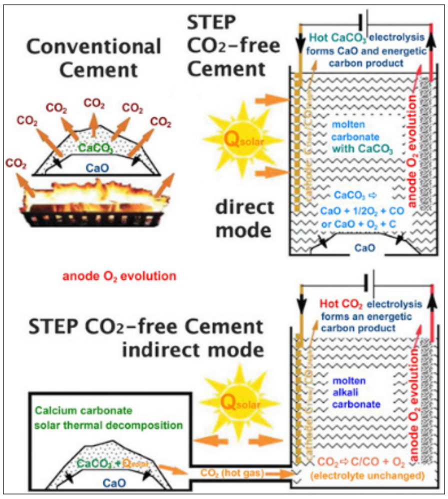

Figure 2: Conventional thermal decomposition production of lime (top left) versus STEP direct solar conversion of calcium carbonate to calcium oxide (top right) eliminating CO_2 [3].

Apart from its negative effects on the climate, CO_2 is also a valuable resource, containing carbon - one of the most used and processed elements on Earth. Coal is predicted to continue to dominate power generation for the next 20 years, and since power generation from coal is a significant source of carbon dioxide emissions, the reduction of these emissions is a critical research need. For example, the US Department of Energy's (DOE) Carbon Sequestration Program, along with related research and development programs throughout the world, continues to make progress toward the goals of lowering the cost of CO_2 capture and ensuring that the CO_2 can be safely and permanently sequestered in geologic formations in a process know as carbon capture and storage (CCS). Another potential approach to reduce CO_2 emissions is CO_2 utilization, sometimes referred to as CO_2 reuse or carbon capture and reuse (CCR). In the literature there can be find several proposals connected with the perspective use of carbon dioxide as a raw material or elaboration of a new technologies without CO_2 emission. Some years ago, there was publish a short communication related to the area of a new molten salt chemistry which allows solar thermal energy to drive calcium oxide production without any carbon dioxide emission. This new approach is called STEP (Solar Thermal Electrochemical Production). In STEP cement limestone undergoes low energy electrolysis to produce lime, oxygen and reduced carbonate without carbon dioxide emission Figure 2; [3].

Reducing our greenhouse gas emissions, while improving the global standard of living, is one of the key fundamental challenges of present century. One of the options that has been proposed to reduce greenhouse gas emissions is the conversion of CO_2 and water into fuels and chemicals. This conversion is challenging because the feedstocks have no energy content, carbon dioxide is usually present as a very dilute molecule (about 400ppm in the air) or present as a mixture of gases, and this process requires substantial amounts of energy that must come from another source. Ideally, the energy for this reaction would come from the sun. A somewhat futuristic solution, however with real possibilities of implementation in the near future, is presented in the figure below Figure 3; [4].

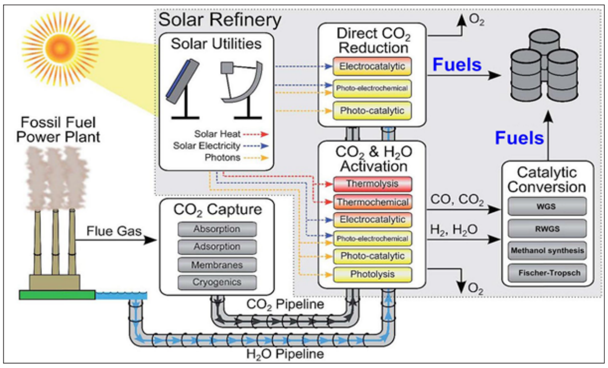

Figure 3: Schematic for solar fuels production. Solar fuel feedstocks (CO_2, H_2O, and solar energy) are captured on-site and/or transported to the solar refinery. Solar energy provides solar utilities in the form of heating, electricity, and photons which are used in the solar refinery to convert CO_2 and H_2O into fuels. CO_2 and H_2O are converted to fuels through two principal routes: (1) direct solar-driven CO_2 reduction by H_2O to fuels or (2) solar activation of CO_2/H_2O to CO/H_2, respectively, and subsequent catalytic conversion to fuels via traditional processing (i.e., methanol synthesis or Fischer-Tropsch). The approximate temperature requirements for the solar-driven conversion processes are color-coded (red = high temperature, yellow = ambient temperature) [4].

It should be noted that technologies for the recovery and reuse of carbon dioxide have been known since the second half of the nineteenth century and include three main processes developed in 1869-1922, namely: the synthesis of salicylic acid from sodium or potassium salt of phenol and CO_2 (1869), the Solvay process for the synthesis of $NaHCO_3$-Na_2CO_3 (1882) and the conversion of NH_3 and CO_2 to urea (1922). With the high-tonnage of urea production, the first two of these technologies are much less exposed as the direction of carbon dioxide management.

Currently, the steam reforming of methane is commonly used in the industrial practice. However, other types of reforming also find practical applications. The sulfur-passivated reforming developed by Haldor Topsøe operates at high carbon concentrations and favorable thermodynamic coke-formation conditions. The process benefits from controlling the amount of hydrogen sulfide in the feed stream that block the carbon nucleation sites on the catalyst through chemisorption of H_2S on the step sites of metallic Ni particles. The SPARG (Sulfur PAssivated ReforminG) process is the first technology used, using CH_4/CO_2 reforming Figure 4; [5,6]. The idea of its development by Sterling Chemical Inc., was the reduction of H_2/CO ratio from about 2.7 to 1.8.

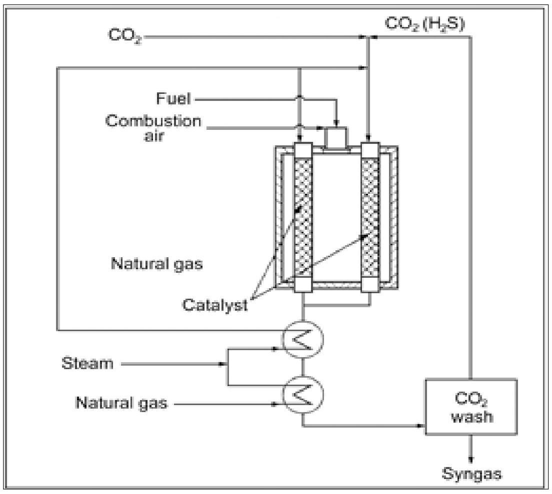

Figure 4: Simplified SPARG process flow diagram [5,6].

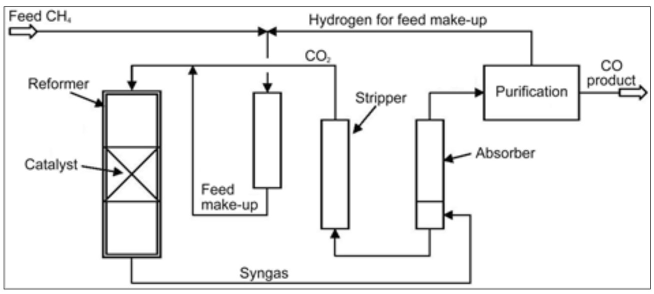

Figure 5: Schematic of the CALCOR standard process [7].

While the SPARG process combines both types of reforming: steam and dry, and its primary goal is to obtain synthesis gas with the appropriate H_2/CO ratio, the CALCOR technology (introduced by Caloric GmbH) is implemented mainly in the aspect of obtaining very high CO purity from natural gas or LPG (liquefied petroleum gas). Dry reforming is the basic reaction on which the mentioned CALCOR (CALoric CO Removal) process is based Figure 5; [7].

Conclusion

An important challenge in the near future will be the further development of methods related to the direct use and conversion of CO_2 towards useful products, as well as the issue of possible storage of carbon dioxide.

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