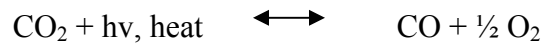


Solar Reduction of CO₂

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I. INTRODUCTION

The reduction of carbon dioxide with solar energy has been investigated as a means to reduce the amount of this green house gas in the atmosphere. This report examines the prospect of solar reduction of carbon dioxide and outlines the implementation of such a system. Project goals include lowering carbon dioxide emissions to the atmosphere and producing viable products. According to the reaction, these possible products from this process are carbon monoxide, oxygen and carbon dioxide



The tasks involved with this project include the following:

- (1) Determining a method of separating the CO₂ from the flue gas
- (2) Optimizing the efficiency of the reduction process
- (3) Determining the most profitable utilization of products
- (4) Maximizing the profit of the overall process

The San Juan power plant in Farmington, New Mexico has been chosen as the location for the proposed CO₂ reduction process. This area of New Mexico receives enough days of sunlight to supply solar energy for the process. The plant produces 14.5 million tons of CO₂ per year and is a major contributor to CO₂ emissions in the area.

II. PROCESS OVERVIEW

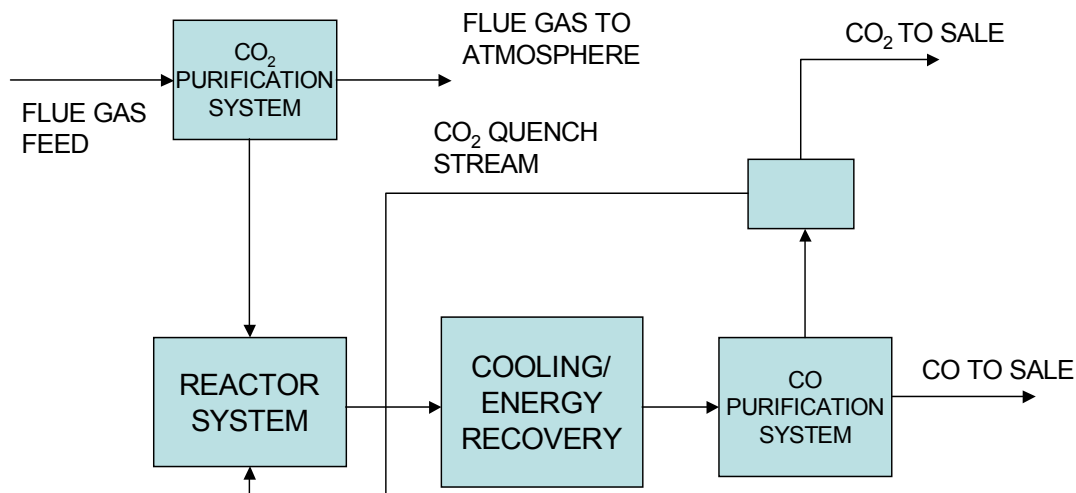


Figure 1: Process schematic

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After the fossil fuel has been burnt to produce power, the CO₂ is separated from flue gas. Studies of a number of types of separation processes have been conducted including amine scrubbing using MEA, adsorption, cryogenic processing, and membrane separation. For the separation of CO₂ from flue gas, the amine based absorption process was chosen. The complete proposed process for the conversion of CO₂ to CO and O₂ is shown in Figure 1. Chemical absorption using MEA is a proven technology for the removal of CO₂ from flue gas streams and has been used in industry for several decades. The flue gas is scrubbed with monoethanolamine (MEA) in an absorption column and the solvent, which is rich in CO₂ is regenerated in a stripper with steam to give a high purity CO₂ product (Figure 2). In the absorption process, the flue gas is initially cooled. It is necessary to remove the sulfur oxides because concentrations of SO_x above 10 ppmv can cause degradation of the MEA solvent by reacting to form corrosive, non-reclaimable salts. Thus, a spray scrubber with a mist eliminator (for SO₃ removal) utilizing caustic soda or soda ash is employed to meet the 10 ppmv requirement. After SO_x scrubbing, the flue gas is passed into an absorption column where it contacts the amine solution counter-currently. The amine solution absorbs the CO₂ from the gas through a reaction, which produces a weakly bonded intermediate. The CO₂-rich amine solution is then pumped from the bottom of the absorber to the lean-rich heat exchanger. Here, the solution is heated from approximately 50 °C to ~105 °C using the CO₂ lean process stream from a regenerator. This solution is then fed to the upper portion of the regenerator where the CO₂ is stripped/ desorbed from the solution using steam. The CO₂ lean amine solution is then fed to the lean-rich heat exchanger from the bottom of the stripper. The product from the top of the stripper is a vapor rich in CO₂, which is the desired product. This vapor stream is then passed through a condenser where the CO₂ is recovered at about 25 psia. The CO₂ is then ready for processing.

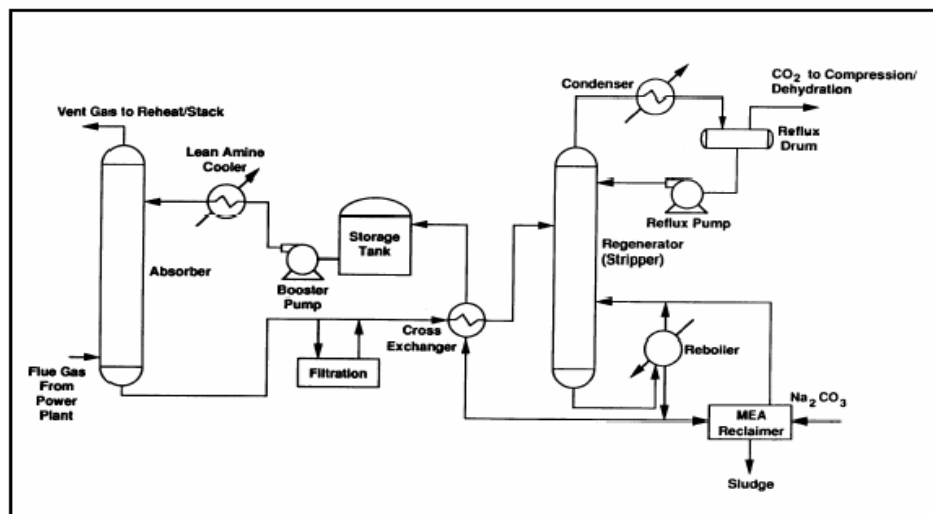


Figure 2: MEA separation process

Reactor System

The reactor design is based on a scale up of the solar reactors designed by the Renewable Energy Corporation at the Los Alamos Research Facilities. This prototype reactor processed 10 L/min of pure CO₂, achieving a six percent conversion. The heat needed to accommodate the reaction is supplied by radiant energy from the sun. The light is reflected by mirror segments built using vacuum-pressed sheet steel, honeycomb aluminum, and silvered glass over a spherical mandrel with appropriate adhesives between each layer. The light is focused into the reactor core through a transparent fused quartz panel to superheat the unit.

Intense preheating of CO₂ occurs in the outer sections of the reactor. The preheating allows for higher processing rates. In the reactor the molecules absorb solar heat as well as UV radiation resulting in the photolysis of CO₂ to the product gases. A number of thermal processes and side reactions occur when CO₂ undergoes the photolytic reaction, resulting in a distribution of the species, CO₂, CO, O₂, and O. The elemental oxygen is unstable at elevated temperatures and can react back to reform CO₂. The reverse reaction is prevented by quenching the hot gas with jets of CO₂ or H₂O. The use of water in the quench jets results in additional undesired reactions and does not effectively inhibit the reverse reaction to preserve the product CO. Experimental analysis at the Los Alamos Research Facility has determined that at least a 2 fold quench using cool CO₂ is needed to effectively preserve the CO produced by photolysis. The achievable conversion of CO₂ for the prototype was approximately 6%, but it is estimated that a conversion over 12 % occurs before back reactions and recombinations take place.

The converters and modular units consisting of a number of mirrors and structural support are actively pointed at the sun during operation. The process stream from the purification system is split and routed to each unit's converter. In each converter, the process stream is preheated to a reaction temperature of 2450°C, using solar energy focused by the mirrors. The preheating is needed to prepare the CO₂ for the absorption of solar light as well as ultraviolet rays, which facilitate the dissociation of CO₂ to CO and O₂. Once passed through the converter a cool stream of CO₂ is introduced into the system in order to quench the reverse oxidation reaction. The streams are then collected to a main line that flows to downstream processing. Instrumentation used in the reaction process provides information regarding process flow rates, temperature histories within the converter and product streams, and histories of CO and O₂ concentrations in the product stream. With a feed flow rate of 120 tons of CO₂ per day to the reaction system, approximately 3350 tons of CO is produced annually.

Scale-up of the prototype was performed assuming cross-sectional area is proportional to the radiant energy and simple light diagrams. The proportions of the reactor core dimensions were maintained and the total flow rate divided among the individual reactors. Optimal conditions were determined to be a surface area of 121 m² and 28 reactor units.

Cooling and Energy Recovery

Upon exiting the reaction system, the process stream is at a temperature of approximately 1350 °F and must be cooled before the products are separated and purified. A heat exchanger/energy generation system has been designed to cool the process stream down to the required temperature for the CO separation process, and produce energy for the overall process. The Energy Recovery system is shown in Figure 3.

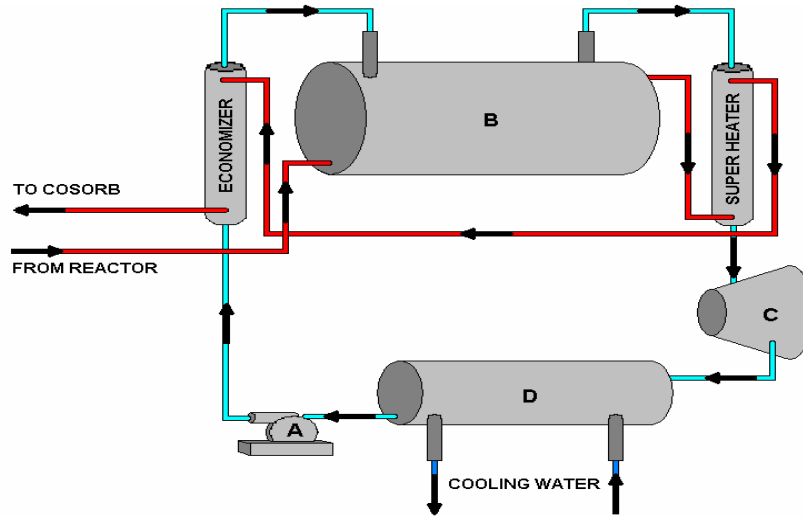


Figure 3: Cooling and energy recovery system

The gas (composed of 91% CO₂, 5.99% CO, and 3.01% O₂) leaves the reactor at a temperature of 1350 °F and enters a boiler where it vaporizes water into steam. The gas then leaves the boiler and superheats the steam in the super-heater, while lowering the temperature of the gas. Finally, the gas enters the economizer where it is cooled to its final temperature of 85 °F.

The steam from the super-heater is sent to a turbine where electricity is generated. The electricity can be used to supply approximately 0.42 MW of power to the rest of the process. The liquid and vapor mixture leaving the turbine is then sent to a condenser, and then pumped into the economizer, and then to the boiler to repeat the process.

CO Separation System

Upon exiting the boiler system, the process stream will be separated to produce a pure stream of CO. Carbon monoxide is purified from CO₂ and O₂ using the COSORB process. The process is recommended over older techniques, such as partial condensation and absorption in liquid methane, for its low corrosion rate, its ability to separate CO in the presence of CO₂, and its low energy consumption. It is also preferred for its ability to produce a high purity product. The process is an absorption/stripper system. A CO-laden feed is sent to an absorber in which it is contacted with a solvent containing cuprous aluminum chloride dissolved in an organic solvent such as toluene. The CO-rich product is then sent to a flash to remove compounds in the feed, which have a physical solubility in the aromatic solvent. The stream is sent to a lean-rich heat exchanger where it is heated

with CO-lean stream from the bottom of a stripping column, and is then passed to the top of the low-pressure column. The stripper is used to regenerate the CO using heat from a reboiler to produce a product stream with a purity of 99%. Once separated, the CO will be compressed and packaged for sale. The stream exiting the top of the absorber column, highly pure in CO₂, is then available to quench the back reaction, requiring 68 % of the stream. The remaining portion of this stream compressed and stored for later sale to Enhanced Oil Recovery. This process was not simulated, and its size and cost was estimated from published information on COSORB from Kinetics Technology Corporation (Keller).

III. ECONOMICS

The basis of this economic evaluation is 10 years. Equipment costs include the systems for purification, reactor, heat exchange, and product separation (Table 1). This amounts to \$20 million. Because land is not being purchased, royalties are paid to the existing plant, the San Juan Plant, for the use of the land that it owns. The sum paid is about \$400,000, which corresponds to 2% of the equipment costs and was obtained from the Department of taxation and revenue in New Mexico. Adding all direct and indirect costs amount to a total capital investment of \$50.0 million.

Table 1: Equipment cost

Equipment	Cost (\$)
MEA system	\$3,300,000.00
Compressor MEA, 1&2	\$804,000.00
2 Storage tanks	\$72,393.44
Solar reactor	\$3,640,000.00
COSORB unit	\$11,700,000.00
CO storage tank*	\$200,000.00
Boiler + turbine	\$429,100.00
Water tower	\$2,000.00
Pump	\$6,000.00
Total Equipment cost	\$20,153,493.44

Based on the cooling water and energy requirement of each system (Table 2), the total operating cost is calculated as \$420,000.

Table 2: Operating cost

Operating Costs	MMBtu/hr	\$/yr	
MEA cooling water	8.02	\$35,150.86	
MEA hot utility	4.58	\$80,291.98	
Water from tower	1.60	\$7,019.46	
COSORB cooling water	1.13	\$4,952.68	
COSORB hot utility	0.21	\$3,681.64	
Total power (MW)	0.5	\$289,271.40	
Cost of water (\$/MMBtu)	0.5	\$420,368.01	Total
Cost of hot utility (\$/MMBtu/hr)	2		
Cost of power (\$/kWhr)	0.066		

The total product cost is based on labor and taxes as well as the operating costs aforementioned. Labor estimations are made based on comparisons with similar projects involving power plants. Obtaining the wages for skilled and unskilled workers from the Bureau of Labor Statistics, labor cost is estimated at \$1.6 million based on an 8-hr/day average.

The sale of carbon monoxide and carbon dioxide amounts to a net earnings of \$27 million, giving a net present worth of \$78.5 million, a payout time of 1.65 years and an IRR of 40.6 %.

IV. CONCLUSION

In conclusion, the reduction of carbon dioxide using solar energy as a means to reduce the amount of the gas in the atmosphere is a process that is in need of further research. The results of the evaluations in this report show that at a rate of 120tons/day of CO₂ being processed; only 0.3% of the total emissions of the gas from the San Juan plant is prevented from being present in the atmosphere. This does not seem like a significant effect, however, it will be a significant decrease in the annual increase of CO₂ concentrations which has been reported to be 1.2% since 1990 according to the National Academy of Sciences.

Although analysis of the economics involved show that the process would be profitable, further research needs to be conducted in order to reach and optimize the goal, which is to reduce the CO₂ concentration in the atmosphere. Research can be done in the area of increasing the conversion of the CO₂ to CO and O₂ in the reactor. The present value of 12% limits the amount of CO₂ that is converted, which makes it necessary to determine an ultimate process that would dispose of the CO₂ adequately. An increased conversion would not only allow more CO₂ to be processed at a time but it will also allow more of CO, the desired product to be obtained, thus increasing profit and reducing the amount of CO₂ in the atmosphere. Increasing the capacity of the entire system is also necessary so that more CO₂ can be processed.

An alternative to this process can use steam to generate power to be sold to power plants so that the need for coal burning is negated. This will ultimately reduce the emission of CO₂ since it is produced from the burning of coal. CO₂ can also be separated from flue gas to be sequestered as an alternative. This involves injecting CO₂ into the ground, ocean or saline aquifers.

Overall, it will be premature to implement this project on an industrial scale as it does not significantly decrease CO₂ emissions. It has potential to be an option to achieve that goal but further research must be conducted on the process to do this.