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# DYNAMICS OF CARBON-DIOXIDE PRODUCTION AND ITS ECONOMIC IMPORTANCE: A REVIEW.

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## ABSTRACT

Carbon dioxide is a by-product of most commercial processes. These processes includes: production of synthetic ammonia, hydrogen gas, natural gas, fermentation, and limestone calcinations. This gas is commonly found in natural gas wells and the effluent stream of most industrial operations. If it is not tapped could constitute a major nuisance as well as a waste to most industrial processes and as environmental pollutant. Although, carbon dioxide has negative effects but when fully harnessed could be very beneficial. This review is centered on how to improve the production, beneficiation, purification, packaging and utilization of carbon dioxide for economic applications.


**KEYWORDS:** Carbon dioxide, Production, Beneficiation, Purification, and Economic applications.

## INTRODUCTION

With the increasing awareness on the need for pollution control, industries operators have come under serious pressure due to their contribution to environmental pollution. Two of the major pollutants released by industries are dust and flue gas, which contains a considerable amount of carbon-dioxide. Concentration of carbon dioxide up to 5vol% in air causes suffocation and also promotes one of the greatest environmental menaces known as global warning (Hesketh, 1979).

From the foregoing, it is clear that the need for pollution control is highly desirable in industrial operations. This can be achieved by treating the effluent gas from industries, thereby removing the dust and the carbon dioxide. In addition to solving of the problems of environmental pollution, the carbon dioxide recovered from flue gas can be packaged and sold, which definitely will contribute in enhancing the financial performance of the industrial operations.

## CONCEPTUALIZATION

Carbon-dioxide is a colourless gas with a faintly pungent odour and acid taste, it was first recognized in the sixteen century as a distinct gas through it presence as a by-product of both charcoal combustion and fermentation processes (Treybal, 1968).

Carbon-dioxide is found nowadays to be a by-product of many commercial processes such as the production of synthetic ammonia, hydrogen gas, natural gas, fermentation, limestone calcinations, and certain chemical synthesis involving carbon monoxide (Boyton, 1980).It is also found in the products of combustion of all carbonaceous fuels, in natural occurring gases as a product of metabolism of animal and in small quantities about 0.5V%, in the atmosphere. Although carbon dioxide is present in the atmosphere and the metabolic processes of plants and animals, it cannot be recovered economically from these sources (Hills, 1968).

## PHYSICAL PROPERTIES OF CARBON-DIOXIDE

Some values of physical properties of $CO_2$ are given in Table 1.0 (Hills, 1968).

### Solubility

The solubility of carbon dioxide in water at 101 kPa pressures and various temperatures is given in Table 2.0 (Hills, 1968).

**Table 1.0:** Physical Properties of Carbon Dioxide

| Property | Value |
|---|---|
| Sublimation point at 101.3 kPa (°C) | - 78.5 |
| Triple point at 518 kPa (°C) | -56.5 |
| Critical temperature (°C) | 31.1 |
| Critical pressure (kPa) | 7383 |
| Critical density (g.L) | 467 |
| At the triple point | 353.4 |
| At 0°C | 231.3 |
| Gas density at 273 K and 101.3 kPa (g/l) | |
| Liquid density | 1.976 |
| At 273 K (g/l) | 928 |
| At 293 K and 101.3 kPa $CO_2$. (vol/vol) | 0.712 |
| Viscosity at 298 K and 101.3 kPa (mPa.s) | 0.015 |
| Heat of formation at 298 K. (kJ/mol) | 393.7 |

**Table 2.0** Solubility of Carbon-dioxide in water at 101 kPa pressure

| Temperature K | Solubility $gCO_2/gH_2O$ |
|---|---|
| 273 | 0.0035 |
| 298 | 0.0015 |
| 313 | 0.0010 |
| 333 | 0.0060 |

At 273K and 101 kPa carbon-dioxide pressures, the solubility is 0.0035 $gCO_2/gH_2O$ and at 298k and 101 kPa it is 0.0015 $gCO_2/gH_2O$. For higher pressures up to about 505 kPa, the solubility is nearly proportional to the pressure in accordance with Henry's law. However, above that pressure the solubility becomes somewhat greater due to the formation of carbonic acid (Perry and Chilton, 1997). The equation for formation of the carbonic acid is shown below.

$H_2O_{(l)} + CO_{2(g)} \rightarrow H2CO_{3(aq)}$

### Toxicity

Although carbon dioxide is a constituent of exhaled air, high concentrations are hazardous, up to 5vol. % Carbon dioxide in air is considered harmful. Because of this, high concentration of carbon dioxide is regarded as a serious environmental hazard.

## CHEMICAL PROPERTIES OF CARBON-DIOXIDE ($CO_2$)

Carbon dioxide, the final oxidation product of carbon is not very reactive at ordinary temperatures. However, some of its chemical properties are:

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Carbon-dioxide, when in water solution produces carbonic acid ($H_2CO_3$), which forms salts and esters through the typical reaction of a weak acid. The reaction is as follows:

$$CO_{2(g)} + H_2O_{(l)} \rightarrow H_2CO_{3(l)}$$

**DECOMPOSITION TO FORM CO**

In spite of the fact that carbon dioxide is very stable at ordinary temperatures, when it is heated to about 1700°C the reaction forming CO proceed to the right to an appreciable extent in the presence of ultraviolet light and electrical discharges.

$$2CO_{2(g)} \rightarrow 2CO_{(g)} + O_{2(g)}$$

**REDUCTION REACTION**

Carbon dioxide may be reduced by several means. The most common of these are the reaction with hydrogen.

$$CO_{2(g)} + H_{2(g)} \rightarrow CO_{(g)} + H_2O_{(l)}$$

This is the reverse of water gas shift reaction in the production of hydrogen and ammonia. Carbon dioxide may also be reduced catalytically with various hydrocarbons and with carbon itself at elevated temperatures.

$$CH_{4(g)} + CO_{2(g)} \rightarrow 2CO_{(g)} + 2H_{2(g)}$$
$$CO_{2(g)} + C_{(s)} \rightarrow 2CO_{(g)}$$

**REACTION WITH AMMONIA**

Carbon dioxide reacts with ammonia as the first stage of urea manufacture to form ammonium carbonate.

$$CO_{2(g)} + 2NH_{3(g)} \rightarrow NH_2COOH_{4(aq)}.$$

This reaction is probably the most important reaction of carbon dioxide and is used world wide in the production of urea, for the synthetic of fertilizers and plastics.

**COMMERCIAL PRODUCTION OF CARBON DIOXIDE ($CO_2$)**

Sources of carbon dioxide from commercial recovery plants are:

I Synthetic ammonia and hydrogen plant in which methane or other hydrocarbons are converted to carbon dioxide and hydrogen.

$$CH_{4(g)} + 2H_2O_{(l)} \rightarrow CO_{2(g)} + 4H_{2(g)}$$

II Flue gases resulting from the combustion of carbonaceous fuels.

$$C_2H_{6(g)} + 7/2O_{2(g)} \rightarrow 2CO_{2(g)} + 3H_2O_{(g)}$$

III Fermentation in which a sugar such as dextrose is converted to ethanol and carbon dioxide.

$$C_6H_{12}O_{6(aq)} \rightarrow 2C_2H_2OH_{(l)} + 2CO_{2(g)} + 3H_{2(g)}$$

IV Sodium phosphate manufacture.

$$3Na_2CO_{3(aq)} + 2H_3PO_{4(aq)} \rightarrow 2Na_3PO_{4(aq)} + 3CO_{2(g)} + 3H_2O_{(l)}$$

V Natural carbon dioxide gas wells

VI Lime-kiln operation in which carbonate are thermally decomposed.

$$CaCO_{3(aq} \rightarrow CaO_{(aq)} + CO_{2(g)}.$$
$$MgCO_{3(aq)} \rightarrow MgO\ (aq) + CO_{2(g)}.$$

**PRODUCTION OF CARBON DIOXIDE FROM AMMONIA AND HYDROGEN PLANTS**

Here methane or other hydrocarbon is being converted to carbon dioxide and hydrogen.

$$CH_{4(g)} + 2H_2O_{(l)} \rightarrow CO_{2(g)} + 4H_{2(g)}$$
$$C_2H_{4(g)} + 4H_2O_{(l)} \rightarrow 2CO_{2(g)} + 6H_{2(g)}$$

More carbon dioxide is generated and recovered from ammonia and hydrogen plants than any other source; in a nutshell, both plants produce hydrogen and carbon dioxide from the reaction between hydrocarbon and steam. A substantial amount of carbon dioxide recovered from ammonia plants are used for Urea productions.

**PRODUCTION OF CARBON DIOXIDE FROM FLUE GASES**

A flue gas is a gas obtained from effluent stream of industrial operation. It consists of gases such as oxygen, carbon dioxide, carbon monoxide, hydrogen sulfide, sulfur dioxide, and nitrogen. (Fig. 1).

In typical plants for producing gaseous carbon dioxide from coke, coal, fuel oil or gas, the fuel is turned under a standard water-tube boiler for the production of 1400 – 1800 kPa steam. At 613k flues gases containing 10-18% carbon dioxide leave the boiler and pass through two packed towers where they are cooled and cleaned by water. The gases are then passed through a booster blower into the base of the absorption tower. In the tower, carbon dioxide is absorbed selectively by a solution of ethanolamine passing counter current to the gas stream. The carbon dioxide from flue gases out of the top of the tower move into the atmosphere, the carbon dioxide bearing solution passes out from the bottom of the tower, through pump and heat exchanger into the top of reactivated tower. Here heat strips the carbon dioxide from amine solution and the reactivated solution rations through the heat exchanger equipment to the absorption tower. Carbon dioxide and steam passes through the top of the reactivated tower into a gas cooler as reflux. The carbon dioxide at this point is available as a gas at a pressure of about 700pa. If liquid or solid carbon dioxide is required it may be further purified for odour removal before compression (Francis and Peters, 1980).

**PRODUCTION OF CARBON DIOXIDE FROM FERMENTATION INDUSTRY**

Large quantities of carbon dioxide are present in gases given off in the fermentation of organic substances such as molasses, corn, wheat and potatoes in production of beer, distilled beverages and industrial alcohol.

These gases may contain impurities such as aldehydes, alkanoic acid, lighter alcohol, glycerol, furfural, glycols, and hydrogen sulfide. Two processes are generally used for removing these contaminants and preparing carbon dioxide for use. In one process, is accomplishment by use of activated carbon absorbers and the other process is the use of chemical purification (Coulson and Richardson, 1980).

**PRODUCTION OF CARBON DIOXIDE FROM NATURAL GAS WELLS**

Natural gas, containing high percentage of carbon dioxide has been found in a number of locations in the world. These include Bonny in Nigeria, New Mexico, Colorado, Utah, and Washington. Several other small $CO_2$ plants have been in operation for a number of years producing commercial solid and liquid carbon dioxide from the these source using well gas as a source of Carbon dioxide.

**PRODUCTION OF CARBON DIOXIDE FROM LIME-KILN OPERATION**

A flue gas containing up to 40% carbon dioxide generated from the lime-kiln operation is pass through a cyclone separator, which removes the bulk of entrained dust, the gas is then flown through the two scrubbers, which removes the finer dust, cooled and pass into an absorption tower. Here carbon dioxide may be recover by the sodium carbonate or Girbotol process (Okonkwo and Adefila, 1995).

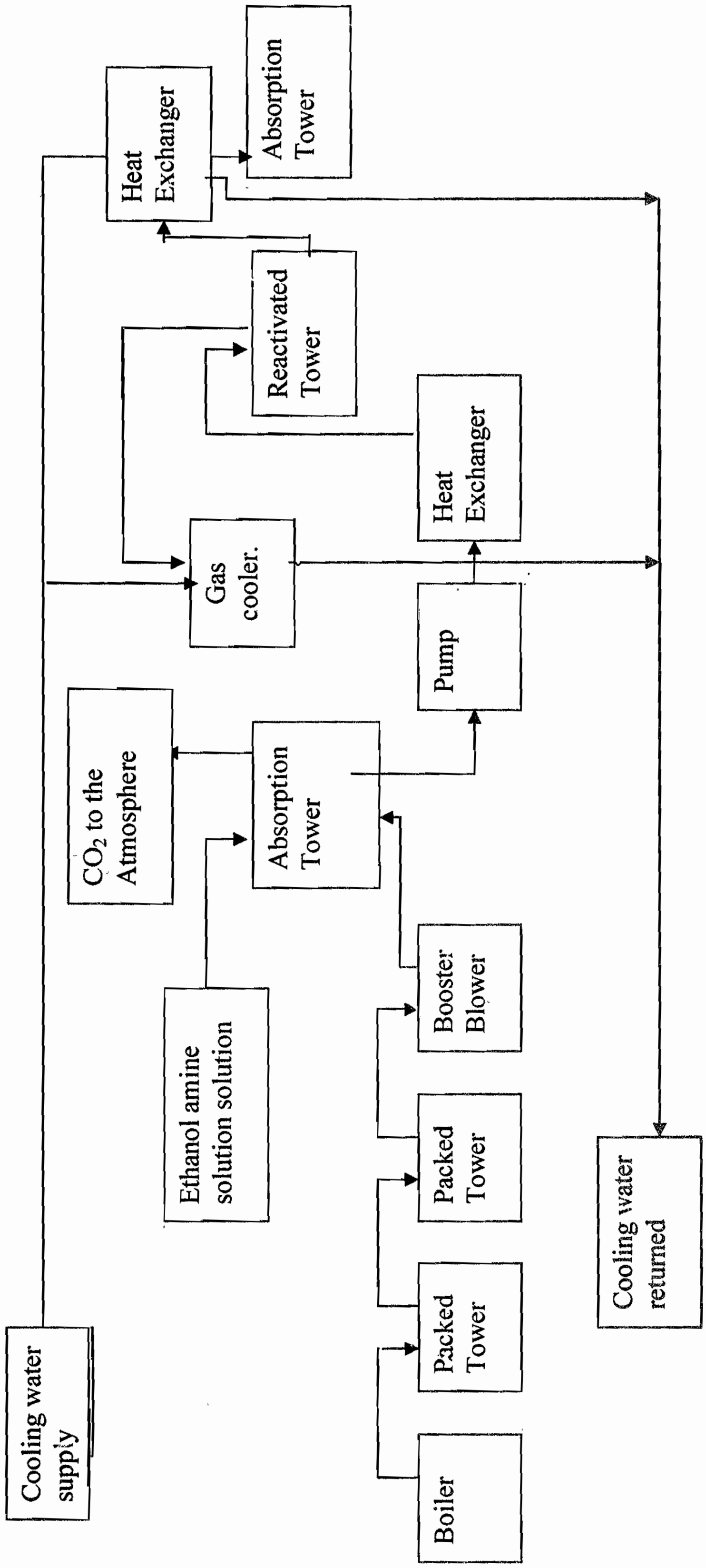
**BENEFICIATION OF CARBON DIOXIDE ($CO_2$)**

This process involves the recovering of carbon dioxide from both industrial and natural gases. Some of the methods in recovering $CO_2$ include: -

**POTASSIUM CARBONATE AND ETHANOL AMINE PROCESS**

These processes are regarded as the common, and usually, the carbon dioxide bearing gases are passed counter current to a solution that removes the $CO_2$ by absorption and retains it until it is desorbed in separate equipment. All these processes are in commercial use and the most suitable choice for a given application depends on individual conditions. Because of the solubility of $CO_2$ in water at normally encountered pressure, water rarely been used as absorbing medium. The higher solubility in the alkali carbonate and ethanolamine solution is the result of a chemical combination

Fig.1: PRODUCTION OF CARBON - DIOXIDE FROM FLUE GAS



of the $CO_2$ with the absorbing medium (Perry and Chilton 1997).

## SODIUM CARBONATE PROCESS

This process of recovering pure $CO_2$ from gas containing other diluents, such as nitrogen and carbon monoxide, is based on the reversibility of the following reaction:

$$Na_2CO_{3\,(aq)} + H_2O_{(l)} \leftrightarrow 2NaHCO_{3\,(aq)}.$$

This reaction proceeds to the right at low temperature and takes place in the absorber where the carbon dioxide – bearing gases are passed counter current to the carbonate solution. The amount of $CO_2$ absorbed in the solution varies with temperature, partial pressure of carbon dioxide in the gas and solution strength, these proceeds to the left when heat is applied. The reaction takes place in a lye boiler.

## FLUOR PROCESS

This is a solvent process that uses propylene carbonate, which has a high solubility for $CO_2$, a low solubility for other light gases, and is chemically stable and non-corrosive to carbon steel. Physical solvent plants represent a higher capital cost than the carbonate or amine plants, but may result in reducing operating cost where high pressure are involved.

## GIRBOTOL AMINE PROCESS

This process developed by the Girdler Corporation in the analysis of $CO_2$ recovery is similar in operation to the alkali carbonate processes. However it uses aqueous solution of ethanolamine. This process depends on the reversible nature of the reaction of $CO_2$ with monoethanolamine to form monoethanolamine carbonate.

$$2HOCH_2CH_2NH_{2\,(aq)} + H_2O_{(l)} + CO_{2\,(g)} \rightarrow (HOCH_2CH_2NH_3)_2\,CO_3{}^{2-}{}_{(aq)}$$

The reaction proceeds in general to the right at low temperatures (300-338k) and absorbs the carbon dioxide from the gas in the absorber. Temperatures, amine solution strength, and $CO_2$ partial pressure affect the solubility of $CO_2$ in ethanolamine.

## SULFUID PROCESS

The sulfuid process was developed during 1960s remove $CO_2$ and other acidic gas from effluent streams at higher partial pressures (Hills, 1968). It uses a circulating solution with a flow pattern similar to those in the amine and carbonate processes. Regeneration occurs at low pressures, and heat is exchange between the regenerated solution and the solution from the absorber. This process is used less often than the amine or carbonate process.

## PURIFICATION OF CARBON DIOXIDE

Although $CO_2$ produced and recovered by the methods outlined above could have high purity, it may sometimes contain some traces of hydrogen sulfide, and sulfur dioxide with slight odour or taste. The most commonly used methods for purification are treatment with potassium permanganate, potassium dichromate or active carbon (Hills, 1968).

## POTASSIUM PERMANGANATE

The most widely used process for removing traces of hydrogen sulfide from carbon dioxide is to scrub the gas with an aqueous solution saturated with potassium permanganate. Sodium carbonate is added to the solution as buffer. The reaction is as follows:-

$$3H_2S_{(g)} + 2KMnO_{4\,(aq)} + 2CO_{2\,(g)} \rightarrow 3S_{(s)} + 2MnO_{2\,(aq)} + 2KHCO_{3\,(aq)} + 2H_2O_{(l)}$$

The precipitated manganese dioxide and sulfur are discarded. The solution is used until it becomes spent or so low in potassium permanganate. It is customary to place two scrubbers in series, to effectively use the permanganate solution. When the solution in the first scrubber is spent with respect to the gas, the positions of the scrubbers are reversed and the scrubber is recharged with fresh solution. Two types of scrubbers are used. The simpler consist of a vessel half or two thirds full of solution. The gas is feeds into the bottom of the vessel and bubbles up through the solution. The other scrubbers is a small packed tower through which the gas stream is passed counter current to a recirculating shower of potassium permanganate and soda ash solution. The latter requires a circulating pump and a solution mix chamber, but has the advantage of reducing the pressure drop through the equipment to a minimum. Use of two scrubbers of this type can improve the efficiency.

## POTASSIUM DICHROMATE

This method is similar in application to the potassium permanganate solution.

$$K_2Cr_2O_{7(aq)} + 3H_2S_{(g)} + H_2O_{(l)} + 2CO_{2(g)} \rightarrow 3S_{(s)} + 2Cr(OH)_{3(aq)} + 2KHCO_{3(aq)}$$

The precipitate chromic hydroxide and sulfur are discarded. This process is used to purify carbon dioxide from fermentation in the Reie process as a final clean up after the alkali carbonate or ethanolamine recovery process.

## ACTIVE CARBON

The process of absorbing impurities from carbon-dioxide on active carbon, charcoal or activated carbon has been described in connection with Backup process of purifying carbon dioxide from fermentation processes. Space-velocity and reactivation cycle vary with each application. The use of active carbon need not to be limited to the fermentation industries, but to other related industries such as lime-kiln and hydrogen gas industries (Kirk, 1980).

## PACKAGING OF CARBON DIOXIDE ($CO_2$)

The main methods of packaging carbon-dioxide include:

Liquefaction

Solidification

## LIQUEFACTION

Carbon dioxide may be liquified at any temperature between its triple point (216.6k) and its critical point (304k) by compressing it to the corresponding liquefaction pressure, and removing the heat of condensation (Perry and Chilton, 1997). There are two types of liquefaction processes.

In the first process, the carbon dioxide is liquefied near the critical temperature; water is used for cooling. This process requires compression of the carbon dioxide gas to pressure of about 7600Kpa, the gas from the final compression stage is cooled to about 305k and then filtered to remove water and entrained lubricating oil. The filtered carbon dioxide gas is then liquefied in a water-cooled condenser.

In the second liquefaction process, the process is carried out at temperature from 261k, with liquefaction pressures of about 1600 – 2400Kpa. The compressed gas is precooled to 277 k, water and entrained oil are separated and the gas is then dehydrated in an activated alumna, bauxite, or silica gel drier and flow to a refrigerant – cooled condenser. The liquid is then distilled in stripper column to remove non-compressible impurities. Liquid carbon dioxide is stored and transported at ambient temperature in cylinder containing up to 22.7kg. Larger quantities can also be stored in refrigerated insulated tanks maintained at 255k and 2070pa and transported in insulated tank trucks and rails or cars especially in developed economies.

## SOLIDIFICATION

Liquid carbon dioxide from a cylinder may be converted to snow by allowing the liquid to expand to atmospheric pressure (Kirk, 1980). This simple process is used only where very small amounts of solid carbon dioxide are required because less than one-half of the liquid is recovered as solid. In most cases when the pressure falls below the triple point (518kpa), the liquid $CO_2$ solidifies to form carbon dioxide snow. Although carbon dioxide may be store without loss in tanks and cylinders, dry ice undergoes continuous loss in storage because of sublimation; this loss can be minimized by keeping the dry ice in insulated boxes. Special insulated rail cars and trucks are used from hauling dry-ice blocks. Most plants produce the material at the time it is sold to avoid storage losses and re-handling costs.

## EFFECTS OF CARBON DIOXIDE ($CO_2$) ON THE ENVIRONMENT

Although carbon dioxide is a constituent of exhaled air high concentrations are hazardous. Up to 0.5Vol% carbon dioxide in air is not considered harmful, but carbon dioxide concentrates in low spots because it is one and one-half time as heavy as air. 5Vol% carbon-dioxide in air cause a threefold increase in breathing rate and prolonged exposure to concentration higher than 5% may cause unconsciousness and death (Shreeve and Brink, 1997). Sufficient ventilation to prevent accumulation of higher percentage of carbon dioxide must be provided where carbon dioxide gas has been released or dry ice has been used for cooking. Carbon dioxide containing known amount of $^{14}C$ has been used as a traces in studying botanical and biological problems involving carbon and carbon compounds (Hesketh, 1979). Increase in carbon dioxide may lead to increase in the level of the oceans, altering rain patterns to make deserts of farmland. Addition of carbon dioxide ($CO_2$) to green house increases the rate of growth of plants.

## USES OF CARBON DIOXIDE ($CO_2$)

Carbon dioxide can be very useful in several fields, some of these fields includes:-

### AGRICULTURE

Carbon dioxide is sometimes added to irrigation water, in the same manner as fertilizer ammonia, in hard water region. It also helps in improving the growth rate of vegetables and flowers.

### FOOD REFRIGERATION

Both liquid and dry carbon dioxide provide the most readily available method of rapid refrigeration of foodstuffs especially, meat product and frozen food. It is especially useful for chilling ice cream products.

### MEDICINE

Carbon dioxide plays an important role in the laboratory, and hospitals, especially useful in treating respiratory problems and in anesthesia, also useful in treating skins in tanning operation.

### BEVERAGES CARBONATION

Carbon dioxide is used for beverages carbonation. Both soft drinks and beer production consume the largest quantity of $CO_2$ carbonation.

### FIRE EXTINGUISHERS

Carbon dioxide averts a pronounced cooling effect helpful in extinguishing. Both fire extinguishing equipment, ranging from hand-type extinguisher to permanent installation in warehouse, chemical plants, ships, and airplanes uses liquid carbon dioxide.

### OTHER USES

Carbon dioxide is widely used in hardening of sand cores and molds in foundries, also useful in welding equipment, immobilizing animals prior to slaughtering, carbonating treated water to prevent scaling and direct injection into the chemical reaction systems to control temperature.

## CONCLUSION

Based on the foregoing, it can be concluded that; carbon dioxide as a by – product when fully tapped from the effluent stream during industrial operations and processed can be economically useful. Some of the major benefits obtained when carbon dioxide is fully harnessed includes:-

(i) Minimization of global warning effects,
(ii) Increase in raw materials for industries,
(iii) Availability of cheap raw material ($CO_2$) for the production of fertilizer for farming,
(iv) Increase in materials for research purpose,
(v) Availability of jobs for both skilled and unskilled personnel,
(vi) Increase in financial performance of industries,
(vii) Diseases control on both plants and animals.

## RECOMMENDATION

(1) Establishment of carbon dioxide generating plants.
(2) Enriching researchers with adequate tools to further investigate ways of improving generation of carbon dioxide.
(3) Improve carbon - dioxide production activities so as to create job opportunities.
(4) Establishment of a body to regulate wastage of carbon - dioxide and educate populace on the danger of its emission.

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