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RECYCLING OF CARBON DIOXIDE TO PROVIDE RENEWABLE ENERGY AND FOR THE MITIGATION OF GREEN HOUSE GAS EMISSIONS

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***Abstract*—In the wake of overall Industrial and social development of a country the need of energy especially Electricity will continue to grow. The use of fossil fuels like coal and oil has become inevitable in the modern times, either for the production of electricity or for driving automobiles and other transport systems. This is a major contributory factor for the rate of increase in the GHG namely carbon dioxide in the atmosphere. Increase in the carbon dioxide content in the atmosphere is a major cause of concern in the conservation of nature and in saving the world from natural disaster which follows atmospheric pollution. Already several procedures are followed to decrease or to prevent the increase in carbon dioxide content in the atmosphere. Capture of carbon dioxide and injecting it into dried up oil wells or deep in the ocean or converting it to some useful organic compounds is already in practice. The procedure we propose is to capture carbon dioxide and convert to carbon monoxide which is a very good industrial fuel gas .This procedure does not involve the use of any expensive catalysts or a new technology. This method does not involve the use of sophisticated equipments and is expected to be cost effective.**

Keywords- green house gas, carbon dioxide, methanol, fuel gas, fossil fuel, sequestration, producer gas

I. INTRODUCTION

The total amount of energy consumed by a country is a measure of the overall development of a country. This depends on the Industrial and social development of a country. This leads to the increase in the need for energy especially Electricity and this will continue to grow. With billions of metric tones of reserves of coal and mineral oils, the coal / oil sectors would remain the main source of power generation for the next few decades. Fossil fuels account for nearly 75% of power generation in many countries especially developing countries as the technology for thermoelectric power plants is well known. The use of fossil fuels is one of the major contributory factors in the increase in the rate of emission of green house gases in the atmosphere. Green house gases absorb the long wavelength Microwave and Infra Red radiation from the sun light or the heat radiation from the earth. Higher the amount of green house gases in the atmosphere higher is the absorption of heat radiation by the atmosphere resulting in increased global warming. This is one of the most important causes for the melting of ice bergs and ice in the polar region resulting in increase in the sea level, submerging of lands by sea and drastic climatic changes. Conservation of Nature and saving the world from natural calamities and disaster caused by global warming is one of the major concerns of modern man. The main green house gas is carbon dioxide. Large quantity of carbon dioxide is produced by the combustion of carbonaceous fuels (fossil fuels like coal and mineral oil). Carbon dioxide emitted from fuel burning is responsible for about 87 percent of global warming. This has increased by about 27 percent since the industrial revolution. It had been estimated that because of increasing global warming the temperature of the earth would rise by 1-3 degree centigrade within a few decades. Burning natural gas, the cleanest of the fossil fuels, instead of other fossil fuels also emits appreciable amounts of carbon dioxide, in addition to carbon monoxide, and other reactive hydrocarbons. It is easily seen that the replacing oils and coal by natural gas for power generation may not the best option to reduce the carbon dioxide emission appreciably.

Fossil Fuel Emission Levels
- Pounds per Billion Btu of Energy Input

Pollutant	Natural Gas	Oil	Coal
Carbon Dioxide	117,000	164,000	208,000
Carbon Monoxide	40	33	208
Nitrogen Oxides	92	448	457
Sulfur Dioxide	1	1,122	2,591

II. DISPOSAL OF CARBON DIOXIDE

In order to reduce the concentration of carbon dioxide in the atmosphere, carbon dioxide sequestration is considered. Many options available for long term storage of carbon dioxide are geological formations like old oil fields, coal formations, saline water aquifers and deep oceans. Many citizens feared burying vast amount of CO_2 waste deep in the ground and sequestration in coal mines would result in man

made earth quake, asphyxiation and ground water contamination. Some chemists believe that simply trapping and burying CO_2 exhausted by power station is a waste of potentially useful valuable resource. Oil companies make use of captured CO_2 to pump out oils from the oil fields and hard to reach oil reserves. Carbon dioxide is injected under high pressure for enhanced oil recovery from oil wells and enhanced coal bed methane recovery from coal seams. In the coal bed methane recovery carbon dioxide displaces sorbed methane from the pores of the coal beds so that carbon dioxide is stored and the released methane can be used as a clean gaseous fuel. Even in this method the methane when used as a fuel is going to produce carbon dioxide which again needs disposal. It would seem timely to find ways to fulfill the potential of the otherwise wasted resource.

Nature of course solves the problem of CO_2 capture in the process of photosynthesis by directly absorbing CO_2 from the atmosphere, in presence of the sunlight releasing oxygen as a byproduct. In this sense CO_2 is very much a renewable resource. But chemists have found that the C-O bond does not break easily at least without expenditure of huge amounts of energy which would defeat the object of recycling the gas in the first place.

Per capita power consumption is said to be a measure of the development of a country. Hence power production and consumption can not be avoided. This situation has forced man to go in search of alternative sources of energy which should be cost effective, easily made available, with intermittent supply and not resulting in atmospheric pollution and be eco friendly.

III. ALTERNATIVE SOURCES OF ENERGY

Any fuel dependant power generation results in the emission of carbon dioxide because fuels are combustible organic substances (except hydrogen as a fuel or nuclear fuel in a nuclear reactor). Hydrogen is a very clean fuel in all sense of the term. But hydrogen does not exist free in nature. It has to be generated by decomposition of hydrogen containing compound especially water. To carryout this process energy has to be spent and hence this may not be cost effective. In addition to this, use of hydrogen has many disadvantages though a lot of research is going on for the utilization of hydrogen for power generation.

Nature has other outlets for energy like the freely available Solar energy, Wind energy, Tidal energy etc.
Utilization of these for power generation does not lead to environmental pollution and they are eco-friendly. But the exploitation of these energy has number of disadvantages. The installation cost involved in trapping and converting the energy into electricity is very high and hence it is not cost effective. The efficiency in trapping and converting the energy is not to any extent appreciable. They are dependant on several factors. This depends on the geographical location, climatic condition and the space available for installing the devices. Hence its utility is limited and at present this energy is not exploited to any appreciable extent.

In order to circumvent these difficulties, to avoid the increase in carbon dioxide content in the atmosphere and to find a (at least partly) renewable source of energy, a method involving trapping of carbon dioxide and converting it to carbon monoxide is proposed.

The chemical, metallurgical industries and thermal plants make use of the conventional fossil fuels as energy sources. All of them inevitably release carbon dioxide in the flue gas. Instead of releasing this to the atmosphere it is trapped and utilized for the preparation of other useful organic compounds. A few procedures are already in practice.

IV. OTHER METHODS OF UTILISATION OF CARBON DIOXIDE

Methanol is produced from carbon dioxide dissolved in water by electrolysis followed by hydrogenation of the carbon monoxide formed. A method of producing methanol by reductive conversion of any available source of carbon dioxide, which comprises electrochemically reducing the carbon dioxide in a divided electrochemical cell comprising an anode in one cell compartment and a metal cathode electrode in another cell compartment that also contains an aqueous solution or aqueous methanolic solution of an electrolyte of one or more alkyl ammonium halides, alkali carbonates or combinations thereof to produce therein a reaction mixture containing carbon monoxide and hydrogen which can be subsequently used to produce methanol while also producing oxygen in the cell at the anode.

$$CO_2+2H_2O \rightarrow CO+2H_2 \text{ (at the cathode) and}$$
$$3/2\ O_2 \text{ (at the anode)}$$

The CO and H_2 produced at the cathode are subsequently reacted over Cu and Ni based catalysts to produce high yields of methanol (CH_3OH).

$$CO + 2H_2 \xrightarrow{\text{Hydrogenation}} CH_3OH$$

Though this method is an efficient method of utilization of carbon dioxide the technology used is a little sophisticated. It involves the installation of a separate unit in an Industry. The carbon dioxide used should be as pure as possible for the method of conversion to be effective.

In another method the production of methanol from reactions between CO_2+ H_2 and CO + H_2 has been studied over platinum catalysts supported on Nb_2O_5, ZrO_2, MgO, SiO_2 and TiO_2. Zirconia- and niobia-supported Pt catalysts showed the highest activity for reactions of both CO_2 and CO. This method is also as effective as the previous method.
But the disadvantage is that the carbon dioxide used should be very pure not containing any gaseous or particulate impurities. In such situation obtaining pure carbon dioxide from flue gases plays a major role.

Institute of Bio-energy and nanotechnology, Singapore developed a novel reaction through which CO_2 is effectively converted into MeOH under milder conditions. This takes place in presence of N-heterocyclic carbene catalyst and the silane as a reducing agent. The final step involves the addition of NaOH solution, when activated CO_2 is converted to methanol. The big advantage of this organic approach to CO_2 conversion is that unlike previous attempts it neatly sidesteps the need for expensive and toxic precious catalysts.

This method uses dry air as the source of CO_2. Normally silanes are very sensitive to oxygen but here in this case the presence of N-carbene catalyst prevents it. One of the disadvantages of this approach is that hydrosilanes are expensive and very sensitive to oxygen.

Gabriel Centi from the University of Messina, Italy was able to convert CO_2 by reduction using hydrogen got from splitting water by solar energy , then binding carbon atom together using Pt, Pd catalysts in carbon nanotubes to produce C_6-C_8 hydrocarbons at room temperature. This method is not cost effective and may not be applicable for large scale reaction. At present this is not a viable method.

Ellen Stechel, Sandhian of Fuels and energy transportation department makes use of cobalt ferrite. On heating to 2600^o F by solar furnace, oxygen was released. On cooling to 600^oF and exposing to CO_2 it snatches oxygen from CO_2 to give CO gas which is the building block for making hydrocarbons. This method has not been tried on a large scale.

A method of conversion of natural gas (Methane) and carbon dioxide to a mixture of CO and H_2 with methanol as an intermediate was proposed by H.W.Koh, S.H.Lee and J.G.Choi. The reaction was carried out in presence of Ni/ SiO_2 catalyst.

$$CO_2 + CH_4 \rightarrow 2CO + 2H_2$$

This method seems to be suitable for the synthesis of valuable organic chemicals. Ni, Pt, Ru based catalysts are known to be effective for the C O_2 – CH_4 reaction. One of the major problems is the deactivation of the catalysts due to the formation of soot on the catalyst during the reaction. The other major problem encountered is the reformation of CH_4 from CO and H_2.

In all the above methods:
i).either free CO_2 is required, ii).the catalyst employed is sensitive to impurities, iii).the catalyst is sensitive to oxygen, iv).the catalyst may be sensitive to moisture, v).catalysts are very expensive, vi).The technology is not cost effective, vii).Erection of new reactors/plants is necessary.

V. THE PROPOSED METHOD

Whenever fossil fuels are burnt not only GHGs are formed but also it leads to oxygen depletion, taking into consideration i).deforestation , ii).Increase in number of plants and industries using fossil fuels , iii).Increase in the number of vehicles using fuels based on mineral oils , iv).Burning of garbage and bio-wastes.

In this procedure there is no isolation of CO_2, no compression, no transportation and no sequestration. This can be equated with considerable energy saving. It would also produce revenue since by using this technology, the amount of petroleum based fuel needed can be reduced to atleast 50%. This technology would be commercially advantageous. This will not only recycle CO_2 but also will result in a more energy efficient way to generate electricity.

Hence a technique, using a chemical based process of already known technology that will convert CO_2 to CO and allow for the production of gasoline or useful organic materials is proposed. The key features of this technique are:

1).CO_2 emitted from coal or oil fired power plants or industries and factories can be used directly, which eliminates the need for clean CO_2.

2).Transformation of large quantities of CO_2 to CO can be done, making this technique a viable one for large scale industrial applications.

With a forecast of 43 billion tons of annual CO_2 emission by 2030, there is an abundant supply of raw material available to produce renewable liquid fuels for global consumption. Not only does CO_2 recycling mitigate CO_2 emission and curb demand for imported oil but it also provides an efficient approach to produce renewable fuels

This method can be easily adopted by chemical, metallurgical industries and thermal power plants which make use of the fossil fuels for power generation, because this method involves simple thermo chemical reaction. It neither involves electrolysis nor the use of any heterogeneous catalysts. This method makes use of a procedure similar to the one adopted for the production of Water gas or producer gas. The same furnace can be used.

The principle is that 'when carbon dioxide is passed over heated coke or coal at 1000^oC chemical reduction takes place, where carbon dioxide is converted to carbon monoxide'.

In presence of limited supply of air and moisture, the following reactions take place:

1). $C + O_2 \rightarrow CO_2 + 97$ K Cals (exothermic)
2). $2C + O_2 \rightarrow 2CO + 61$ K Cals (exothermic)
3). $C + H_2O \rightarrow CO + H_2$ -29 K cals (endothermic)
4). $C + CO_2 \rightarrow 2CO$ - 36 K cals (endothermic)

Flue gases from the chimney of furnaces contains CO_2 , C (soot), O_2 , N_2 and some SO_2. After scrubbing through water, SO_2 and tar can be removed. The emerging gaseous mixture contains mainly CO_2, a little O_2, N_2 and moisture. This is passed over heated coke where chemical reduction takes place converting CO_2 to CO. From the thermo chemical data of the above reactions it is seen that the net result is exothermic. Hence energy needed to keep the coal/coke red hot is small and hence it is cost effective. This is more advantageous than the production of water gas.

The presence of little oxygen in the flue gas brings forth [1] and [2] reactions. These reactions being exothermic would be expected to maintain the temperature of the furnace. Presence of any kind of impurities is not going to affect the reaction and hence the process of removal of impurities is not necessary. The presence of moisture increases the quality of the fuel gas produced by forming hydrogen by the reaction [3]. The furnace needed and the technology involved is the same as the one already in use for the production of producer gas. Hence this method is cost effective in all sense of the term.

The gas obtained as a product contains mainly carbon monoxide and hence this can be used as a good gaseous industrial fuel especially for chemical and metallurgical

industries. When this is used as a fuel the following reaction takes place.

$CO + 1/2\ O_2 \rightarrow CO_2 + 67$ K Cals.

From the carbon monoxide formed by the above method, other useful organic compounds like methanol or long chain hydrocarbons can be prepared (by Bergius process or Fischer Troph process)

VI. CONCLUSION

Formation of CO_2 and its increase in the atmosphere cannot be prevented in the near future since the use of fossil fuels continues to be the source of energy. This causes global warming which is the causative factor for drastic climatic changes and natural disaster. Just removal of CO_2 from the atmosphere and dumping in deep sea or coal mines is not an attractive method. In this situation, trapping of CO_2 and converting it to some useful organic compounds like fuel gas, gasoline, methanol and so on is widely accepted to be a fruitful method .Because this method removes the GHG from the atmosphere and recycles the CO_2 as a renewable source of energy. Several methods were proposed and are in practice. The method we have proposed is 'converting CO_2 to CO by passing the flue gas from the Industries over red hot coke or coal'.

This method has the following advantages:

a).By adopting this method we can avoid the increase in the carbon dioxide content in the atmosphere.

b).The amount of fossil fuel required for the industry is halved by the formation of fuel gas by recycling the so called green house gas CO_2 in the flue gas.

c).The amount of Oxygen depletion in the atmosphere is also halved by this process.

d).This method is cost effective and does not involve any new technology.

e).This method produces fuel gas (carbon monoxide) and so, after purification several organic compounds like methanol and fuels like gasoline can be prepared.

Hence the method we have proposed is simple, cost effective and more viable for the recycling of CO_2 and the gases emitted from the industries. Thus it also helps in the mitigation of CO_2 and the other gases, from polluting the atmosphere.

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