PURIFICATION OF WASTE CARBON DIOXIDE FROM ETHYLENE GLYCOL PLANTS AND ITS COMMERICAL APPLICATION

ABSTRACT

Reduction of waste and conversion to the valuable products is the key challenge in today's competitive petrochemical business. Large amounts of the carbon dioxide is treated as waste and vented to atmosphere from ethylene glycol plants. Carbon dioxide (CO_2) is one of the byproducts produced during the manufacturing process of ethylene glycol. Carbon dioxide may be used as one of the raw material in urea and methanol plants. Moreover, CO_2 can be liquefied up to a food grade product or can be utilized for dry ice, cold drinks, beverage preparation, or even as a preservative. This study will examine opportunities to reduce carbon dioxide emission to the atmosphere and utilization in eco-friendly manners by conversion into competitive petrochemical products. This study also describes technologies designed to recover and purify the waste carbon dioxide. The recovery and purification of waste CO_2 will provide two benefits. First, a reduction in the large amount of CO_2 vented to the atmosphere and the subsequent reduction of pollution and global warming which could be realized. Secondly, the availability of raw materials from waste stream, which will reducing the production cost.

INTRODUCTION

The threat of global warming is considered by many to be a serious issue. Today almost 98% of global environmental scientists agree that this threat exists and urge global leaders to take drastic measures to reduce the emission of CO_2.

One of the most alarming global environmental problems of today is the unexpected increase of the natural greenhouse effect. This problem is mainly caused by the increased in the atmospheric CO_2 concentrations. Ethylene glycol plants represent an opportunity to control CO_2 emissions. The removal of CO_2 from the plant's vent gases is no longer a major technological challenge. Many technologies have been developed for this purpose. The real problem in the near future is what to do with enormous quantity of CO_2 that can be recovered. So in the present study, a brief description has been given for waste carbon dioxide recovery and purification, then various options for utilization of purified carbon dioxide are explored.

PROCESS DESCRIPTION OF CARBON DIOXIDE VENTING :

In ethylene glycol plants there are two sections: ethylene oxide and the ethylene glycol section. In the ethylene oxide plant, ethylene and oxygen react over a silver catalyst in a shell & tube reactor. The reaction is a heterogeneous catalytic exothermic reaction which produces ethylene oxide by partial oxidation of ethylene on the catalyst. Some amount of carbon dioxide and water is also produced in the reactor as side reaction between ethylene and oxygen (complete combustion). The reaction is a high temperature (230 - 270 °C), high pressure (20 – 21 bar g) reaction in which pressure and temperature play a major role in controlling the performance of the catalyst and maintaining the reaction components in a non flammable regime. Methane is added as a ballast gas. The reactions involved in this process are given below.

$$\mathbf{CH_2 = CH_2 + 1/2\ O_2 \xrightarrow{Ag - CATALYST} \overset{\quad O \quad}{CH_2 - CH_2}\ -106.901\ KJ/Kgmol\ \ of\ _{C2H4}} \qquad \mathbf{(1)}$$

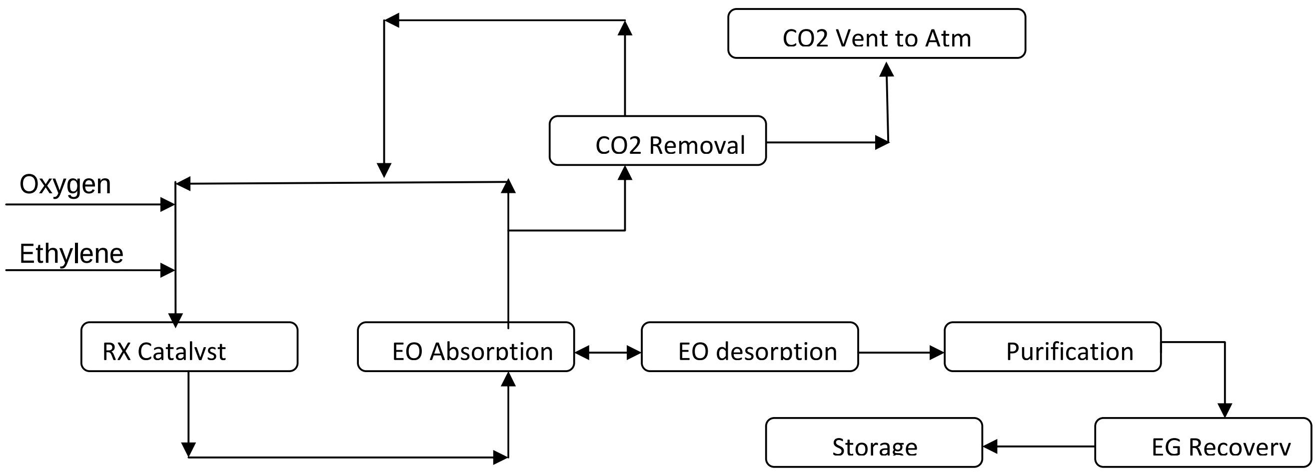
In this first reaction carbon dioxide and water are formed by the ethylene oxidation reaction competing with the main reaction.

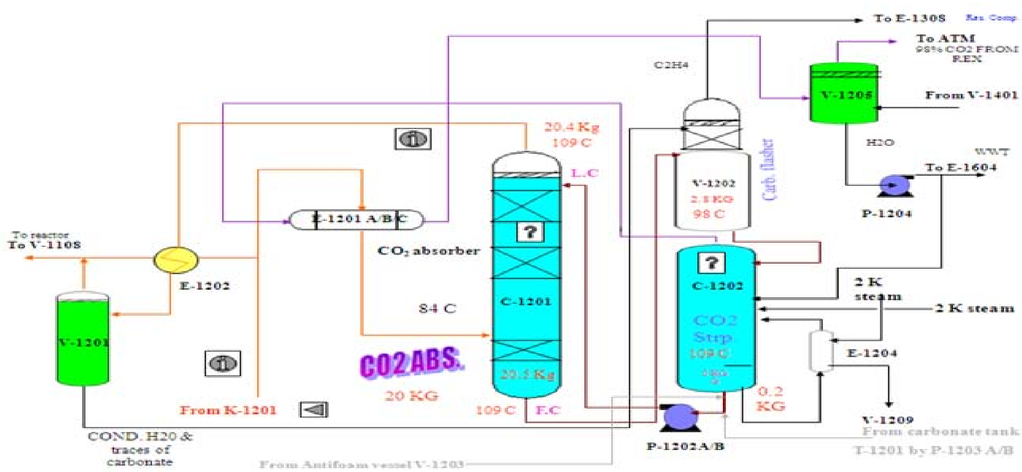
In a second reaction, some of the EO forms isomerizes to acetaldehyde (ACH) which in turn is rapidly oxidized to carbon dioxide and water:

$$\mathbf{CH_2 = CH_2 + 3\ O_2 \longrightarrow 2CO_2 + 2\ H_2O\ -1323.605\ KJ/kgmol\ of\ C2H4} \qquad \mathbf{(2)}$$

Ethylene oxide (EO) is absorbed from the reaction gas in the EO scrubber, the remaining gas is then passed through a carbon dioxide (CO_2) removal system to maintain the reactor inlet CO_2 concentration at design value. At first CO_2 is absorbed in hot potassium carbonate solution, it is then stripped off in a CO_2 regenerator/stripper unit. The hot CO_2 is cooled and vented to atmosphere at 60-95 °C. The vented CO_2 is saturated with steam. There are many technology suppliers of ethylene glycol processes. The most widely used technologies are from Scientific Design (SD), Shell and Dow Chemical. A simplified process flow is described below:

Carbon Dioxide (CO_2) Vent Process Flow Diagram





A. Carbon Dioxide Vent Gas Composition

Sr.No.		Unit	Technology-I	Technology-II
1.	Total Organic Chloride	PPMV	3	3
2.	Methane	PPMV	1500	500
3.	Ethylene	PPMV	2500	2000
4.	Ethane	PPMV	NIL	NIL
5.	Ethylene Oxide	PPMV	16	16
6.	Carbon Dioxide (CO_2)	%	59	95
7.	Water	%	40.5	4.75

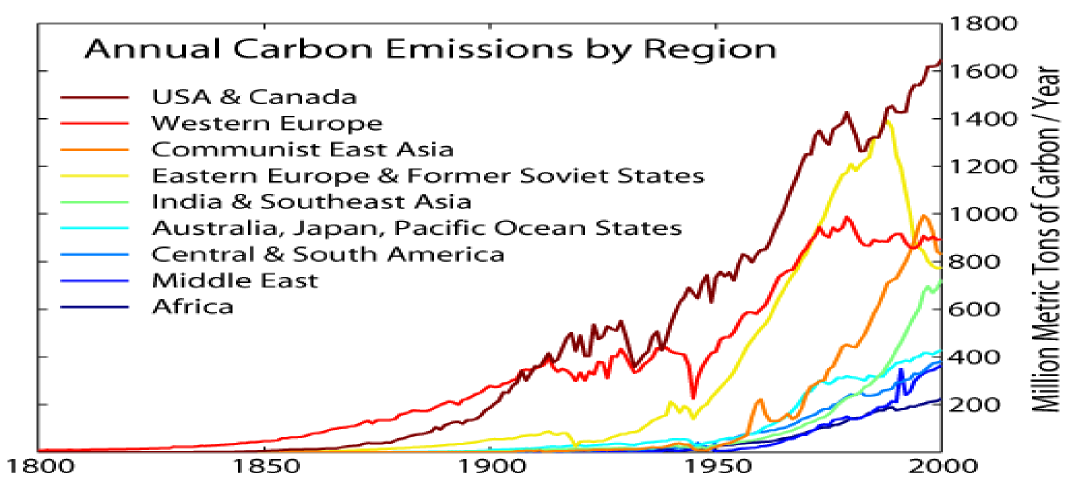
B. **Process parameters of Carbon Dioxide Vent:**

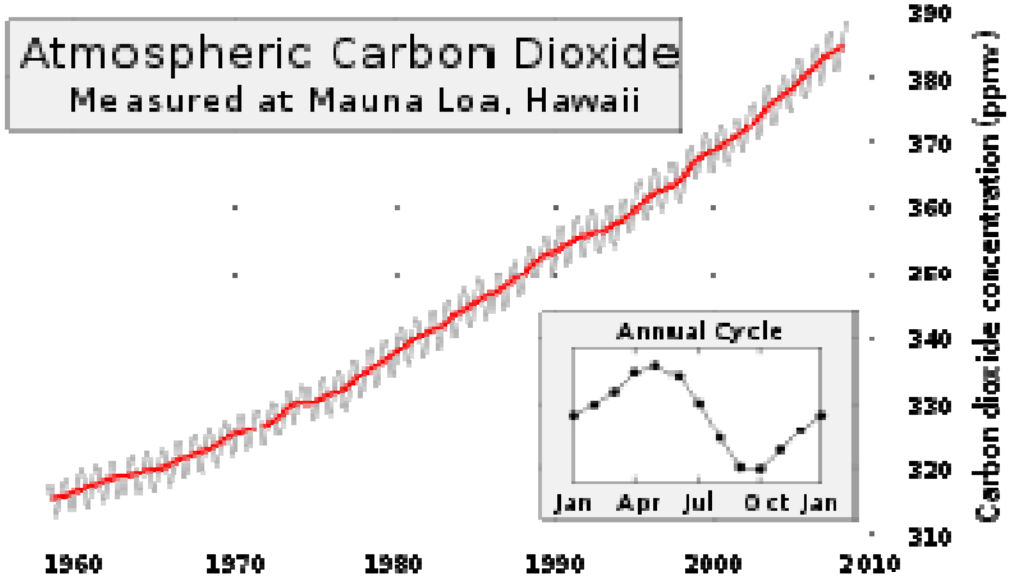
Sr.No.		Unit	Technology-I	Technology-II
1.	Temperature	°C	60 - 90	60
2.	Pressure	bar a	1.5	1.0

The gas composition from the technologies is somewhat different and its main components are CO_2--90.85%, water—9.14% and ethylene—0.01 %. Though chlorides are present in the gases at ppm level (1-1.2 ppm), this chloride level plays a major role in CO_2 recovery and cleaning techniques, especially for food grade CO_2.

CARBON DIOXIDE EMMISSION UPDATE:

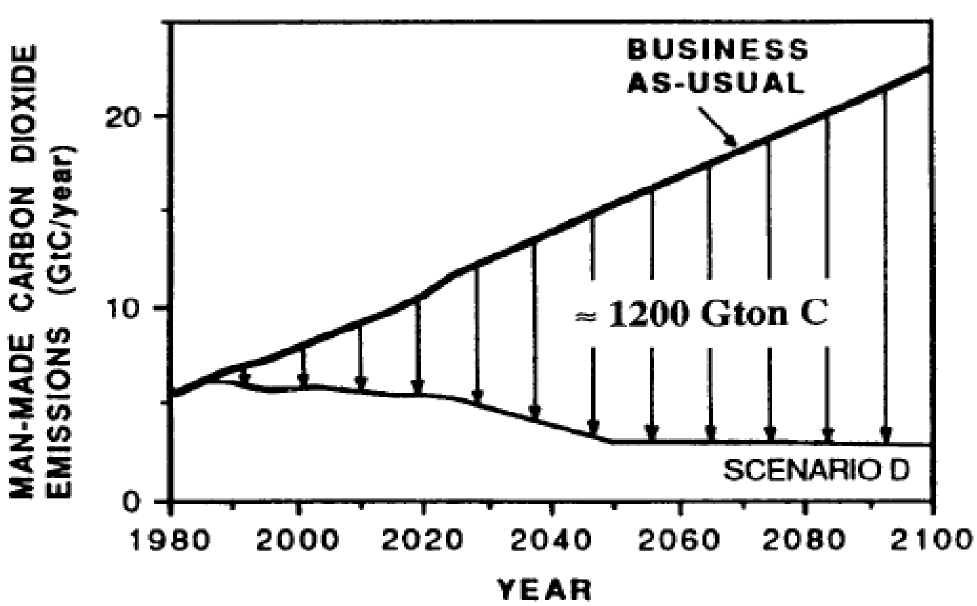
This carbon dioxide (CO_2) vent gas can be considered a waste but carbon dioxide is one of the main constituent of green house gases which are responsible for global warming. So as per the Kyoto Protocol, recovery and reuse of this waste CO_2 is a real challenge facing engineers. Annual carbon emissions by region and the global trend of CO_2 gases are given below (as measured in Hawaii). About 27 billion tones of pure carbon dioxide are pumped into the atmosphere every year — equivalent to 7.3 billion tones of pure carbon.





The total atmospheric concentration of carbon dioxide is now at 387 parts per million as measured at this site, up from an historic average of 180 to 280 ppm. Even if radical cuts were adopted by world governments and adhered to, the lowest level at which they could be expected to stabilize is 450 ppm, say scientists. To prevent a further temperature rise of more than 2 °C, emissions would need to be stabilized around that level. This may be insufficient to prevent catastrophic warming impacts such as a rise in sea levels of between 0.5 m and 1.4 m (1.6 ft and 4.6 ft) which may devastate many coastal cities around the world such as Shanghai, Calcutta and Dhaka. Instead, some scientist feel that a 1.5 °C rise as a safer target.

TURKENBURG: CO_2 REMOVAL; SOME CONCLUSIONS



In the coming decades, due to human activity in my opinion, the emission of carbon dioxide may increase from a level of about 7 GtC in the year 1990 to more than 20 GtC in the year 2100. This may enhance the greenhouse effect resulting, on average, in an additional warming of the Earth's surface. As a consequence the climate on Earth may change significantly. To limit the risk of climate change to sustainable levels, many believe we should reduce the emission of carbon dioxide and other greenhouse gases. Carbon dioxide (CO_2) level should be below the 3GtC per year.

SABIC APPROACH

Saudi Basic Industry (SABIC) owns and operates seven ethylene glycol plant located in Al-Jubail in Saudi Arabia. These ethylene glycol plants vent a substantial quantity of carbon dioxide (CO_2) into the atmosphere. Thus, SABIC wanted to study the possibility of recovering this CO_2 from the vent gas to protect the environment and provide a positive economic impact. The maximum amount of carbon dioxide vented to the atmosphere from these ethylene glycol plants is 115T/hr (approx). A study has been conducted to recover, purify and convert this CO_2 into either urea or methanol.

TECHNOLOGY

Highly efficient carbon dioxide (CO_2) purification and liquefaction technologies are available as per United States Patent 6224843 that recover the carbon dioxide from the vent gases from ethylene glycol manufacture and remove the unwanted impurities and produce highly concentrated carbon dioxide. These purified CO_2 streams can be sent to food and beverage industries as well as to a broad range of industrial application such as the urea and methanol process units identified at Al-Jubail. The few technology supplier are listed below:

1. UNION Engineering
2. Toromont Energy system (ENERFLEX) UK.
3. Linde Ag Germany
4. Johnson Matthey USA.

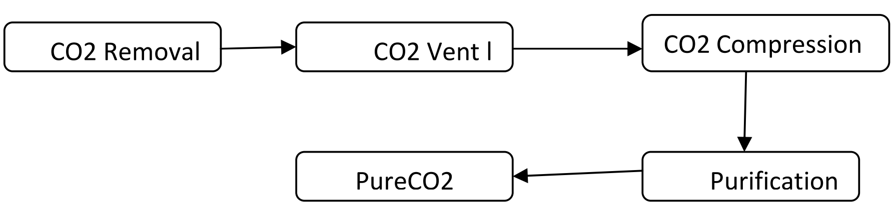
They are the international leaders in supplying technology for the design, engineering, and fabrication of modular CO_2 plants. These technologies are capable of reducing the chloride level in the vent gas below 1 PPB. The technology is commercially viable for a variety of CO_2 applications, from low pressure gathering to water dehydration to high pressure (200 to 400 bar) disposal.

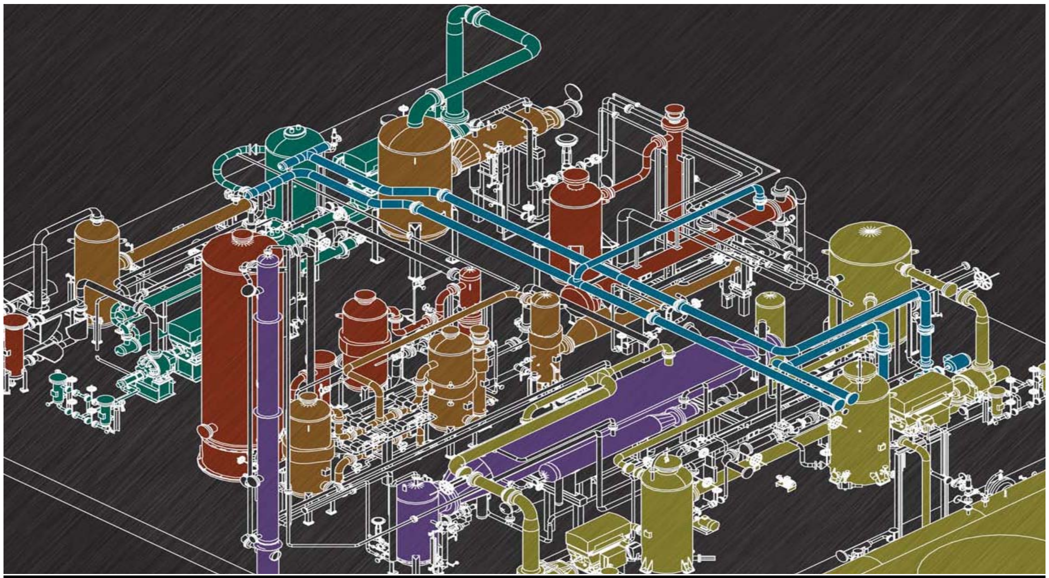
Carbon Dioxide Purification Process Description Highlight

The carbon dioxide (CO_2) stripper top vent gas is at a low pressure, the pressure of this stream is increased by a compressor. To remove the contaminants, a stripping column, catalytic oxidation reactor, regenearable carbon bed, sacrificial absorption bed, and a low catalytic sulfur removal system are used. Carbon dioxide (CO_2) is condensed in large kettle type shell & tube heat exchangers and purified in purification column. A 50%-50% water and glycol mixture is used for cooling the compressor lube oil. Special care is taken in the process to avoid ice formation during CO_2 condensation by providing a refrigeration system and a regenearable activated alumina and molecular sieve vessels.

The carbon dioxide (CO_2) is saturated with water. Thus, during purification, a significant amount of water will be generated which will contains mainly glycol and hydrocarbons. We have contacted some water treatment companies like Aquatech, GE Water Treatment, Thermax, and Metito Chemicals. They have suggested that technologies are available to recover this waste water as potable water and can be used as cooling water make up. Most of the cases show a payback period of 1 to 2 years. Since present cost of utilities are increasing day by day, this waste water recovery will further our effort to reuse and recycle waste.

CO2 Purification Process Plant





APPLICATION WITHIN SABIC

A. SAFCO & IBB (SABIC affiliates): Both affiliates have urea plants. The raw material of urea plant is purified and compressed carbon dioxide (CO_2) and ammonia (NH_3). Waste carbon dioxide can be purified and compressed to a desired specification. The quality of the CO_2 after purification almost meets the specification of the urea plants and only minor additional treatment should be required. This source should still be economically favorable for the urea plant.

B. AR-Razi & IBN-SINA (SABIC affiliates): Both affiliates have a methanol plant. The raw materials for the production of methanol are carbon dioxide (CO_2) and hydrogen (H_2). Hydrogen can be extracted from the purge gases of various plants. Hydrogen and compressed purified carbon dioxide (CO_2) can be used to produced or enhance the methanol production. Again, this source of carbon dioxide should prove favorable for the economics of these plants as well.

Waste CO_2 will be utilized as a key raw material and at the same time SABIC can claim carbon credit to control green house gas.

DEMAND AND GROWTH OF THE CARBON DIOXIDE MARKET

The carbon dioxide (CO_2) industry has seen strong growth in demand in both established and emerging markets. The majority of customers use CO_2 in the food and beverage industry. It is a highly stable and non-cyclic market. New and interesting applications are developed on regular basis and include:

1. Carbonation of water, soft drinks, and beer
2. Food chilling
3. Re-mineralization in desalination process
4. Food packaging
5. Welding
6. Waste water treatment
7. Medical
8. Degreasing application

The above mentioned applications represent an established market. There are other major commercial uses of carbon dioxide (CO_2) that can be divided into two main categories:

A. **Use of carbon dioxide (CO_2) as a raw material for chemical process:** The utilization of CO_2 in which the entire molecule is incorporated into the product. Producing chemicals such as urea, organic carbonates (including dimethyl carbonate (DMC)), inorganic carbonates, salicylic acids and its derivatives, polymers, and other organic intermediates.

B. **Use of CO_2 as resources in technological processes:** The utilization of CO_2 in reduction processes to yield other C_2 molecules richer in energy such as methanol, carbon monoxide, methane, formic acid and formaldehyde.

The most promising chemicals/products synthesized from CO_2 on the basis of expected future production capacities are methanol, urea, new materials, polycarbonates (including DMC), polyurethanes, carbamates, and pharmaceutical.

FUTURE TREND OF CARBON DIOXIDE:

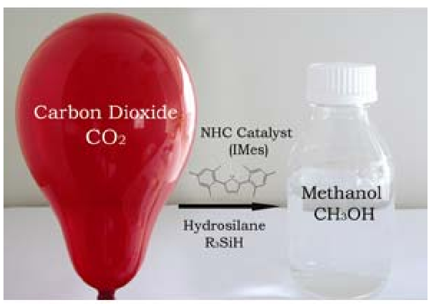
The present use of CO_2 as resource in technological processes can vary from higher to lower capacity and include: enhanced oil recovery (EOR), industrial extraction processes, food packaging and freezing, and as a additive in beverages and soft drinks. A massive shift towards carbon dioxide-based products has occurred in the production of pigments that are used in paper, plastics, and and paint. The application of CO_2 in chemical products might create a market of several hundred megatons of carbon per year.

Further study is needed to investigate what could be the net effect of these applications on carbon dioxide (CO_2) emission reductions.

To be sure that the technologies to remove CO_2 are environmentally and ecologically sound, specific attention should be paid to the storage and disposal of CO_2.

One issue is safety. In 1986 a volcanic in Africa sent carbon dioxide (CO_2) into the atmosphere from Lake Nyos, killing more than 1700 people. Investigations of CO_2 injection in underground wells suggest that safety aspects are not a limiting factor if advanced planning, intensive control, adequate maintenance and appropriate materials are applied. Further research on the probability and the effects of a CO_2 escape is needed to create a better understanding of the risks of storing CO_2 underground.

The reaction pathway for producing methanol via CO_2 is already developed.



IBN scientists convert carbon dioxide into methanol.

Scientists made carbon dioxide react by using N-heterocyclic carbenes (NHCs), a novel organ catalyst. In contrast to heavy metal catalysts that contain toxic and unstable components, NHCs are stable, even in the presence of oxygen. Hence, the reaction with NHCs and carbon dioxide can take place under mild conditions in dry air.

One might ask whether the application of CO_2 removal can be done in a cost-effective way when there are also other options to reduce the CO_2 emissions, especially when these options are developed further. Several groups have studied this question, using advanced computer models and detailed information about the possible development of all the different options. The results clearly indicate that in the near future CO_2 removal can indeed be a cost-effective option. Decarburization of fuels and of flue gases are promising application for the use of CO_2 especially with tight CO_2 emission constraints. The main limiting factor for the application of CO_2 in decarburization might not be its competitiveness but the availability of enough storage capacity.

ECONOMICES:

The sale price of pure carbon dioxide on the international market has varied from 20 to 100 USD per ton as per geographical location. Even though, the average sale price is approx. 50 USD per ton. Methanol and urea processes have been identified as potential industrial consumers. If a carbon dioxide purification plant was integrated with either a methanol or urea process, the pay back is an estimated 3 to 4 years. If a carbon dioxide purification unit is installed on a stand-alone basis, then the sale price would vary from 25 to 45 USD per ton making these plants economically feasible as well.

CONLUSIONS:

Petroleum industries are a major contributor to carbon dioxide emissions (CO_2) in to the atmosphere. Technologies are being developed and improved to focus their attention on mitigation and reducing company's carbon output. Drastic cuts in carbon emissions may not be sufficient to avoid the worst effects of global warming and the world will need to suck carbon from the atmosphere to avert permanent damage to the climate, according to a leading world authority on climate science. Individual efforts by industrial producers such as SABIC may help to convert the waste carbon dioxide into usable petroleum products. This may be a good first step in the reduction of carbon dioxide emissions.

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