

What To Do With CO₂? Storage Vs. EOR Vs. CO₂ As A Chemical Feedstock

Udara S. P. R. Arachchige, Sakuna Sandupama P.W

Faculty of Technology, University of Sri Jayewardenepura,
Nugegoda, Sri Lanka
udara@sjp.ac.lk

Faculty of Technology, University of Sri Jayewardenepura,
Nugegoda, Sri Lanka
ssakunas@gmail.com

Abstract: Atmospheric carbon dioxide concentration tremendously increased over the years due to fossil-fuel based power generation, industrialization, and deforestation. Therefore carbon dioxide capture technologies are essential to maintaining a better living environment. However, there should be a utilizing method with captured carbon dioxide. There are mainly three mechanisms involving captured carbon dioxide, Permanently storage, enhanced oil recovery, and carbon dioxide as a chemical feedstock. All of them have an advantage as well as disadvantages over the others.

Keywords: Carbon Dioxide capture, Storage, Enhanced Oil recovery, Chemical feedstock

1. Introduction

CO₂ is considered as the main anthropogenic contributor for greenhouse gas effect as a result of a major contribution to the global temperature rise. Recent emphasis on carbon dioxide emissions and the resulting potential for global warming and climate change has gained important consideration [1]. The atmospheric concentration of carbon dioxide (CO₂) has increased tremendously during the last few decades. CO₂ emissions in a large amount by many industries like coal and gas-fired power plants, steel production, cement production, chemical, and petrochemical production are the leading emission sources. Global greenhouse gas emissions are rapidly increasing and in 2019 carbon-dioxide (CO₂) composition in the atmosphere reached 410 parts per million (ppm). CO₂ releases to the atmosphere must be reduced to maintain a better environment for living. Figure 1 show the CO₂ concentration variation in the atmosphere over with time [2].

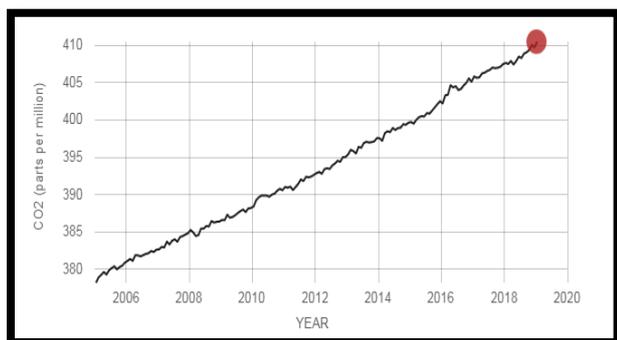


Figure 1: Atmospheric CO₂ concentration [1]

Fossil fuel (especially coal) still plays the most important role in the energy sector. On the other hand, fossil fuel is the leading CO₂ emission source to the atmosphere. Therefore, carbon dioxide capture and storage (CCS) technologies are important to continue uses of fossil fuel [3]. There are mainly three methods are involving with the storing mechanisms of captured CO₂. The captured CO₂ has to storage permanently, use for enhanced oil recovery (EOR) or

can be utilized as a chemical feedstock in many different industries [4].

2. CO₂ Storage

CO₂ can be stored in three main ways: in deep geological formations, in deep ocean water-ocean storage, in the form of mineral carbonates-mineral storage [5].

2.1. Deep Geological Formations

The CO₂ can be captured either from the flue gases or is the carbon captured from the fuel before the combustion process. The captured CO₂ has to be cleaned and compressed before it is pumped. Then it is pumped as a liquid down into a porous rock formation for permanent storage. Storage in deep geological formations is also known as 'geo-sequestration'. In this technique, carbon dioxide is converted into a high-pressure liquid-like form known as 'supercritical CO₂' and that supercritical CO₂ behaves like a runny liquid. Once it is formed as supercritical CO₂, that is injected directly into sedimentary rocks. The rocks may be in **old oil and gas fields**, **Unminable coal seams** and **saline formations** have also been suggested as storage sites [6].

2.1.1. Old Oil and Gas Field

The CO₂ storage potential in old oil and gas fields are found in world wide. It has storage capacity equates to over 60 years of current CO₂ emissions from all uses of fossil fuels worldwide. The major purpose of these injections was to disposing of "acid gas," a mixture of CO₂, H₂S and other byproducts of oil and gas exploitation and refining. Essentially, CO₂ and H₂S from the produced oil or gas stream can be removed by acid gas injection and, compress and transport the gases via pipeline to an injection well, and re-inject the gases into a different formation for disposal. In most of these schemes, CO₂ represents the largest component of the acid gas, typically up to 90% of the total volume injected for disposal. Successful acid gas injection requires a nearby reservoir with sufficient porosity.

2.1.2. Unminable coal seams

Unminable coal seams (or coal that is too deep or difficult to mine) can be used to store CO₂ because it is adsorbed in the coal if the coal is permeable enough to allow CO₂ to penetrate. The abandoned or uneconomic coal seams are another potential storage site as it can be reused for storage facility. The captured CO₂ diffuses through the pore structure of coal and is physically adsorbed to it. This process is exactly having similarity with the way in which activated carbon removes impurities from air or water. During the process of absorption the coal releases previously absorbed methane, and the methane can be recovered. This recovered methane can be used and the process of extracting useful methane from a coal seam when it is injected with CO₂ is called ECBM (or enhanced coal bed methane). The sale of recovered methane can be used to offset a portion of the cost associated with the CO₂ storage. However, burning the resultant methane would produce CO₂ which would reduce some of the benefits of storing the original CO₂.

2.1.3. Saline aquifers

A highly concentrated brine solution is contained in some deep rock formations which are present in the rock pores (which act together like a huge sponge), and have so far been considered of no benefit to humans. These are known as 'saline aquifers'. In the past they have been rarely used for storage of chemical waste. However the value of saline aquifers is being re-examined. Their main advantage for saline aquifer is their large potential storage volume and their common occurrence. The main drawback of this method is, that relatively little is known about them, compared to oil fields. Unlike storage in oil fields or coal beds, no useful by-product will offset the cost of storage. Therefore, it is important to understand more about saline aquifer storage, but current research shows that several trapping mechanisms immobilize the CO₂ underground, reducing the risk of leakage.

2.2. Ocean storage

Another proposed form of carbon dioxide storage is in the deep oceans, but the environmental effects of this are generally believed to be bad, and the process is not well understood. A large quantity of CO₂ kills ocean organisms as CO₂ acts as an asphyxiant. Also, as CO₂ reacts with the water to form carbonic acid, H₂CO₃, the acidity of ocean water would increase and make an acidic environment which extremely creates a deadly situation for living organisms. However, with careful consideration, ocean storage facility can be implemented. The compressed CO₂ would be injected into the deep ocean. Various methods to achieve this have been proposed including CO₂ dispersal in a very dilute form at depths of 1000-2000m, discharge at 3000m to form a lake of liquid CO₂ on the seabed or formation of a sinking plume to carry most of the CO₂ into deeper water. A release of solid CO₂ at depth of ocean can also be suggested. Of these options, the first is thought to be the most promising in the short-term.

2.3. Mineral storage

Mineral storage is the next CO₂ storage mechanism available today. In mineral storage, captured CO₂ is reacted with naturally occurring magnesium-(Mg) and calcium-(Ca) containing minerals. This is called mineral carbonation and occurs naturally as the weathering of rock over geologic time

periods. Such magnesium and calcium minerals are very abundant and are very stable. As a result, the re-release of CO₂ into the atmosphere does not happen. However, these carbonation reactions are very slow under normal temperatures and pressures and to speed it up would need energy to further continue. The reaction rate can be made faster, by reacting at higher temperatures and pressures, or by pre-treatment of the minerals before storing. Mineral carbonation can be carried out in two ways, in-situ and ex-situ. In the in-situ method where the CO₂ is injected into a geologic formation for the production of stable carbonates, such as calcite (CaCO₃), dolomite, magnesite (MgCO₃), and siderite (FeCO₃). The products that are formed are thermodynamically stable, therefore, the sequestration is permanent and safe. This method differs from the conventional geological storage because CO₂ is injected underground under the appropriate conditions to accelerate the natural process of mineral carbonization. The second one is the ex-situ method where the process takes place above ground in a processing plant. However, in this method, the processing plant has to be installed. In situ mineralization is preferable because there is no need for additional facilities and mining, the CO₂ is injected directly into porous rocks in the subsurface and reacts directly with the rocks. Overall CO₂ storage mechanism is given in the Figure 2 [7].

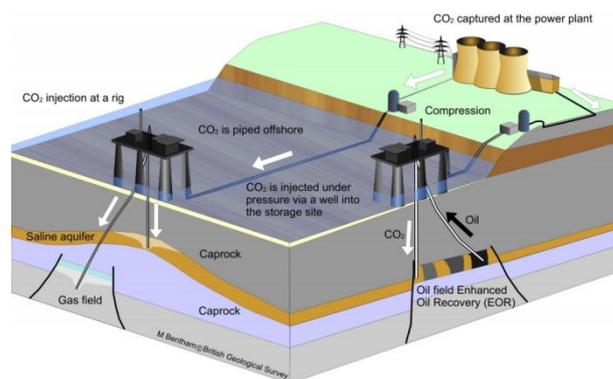


Figure 2: CO₂ storage in Geological formation, saline aquifer and EOR [7]

3. How do we store CO₂ safely and permanently underground?

There should be key geological features in a storage facility to safely store the CO₂. It needs a layer of porous rock, sufficient capacity and the impermeable layer of caprock to seal the porous layer underneath. Various physical, e.g. impermeable 'caprock', and geochemical trapping mechanisms prevent CO₂ from escaping to the surface. By exploiting the same trapping mechanisms are used by nature to store CO₂, gas, and oil for millions of years; and by using existing technology to transport and inject the CO₂. Once CO₂ stored, storage regulations will require that storage operations are rigorously monitored for a number of reasons, including:

- verifying the amount and composition of CO₂ being put into underground storage
- understanding how the CO₂ is behaving once underground
- providing early warning if things are not going as planned

- providing assurance of long-term storage integrity
- measuring any leakage that might occur

A broad range of tools and technologies is available to monitor CO₂ storage sites at a range of locations both onshore and offshore. Monitoring systems can be categorized into deep-focused and shallow-focused monitoring according to the procedure that uses. Deep-focused monitoring can be run from the surface (e.g. surface seismic or gravimetric) or from wellbores (e.g. well logging, pressure/temperature measurement) and is aimed at identifying and characterizing changes that occur within the storage reservoir as injection proceeds, including the movement of CO₂ within the storage reservoir and its immediate surroundings. Deep monitoring systems will also give early warning should CO₂ migrate to shallower depths. Shallow monitoring systems are designed to detect and measure CO₂ that has migrated into shallow geological formations, to the soil or seabed, or leaked to the atmosphere or into seawater. Shallow focused methods can be airborne (e.g. satellite interferometry), deployed at the surface (e.g. atmospheric measurements and surface flux), or can be run from shallow wellbores (e.g. geochemical sampling). The most important public concern about CCS is whether stored CO₂ will leak back to the surface (land or sea) and into the atmosphere. This would be a hazard because CO₂ at high concentrations is an asphyxiant, but it would also mean that the process would not be working as a climate change mitigation method. However, for well-selected, designed and managed geological storage sites, the Intergovernmental Panel on Climate Change (IPCC) says that risks are low. CO₂ could be trapped for millions of years, and well selected stores are likely to retain over 99 percent of the injected CO₂ over 1000 years [8].

4. Barriers to use CO₂ storages

There are several factors that we have to consider for CO₂ storage process. Mostly those are considered as barriers for CO₂ storing mechanisms. The high cost of capturing, processing and transporting anthropogenic CO₂ is one of the major problems with CO₂ storage mechanism. To overcome this, CO₂ capture technologies have to implement. Monitoring, verification, and environmental safety have to be performed before the CO₂ storing process start, and during the storing time period and even after the store and well closed. The continuous monitoring system has to be implemented to check whether stored CO₂ are in safe condition. Therefore, it is a time consuming costly process. In order to overcome that, the programmable advance monitoring system has to be developed and implemented on storage sites. At the same time, lack of functioning emission trading system also a disadvantage of the CO₂ storage process. To overcome that, the joint industry, governmental regulation system has to be implemented. One of the critical barriers is the conflict between CO₂ storage and EOR process. Depleted oil and gas fields always leave behind some amount of residual petroleum within the reservoir. New technologies or change in price in the future can change the abandoned petroleum field once again into a valuable asset. But converting a depleted oil field into CO₂ storage may be irreversible.

5. Enhanced Oil Recovery (EOR)

Once Oil field is discovered, it is initially developed and produced oil and gas using primary recovery mechanisms in which natural reservoir energy, expansion of dissolved gases, change in rock volume, gravity, and aquifer influx, drive the hydrocarbon fluids from the reservoir to the wellbores as pressure reduction with the fluid production. Due to primary oil recoveries, it can be recovered around 5-20 percent of the original oil in place (OOIP). However, low recoveries prompt field operators to find ways to improve recovery through the application of secondary recovery methods, which provide additional energy to the reservoir. In the secondary recovery method, it entails injecting either water and (or) natural gas into the reservoir for re-pressurizing and (or) pressure maintenance and to potentially act as a water and (or) gas drive to displace oil. This helps to sustain higher production rates and extends the productive life of the reservoir. However, the end of both primary and secondary recoveries, it can totally recover around 40 percent of OOIP [9]. When an oil field begins to age, oil production begins to tail off and it can apply various ways to get at the remaining oil and extend the life of the field. One of them is to pump high pressurized CO₂ underground to raise the pressure and drive oil to the surface. However, currently, oil companies buy in the CO₂ from fertilizer factories or power stations that have CCS fitted and pump it to the wellhead by pipelines. Some CO₂ is sequestered in this way, but only as a byproduct. The main goal is more oil, which means more CO₂ produce and release. So while this is potentially a green technology, it can equally be used in ways that are environmentally damaging. The EOR method to gain more oil from the oil reservoir can be illustrated in Figure 3 [10].

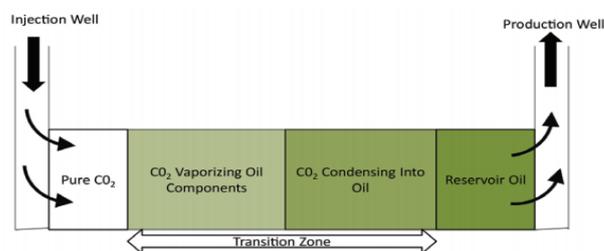


Figure 3: CO₂ Enhanced Oil Recovery: Process Schematic

6. CO₂ as a chemical feedstock

CO₂ can be used in many different industries as a chemical feedstock. In those industries, it is using as CO₂ in the liquid form, gaseous form or as a supercritical CO₂. Few of them will briefly discuss under this section.

6.1. Urea yield boosting

When natural gas is used as the feedstock for urea production, surplus ammonia is usually produced. A typical surplus of ammonia may be 5 percent to 10 percent of total ammonia production. If additional CO₂ can be obtained, this can be compressed and combined with the surplus ammonia to produce additional urea. A number of projects has been implemented to capture CO₂ from ammonia reformer flue gas for injection into the urea production process [11].

6.2. Algae cultivation

CO₂ can be added to the growth process of algae, significantly increasing its productivity. CO₂ can be combined with (bubbled through) algae cultivation systems to increase algae yield. The increased algae product can be a feedstock for biodiesel production. Biodiesel is a renewable energy source will be one of the best solutions to overcome fossil fuel based power generation issues.

6.3. Food processing, preservation and packaging

CO₂ is used for various applications in the food industry, including cooling while grinding powders such as spices and as an inert atmosphere to prevent food spoilage. In packaging applications, CO₂ is used in modified atmosphere packaging (MAP) with products such as cheese, poultry, snacks, produce and red meat, or in controlled atmosphere packaging (CAP), where food products are packaged in an atmosphere designed to extend shelf life.

6.4. Supercritical CO₂ as a solvent

CO₂ is useful in the industrial processes for high-pressure extraction and as a solvent to isolate targeted compounds, such as fragrances and flavors. Because of its low critical temperature and moderate pressure requirements, it can be treated with natural substances particularly gently. It is gaining favor as a solvent in the dry cleaning industry. Organic solvents are replaced by super critical carbon dioxide as it is a hydrophobic solvent. It has a very low viscosity. Carbon dioxide when substituted for an organic solvent, solvent costs and emission of toxic organics are minimized. By changing the carbon dioxide pressure separation of the products and catalyst can be controlled easily. Currently, supercritical carbon dioxide is used in the manufacture of di-methyl carbonate, caffeine extraction, dry cleaning, and parts degreasing [12].

6.5. Food and Beverages Industry

Liquid or solid carbon dioxide is used for quick freezing, surface freezing, chilling and refrigeration in the transport of foods. In cryogenic tunnel and spiral freezers, high-pressure liquid CO₂ is injected through nozzles that convert it to a mixture of CO₂ gas and dry ice "snow" that covers the surface of the food product. As it sublimates (goes directly from solid to gas states) refrigeration is transferred to the product. Carbon dioxide gas is used to carbonated soft drinks, beers, and wine and to prevent fungal and bacterial growth. Liquid carbon dioxide is a good solvent for many organic compounds. It is used to de-caffeinate coffee. It is used as an inert "blanket", as a product-dispensing propellant and an extraction agent. It can also be used to displace air during canning. Supercritical CO₂ extraction coupled with a fractional separation technique is used by producers of flavors and fragrances to separate and purify volatile flavor and fragrances concentrate.

6.6. Fire suppression technology

When applied to a fire, CO₂ provides a heavy blanket of gas that reduces the oxygen level to a point where combustion cannot occur. CO₂ is used in fire extinguishers, as well as in industrial fire protection systems.

7. Conclusion

There are several advantages and disadvantages over storage, EOR or CO₂ as a chemical feedstock method. It can be concluded as follows.

CO₂-Storage

Advantages:

- Possible storage sites are available all around the world.
- Store in Unminable coal seams: CO₂ adsorption to the coal releases previously adsorbed methane, and the methane can be recovered.
- Saline aquifers: their large potential storage volume and their common occurrence.

Disadvantages

- It needs layer of porous rock, sufficient capacity and the impermeable layer of caprock to seal the porous layer underneath.
- Ocean storage : Large concentrations of CO₂ kill ocean organisms as CO₂ acts as an asphyxiant. Also, as CO₂ reacts with the water to form carbonic acid, H₂CO₃, the acidity of ocean water would increase.
- The high cost of transporting anthropogenic CO₂ if the sites are not very closer to the capturing plant.
- Monitoring , verification and environmental safety- Before the CO₂ storing process start, and during the storing time period and even after the store and well closed, continuous monitoring system has to be implemented to check whether stored CO₂ are in safe condition.
- Lack of functioning emission trading system-Lack of provide financial benefits to the operator of the CO₂ storage
- Another potential risk is that dissolved CO₂ can change the acidity of the deep aquifer. A different acidity may cause certain trace elements, such as the toxic elements lead and arsenic, to become mobilized and travel to the shallow aquifer (which is what we use for drink water and irrigation). We don't want that either.

CO₂-EOR

Advantages:

- Every oil field after first and second recovery large amount of oil remained and can take out with the EOR.
- The main goal is more oil, which means more CO₂ of course can be utilized for the EOR.
- This option is attractive for geological storage because the geological character of hydrocarbon reservoirs is well known, and because costs of injection may be partly offset by the sale of additional oil that is recovered.
- additional hydrocarbon recovery that promotes energy independence
- The largest difference compared to other gases is that CO₂ can extract heavier components up to C30. The solubility of CO₂ in hydrocarbon oil causes the oil to swell. CO₂ expands oil to a greater extent than methane does.

- CO₂ has the following characteristics in a flood process:
 - It promotes swelling
 - It decreases oil viscosity
 - It increases oil density
 - It is soluble in water
 - It can vaporize and extract portions of the oil
 - It achieves miscibility at pressures of only 100 to 300 bars
 - It reduces water density
 - It reduces the difference between oil and water density, and then reduce the change for gravity segregation
 - It reduces the surface tension of oil and water, and result in a more effective displacement

Disadvantages:

- One of the main problems in achieving profitable CO₂ flooding has been the high mobility of the CO₂. The relative low density and viscosity of CO₂ compared to reservoir oil are responsible for gravity tonguing and viscous fingering. The effect of CO₂ is more severe than those problem are in a water flood.
- high cost of CO₂
- Surface facilities has to be modified
- In addition, some phenomenons such as gravity override, viscous fingering and channeling of CO₂ can lead to poor contact between injected CO₂ and thus cause low sweep efficiency.

CO₂-Chemical Feedstock

Advantages

- CO₂ can be used to produce something useful. (soft drinks, beer)
- Raw material cost can be minimized by using captured CO₂.
- Chemical production rate can be implemented. (urea, algae)
- Product quality improvement (seal gas for wine industry)

Disadvantages

- CO₂ captured and storage is costly compared to the product that is using CO₂ as a chemical feedstock.

The overall idea of uses of captured CO₂ can be illustrated in the Figure 4.

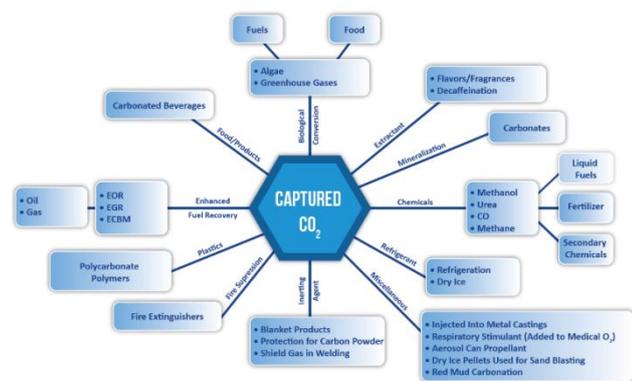


Figure 4: Applications of CO₂ [13]

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Author Profile

Udara S.P.R. Arachchige received his B.Sc Degree (2007) in Chemical and Process Engineering from University of Moratuwa, Sri Lanka and M.Sc degree (2010) in Energy and Environmental Engineering from Telemark University College, Porsgrunn, Norway. He received his Ph.D in Carbon dioxide capture from power plants- modeling and simulation studies at South Eastern University of Norway in year 2014. He has presented and published 23 papers in International Conferences and journals. His research

interests are CO₂ capture, modeling and simulation, air pollution control and energy optimization. Currently he is working as a senior Lecturer in Faculty of Technology, University of Sri Jayewardenepura, Sri Lanka.

E-mail address: udara@sjp.ac.lk



Sakuna Sandupama is presently pursuing his Bachelor's degree in Engineering Technology at Faculty of Technology, University of Sri Jayewardenepura, Sri Lanka. His research interest are environmental pollution and control, information communication technology, technology for sustainable development.

E-mail address: ssakunas@gmail.com

