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Chapter

Carbon capture utilization and storage supply chain: analysis, modeling and optimization

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Abstract

In 2016, CO₂ emissions in the world was about 32.3 Gt with the combustion of fossil fuel being the highest contributor. A target for the reduction of CO₂ emissions of 60% was set in the Paris Agreement. Thereafter, this topic has acquired much importance in the world, especially in recent years. In this context, carbon capture utilization and its storage supply chain is highly considered as a strategic solution that can solve the problems related to CO₂ emissions. In this work an overview about carbon capture utilization and its storage supply chain is developed. Due to their important environmental role, mathematical models are required for the design and optimization. Hierarchical or simultaneous methodology can be used, and one procedure is suggested for minimizing the total cost of the supply chain. Following this, equations related to capture and compression costs, transportation costs, utilization and storage costs are revised. This work, in addition, reviews systems for CO₂ capture and compression, and options for CO₂ utilization and storage. Many works are present in literature regarding this technology, however more studies should be developed on dynamic state considering uncertainties.

Keywords: carbon capture utilization and storage supply chain, mathematical modeling, optimization, design, CO₂ capture technology, CO₂ utilization, CO₂ storage, CO₂ reduction, economic analysis, uncertainties.

1. Introduction

The variation of climate has a high influence on all aspects of society and it is recognized as public concern in the United Nations Framework Convention on Climate Change (UNFCCC) (Pires et al., 2011; Han and Lee, 2011a). In this context, carbon capture, utilization and storage (CCUS) systems have an important role and researchers worldwide have focused their attention on carbon capture utilization and storage supply chains. Figure 1 shows the main elements of carbon capture utilization and storage supply chain: CO₂ source, CO₂ capture technology/material and compression, CO₂ transportation, CO₂ storage and CO₂ utilization (Hasan et al., 2015).

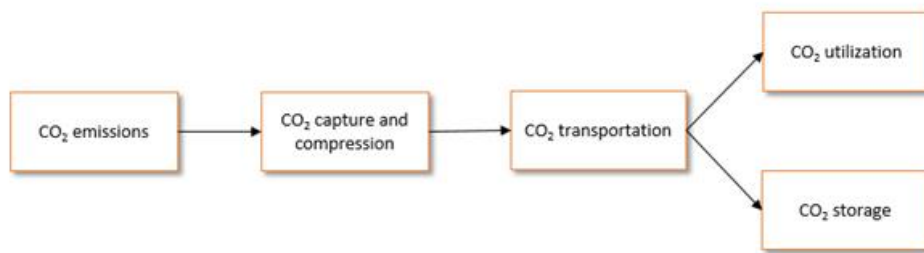


Figure 1 Block diagram for the main elements (CO₂ source, CO₂ capture and compression, CO₂ transportation, CO₂ utilization and CO₂ storage) of carbon capture utilization and storage supply chain (Hasan et al., 2015)

When more than one CO₂ sources, capture technologies/materials, CO₂ utilization and storage sites are present, the system is known as carbon capture utilization and storage supply chain network and the best combination between single elements then the best supply chain should be found.

There is international interest to carbon capture utilization and storage systems, because inside the sustainable economy they can limit the increase of temperature to 2 °C, as established by the Paris Agreement (COP21) setting a reduction target of 50% for CO₂ emissions by 2050 (Tapia et al., 2018). The Intergovernmental Panel on Climate Change (IPCC) suggests that the cost of actions to solve this environmental problem should increase by 138% without carbon capture utilization and storage systems and the certainty to achieve the fixed objective is not present. In particular, climate action without CCUS systems are calculated around \$2 trillion over 40 years. The application of carbon capture utilization and storage systems in industrial and power sectors should reduce greenhouse gas emissions of 7 Gigatonnes per year by 2050 with the aim to constrain the increase of heating of 2 °C. The importance of carbon capture utilization and storage system can be understood by looking at emission data: despite traditional climate change mitigation initiatives and policies, global greenhouse gas emissions grew by 2.2% every year between 2000 and 2010 compared to the increase of 1.3% every year between 1970 and 2000 (Milani et al., 2015). Therefore, in order to reach the objectives set by the Paris Climate Change Agreement, carbon capture utilization and storage will be an important technology, especially for the long term and will have a promising value (Sun and Cheng, 2017).

Many mathematical models are performed with the aim to design and optimize carbon capture utilization and storage supply chain by minimizing the total costs or by maximizing the amount of captured CO₂. The aim is to find, inside a carbon capture utilization and storage supply chain network, the best combination between CO₂ source, CO₂ capture and compression, CO₂ transportation, CO₂ storage and CO₂ utilization. CO₂ sources and CO₂ utilization/storage sites are connected as in a combinatorial problem: more alternatives are present by increasing CO₂ sources and utilization/storage sites. An overview of CO₂ capture technology, CO₂ storage and CO₂ utilization is suggested in this work and its aim is to suggest a guide to model carbon capture utilization and storage supply chain. Then a review of works presented in literature is shown.

2. Status of carbon capture utilization and storage supply chain

Overall, in the world the realization of carbon capture utilization and storage supply chains is slower than the objectives established by Paris Agreement cannot be satisfied.

70 carbon capture utilization and storage projects at pilot scale are present in the world: 22 are in North America, 1 in South America, 22 in Europe, 20 in Asia, 4 in Australia, and 1 in South Africa, as shown in figure 2 (Liu et al., 2015).

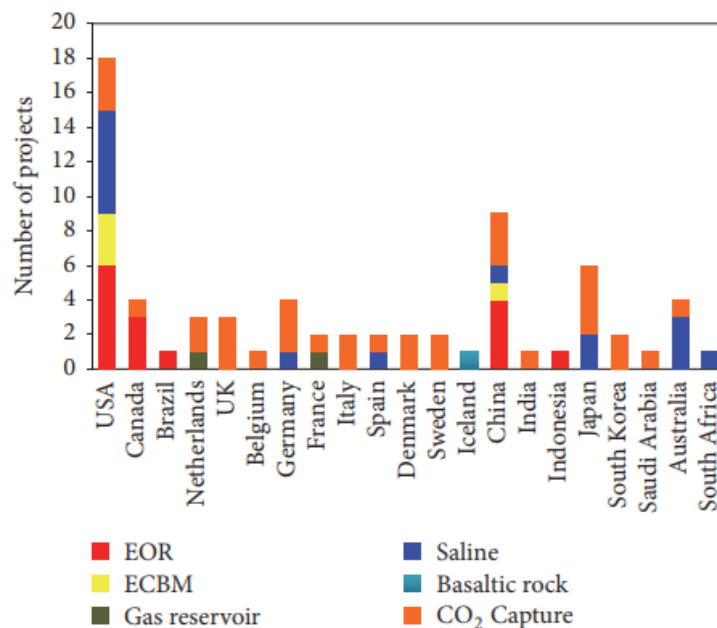


Figure 2 Global distribution of pilot-scale carbon capture utilization and storage engineering projects based on project purpose and reservoir types (<http://www.globalccsinstitute.com/>) (EOR=enhanced oil recovery, ECBM= enhance coal-bed methane).

Some important projects related to carbon capture utilization and storage supply chains are: Petra Nova in Texas (CO₂ emitted by coal-fired power plant is used to enhanced oil recovery), Al Reyadah in Abu Dhabi (CO₂ from iron and steel industry is used to enhanced oil recovery), Tuticorin in India (CO₂ emitted by coal powered boiler is used to make baking soda), Boundary Dam 3 in Canada (CO₂ from power plant is used to

enhanced oil recovery), Air Products in Texas (CO₂ from hydrogen refining is used to enhanced oil recovery), Emirates Steel Project in UAE (CO₂ from steel industry is utilized to enhanced oil recovery), Yangchang Petroleum in China (CO₂ from coal industry is used to enhanced oil recovery). Other small- or large-scale carbon capture utilization and storage projects have been developed showing significant reductions of CO₂. However, many studies and research has been carried out to estimate the costs of these supply chains, the main obstacle for their development at industrial scale.

3. Carbon capture utilization and storage technology overview

3.1 CO₂ capture options

CO₂ can be captured from flue gases with three strategies: post-combustion, pre-combustion, oxy-combustion, as present in figure 3.

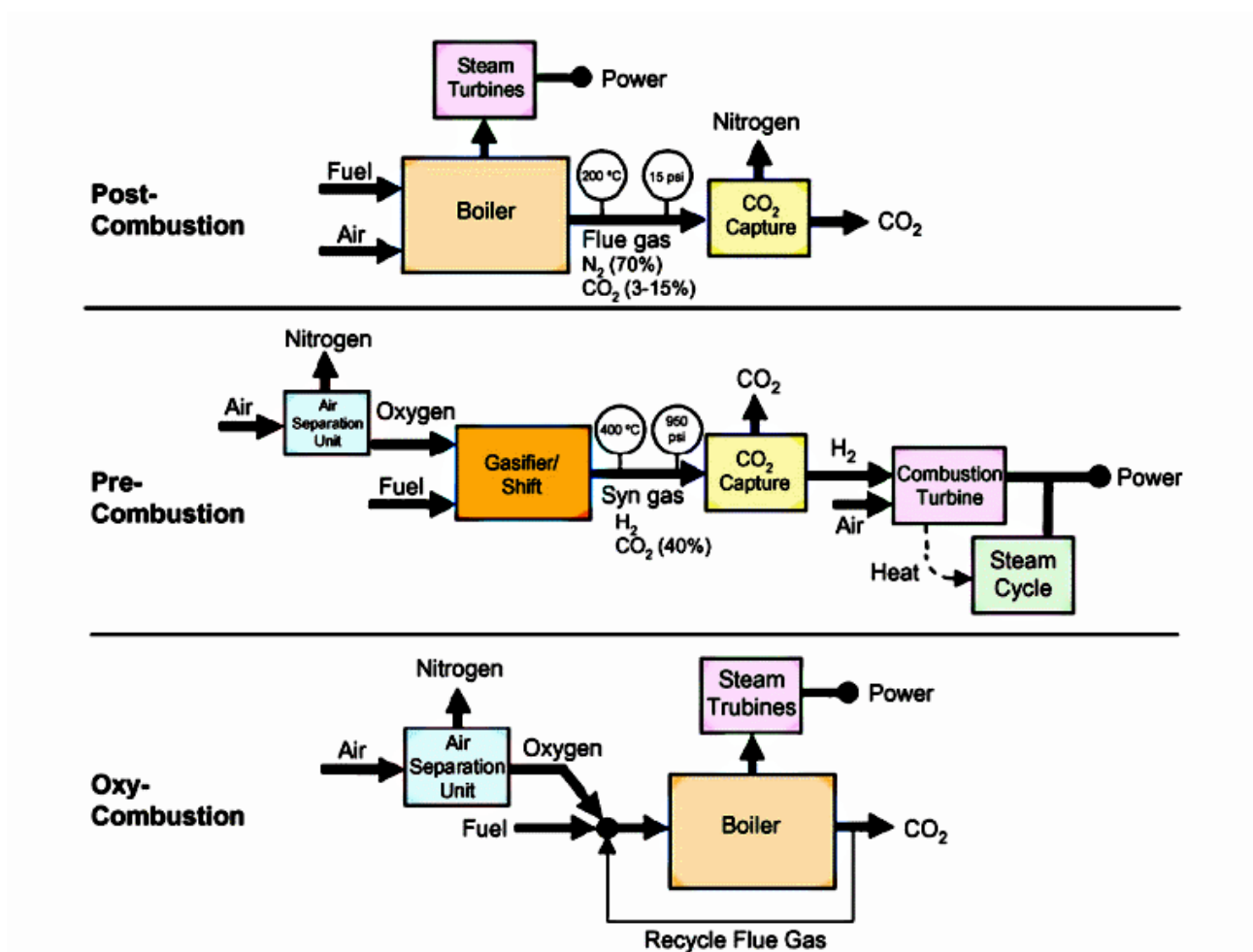


Figure 3 Block diagram for different CO₂ capture strategies (post-combustion, pre-combustion and oxy-combustion) (Figuerola et al., 2008, reproduced with permission number 4563270013378)

In post-combustion capture, CO₂ is captured from flue gas obtained by the burning with air. In pre-combustion capture, CO₂ is removed by syngas obtained by gasification process, before the combustion. In oxy-combustion, unlike to post-combustion, heat source is combusted with oxygen containing little or no nitrogen and flue gas is recycled after that CO₂ is captured. The selection of one of these strategies depends on

advantages and disadvantages, CO₂ concentration and pressure. Advantages for post-combustion capture are: a straightforward approach to be retrofitted and it is a more mature strategy respect to other strategies so that can be more applied to existing power plant. However, some disadvantages are: a low CO₂ concentration (about 5–15 vol%) that due to the near atmospheric pressure does not cause high CO₂ partial pressure (about lower than 0.15 atm), the requirement of higher circulation volume for high capture level producing energy lost during solvent/sorbent regeneration (Figueroa et al., 2008; Song et al., 2019). Advantages for pre-combustion are: a high CO₂ concentration (about 45 vol%) and pressure, then a high CO₂ partial pressure and driving force for the separation. For these reasons, a lot of systems can be used for CO₂ capture, however severe operating conditions are required (15-20 bar and 190-210 °C) and as the previous strategy energy penalties are present due to sorbent regeneration (Figueroa et al., 2008; Song et al., 2019; Dai et al., 2016; Nandi et al., 2015). Advantages for oxy-combustion are: a low investment cost caused by a high CO₂ concentration (80-98 vol%); however, efficiencies are not so high determining energy penalties, the production of O₂ can be very expensive and auxiliary load are added (Figueroa et al., 2008; Song et al., 2019; Hedin et al., 2013; Tonziello et al., 2011; Leung et al., 2014). Generally, post-combustion strategies are used for power generators fueled by coal and air. Pre-combustion strategies are used for gasification process. Oxy-combustion strategy is generally used for already existing plants. Different technologies as absorption, adsorption, membrane, chemical looping and cryogenic can be used to capture CO₂ in the above strategies. These are based on different principles.

Table 1

Suggested CO₂ capture technologies for different CO₂ capture strategies with the description of methodology and applications (Cuellar-Franca and Azapagic, 2015)

Capture option	Separation technology	Method	Applications
Post-conversion	Absorption by chemical solvent	Amine-based solvent, e.g. monoethanolamine (MEA), diethanolamine (DEA), and hindered amine (KS-1)	Power plants; iron and steel industry; cement industry; oil refineries
		Alkaline solvents, e.g. NaOH and Ca(OH) ₂	
		Ionic liquids	
	Adsorption by solid sorbents	Amine-based solid sorbents	No application reported
		Alkali earth metal-based solid sorbents, e.g. CaCO ₃	
		Alkali metal carbonate solid sorbents, e.g. Na ₂ CO ₃ and K ₂ CO ₃	
		Porous organic frameworks – polymers	Power plants
Membrane separation	Polymeric membranes, e.g. polymeric gas permeation membranes	Power plants; natural gas sweetening	
	Inorganic membranes, e.g. zeolites		
	Hybrid membranes		
Cryogenic separation	Cryogenic separation	Power plants	
Pressure/vacuum swing adsorption	Zeolites	Power plants; iron and steel industry	
	Activated carbon		
Pre-conversion	Absorption by physical solvents	Selexol, rectisol	Power plants (IGCC)
	Absorption by chemical solvents	Amine-based solvent, e.g. Monoethanolamine (MEA)	Ammonia production
	Adsorption by porous organic framework	Porous organic frameworks membranes	Gas separations
Oxy-fuel combustion	Separation of oxygen from air	Oxy-fuel process	Power plants; iron and steel industry; cement industry
		Chemical looping combustion	Power plants
		Chemical looping reforming	Power plants; syngas production and upgrading

3.1.1 Absorption technology

Absorption process can be physical or chemical (Song et al., 2019). Absorber and regenerator work in a continuous way: flue gas (fed at the bottom of the absorber) and solvent (fed at the top of the absorber) are working in counter current way then a selective capture of CO₂ is present. Stream with a high CO₂ content from the absorber is sent to the regenerator: CO₂ is desorbed and it can be used or stored, while the solvent is regenerated and recycled for further use in the absorber. Chemical solution for absorption such as monoethanol amine (MEA), diethanol amine (DEA), N-methyldiethanolamine (MDEA), and di-2-propanolamine (DIPA) are generally used (Mamun et al., 2007). Diglycolamine (DGA), 2-(2-aminoethylamino) ethanol (AEE), 2-amino 2-methyl 1-propanol (AMP), N-2-aminoethyl 1,3-propanediamine (AEPDNH₂), triethanol amine (TEA), triethylene tetra amine (TETA), piperazine (PZ), glucosamine (GA), NaOH, NH₃, K₂CO₃, KOH, Na₂CO₃, etc. are other absorbent solutions that can be used, but with some limitations for application in large scale plants (degradation, corrosion, regeneration efficiency). In recent years, ionic liquids are under research

for application in CO₂ absorption process. Due to their physical-chemical properties (low volatility, good dissolution, high decomposition temperature and stability, excellent chemical tunabilities), they can reduce regeneration energy but until now they have a higher cost compared to other solvents (Luo and Wang, 2017; Ma et al., 2018). Some advantages of absorption process are: chemical solvents ensure a high driving force to capture CO₂ also at low concentration, while wet-scrubbing guarantees a recovery of heat especially for exothermic absorption reactions (National Energy Technology Laboratory, 2010). Absorption technology is less expensive for large-scale plants, simpler and more robust than other technologies. For these reasons, they are preferred and applied among capture technologies (Bhown, 2014). Actually, researches in absorption system for CO₂ capture are regarding the improvements of solvents and gas-liquid contactor, the study of inhibitors for degradation and corrosion, the study of alternative solvents and blended solvents, etc.

3.1.2 Adsorption technology

In the first section of this process, flue gas is dried for the condensation of water and after compression it is sent to chambers packed with solid adsorbent (activated carbon, zeolites, or metal organic frameworks, etc.) (Gao et al., 2017; Samanta et al., 2012). Generally, in one system, two or three adsorption chambers are present: the first receives the feed for CO₂ adsorption, the second for its desorption, while the last is in stand-by for the first one (Thiruvengkatahari et al., 2009). The system operates continuously, changing pressure in PSA (pressure swing adsorption) and VPSA (vacuum pressure swing adsorption) systems, temperature in TSA (temperature swing adsorption) systems or voltage electric current in electrical swing adsorption (ESA) systems. It is possible to combine pressure swing adsorption and temperature swing adsorption in PTSA systems (pressure and temperature swing adsorption) that could reduce power consumption by 11% respect to pressure swing adsorption system (Gupta, 2003). However, adsorption is lower used for large scale processes than absorption process (Bhown, 2014). In any cases, some advantages for adsorption process are: fast kinetic, the large adsorption capacity of sites and low sensible heat, it allows to work with low CO₂ concentration and at a higher capacities than absorption (National Energy Technology Laboratory, 2010). Some disadvantages for adsorption are related to the regeneration and reusability of adsorbents and a lower efficiency and selectivity respect to absorption or cryogenic technology (Bamdad et al., 2018; Mondal et al., 2012). Researches in adsorption process are about the study of novel adsorbents or the modification of already present (their surface) with the aim to work at high temperatures and with steam, resulting in a high capacity and selectivity. In this context, a good solution is presented by activated carbon fibers and carbon fiber composites.

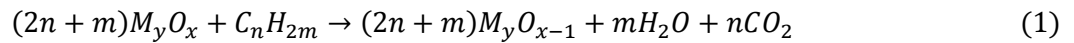
3.1.3 Membrane technology

Membrane technology is introduced in last years and it is divided in gas separation and gas absorption. In the suggested process the permeate of the first stage is divided in two parts: 70% is fed to the second-stage while 30% is recycled to the first stage as sweep (Hussain et al., 2010). Instead, the permeate of the second stage is recycled to the same stage as a sweep for only 5%. These systems are a new technologies and have some disadvantages related to higher temperature than 100 °C, sensibility to corrosion due to particular gases, high performance for long term operation, the requirement of multiple stages for diluted feed stream (below 20%)

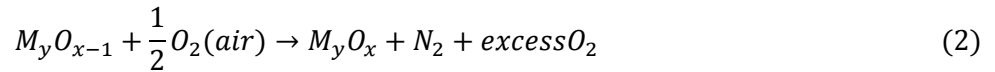
and inability to handle high flue gas flow rate (Zhang et al., 2013; Mondal et al., 2012). Some advantages are due to the no use of steam, chemicals and its simple design (National Energy Technology Laboratory, 2010). Also, membrane systems are competitive due its energy efficiency and sustainability (Evangelos et al., 2017). Generally, polymer membranes and composite membranes are used in addition to inorganic one (carbon, zeolite, ceramic or metallic) and can be porous and not. In last years, mixed matrix membranes are developed and are composed by a polymer with dispersed zeolites inside. This solution can improve the selectivity of membrane compared to traditional one (Li et al., 2013). It is evident, that today researches are about the finding new efficient materials.

3.1.4 Chemical looping combustion

In a chemical looping combustion (CLC) for carbon capture system, combustion is divided in two steps: oxidation and reduction reaction by using oxygen (in the form of solid metal oxides as Fe_2O_3 , NiO , CuO , Mn_2O_3 called solid oxygen carrier), moving between the two separated phases, with two fluidized bed reactors, one for air and one for fuel (Song et al., 2019). In the first reactor, metal oxides are oxidized by the oxygen of air. In the second reactor, metal oxides are reduced by fuel, which is oxidized to CO_2 and H_2O . The generalized reaction for fuel reactor is the following (Mondal et al., 2012) (see Eq. 1):



while for air reactor, the following reaction take places (Mondal et al., 2012) (see Eq. 2)



Advantages of this technology are: the production of no toxic N_2 from air reactor and the production of CO_2 from fuel reactor that can be separated by H_2O by condensation then reducing capital costs (Olajire, 2010). In addition, NO_x formations are minimized, because combustion is carried out with air reducing oxygen that is re-oxidized in the air reactor at lower temperature. However, there are few large-scale plants using this process (most of them are in laboratory scale) with some problems, as the low stability of oxygen carrier, the slow reaction rate of redox reaction and the removal of sulfur by fuel to avoid poisoning problems (Solunke et al., 2011). Chemical looping is especially used in gasification process capturing at least 90% of CO_2 : however, the cost of electricity is increased of 16% respect to air fired circulating fluidized bed plant (Nsakala and Liljedahl, 2003).

3.1.5 Cryogenic technology

Cryogenic technologies are also known as low temperature CO_2 capture technologies. CO_2 is separated by flue gas due to the different condensation and desublimation properties. High CO_2 recovery (99.99%) and purity (99.99%) can be obtained with this technology (Brunetti et al., 2010). In the process scheme for cryogenic capture a steel monolith structure is used as packed material while liquefied natural gas is used for refrigeration. Energy consumption and installation investment costs are lower than vacuum pressure swing adsorption due to a smaller bed size and even if it has more potential than absorption it is not yet marketable,

due to some problems as the losses of sensible and latent heat due to the no good thermal insulation. In addition, in order to remove H₂S, the temperature of system should be about 150 °C, so increasing operating costs. Also, an additional refrigerator is required for liquified natural gas, increasing then the energy consumption of the system (Abatzoglou and Boivin, 2009). Other limitations of cryogenic technology are related to the presence of other gases (SO_x, NO_x, H₂O), that during condensation can determine corrosion, fouling phenomena (AxeL and Xiaoshan, 1997). Also, CO₂ can produce solids reducing heat transfer and then the efficiency. However, the main advantages of cryogenic technology are that chemical solvents are not necessary and that atmospheric pressure can be set. Also, liquid CO₂ is obtained and it is needed for economical transport in ship and pipeline. In addition to packed bed scheme, other processes are developed with cryogenic technology: anti-sublimation CO₂ capture process (AnSU), CryoCell process, cryogenic distillation and stirling cooler system ensuring a CO₂ recovery between 85% an 99% (Song et al., 2019). Advantages and limitations of these different schemes are reported in table 2. CO₂ can be captured without organic solvents: it is then a green process and it is competitive with refrigerant at low costs. Cryogenic can be used in cases with high CO₂ partial pressure, that it is typical of pre-combustion or oxyfuel combustion process (Gupta et al., 2003). Then, it is not economically favorable for dilute CO₂ stream due the high amount of required energy.

Table 2

Convenience and limitations of cryogenic capture technology (packed bed, AnSU, CryoCell, distillation, stirling cooler)

Category	Cold energy source	Advantages	Limitations
Packed bed	Liquid nitrogen gas (LNG)	Atmosphere	Depends on the availability of LNG
		Simultaneous H ₂ O and CO ₂ removal	Lab scale
		Avoiding high pressure drop surface area-to-volume ratio of the column	
AnSU	Liquefied natural gas (LNG)	Atmosphere	Depends on the location of natural gas station
		Lower energy penalty than MEA absorption	No H ₂ O can be tolerated
		Pilot demonstration	Frost CO ₂ adversely affects heat conduction undesired mechanical stresses
CryoCell	Chiller	No process heating system required	More suitable for high CO ₂ concentration (higher than 20%)
		No corrosion potential	High compression power requirement
		No foaming potential	
		Avoid compression cost	
Distillation	Compressor and cooler	Avoid compression cost	Capital cost for pressure difference
		Easy to be pumped to storage site	High installation cost
		Energy storage potential	
		Water saving potential	
		Simultaneous removal of other pollutants (Hg, SO _x , NO ₂ , HCl, etc.)	
Stirling cooler	Stirling cooler	Atmosphere	Exergy loss due to temperature difference
		Simultaneous H ₂ O and CO ₂ removal	Difficulty of frost layer scrapping
		Lower energy penalty than MEA absorption	Lab scale
		Energy storage potential	

3.1.6 Hybrid technology

With the aim to overcome the limitations of each technology, hybrid capture technology are developed by the combination of different technology as shown in figure 4. Hybrid processes ensure a higher CO₂ recovery and lower energy penalties and installation investment costs. The combination of membrane with absorption process (membrane contactor), catalysis process (adsorption-catalysis-membrane) and cryogenic process (low-temperature-membrane-cryogenic) shows significant development. These hybrid technologies can be combined in serie, parallel or integrated. Therefore, hybrid processes is a hopeful alternative for the future.

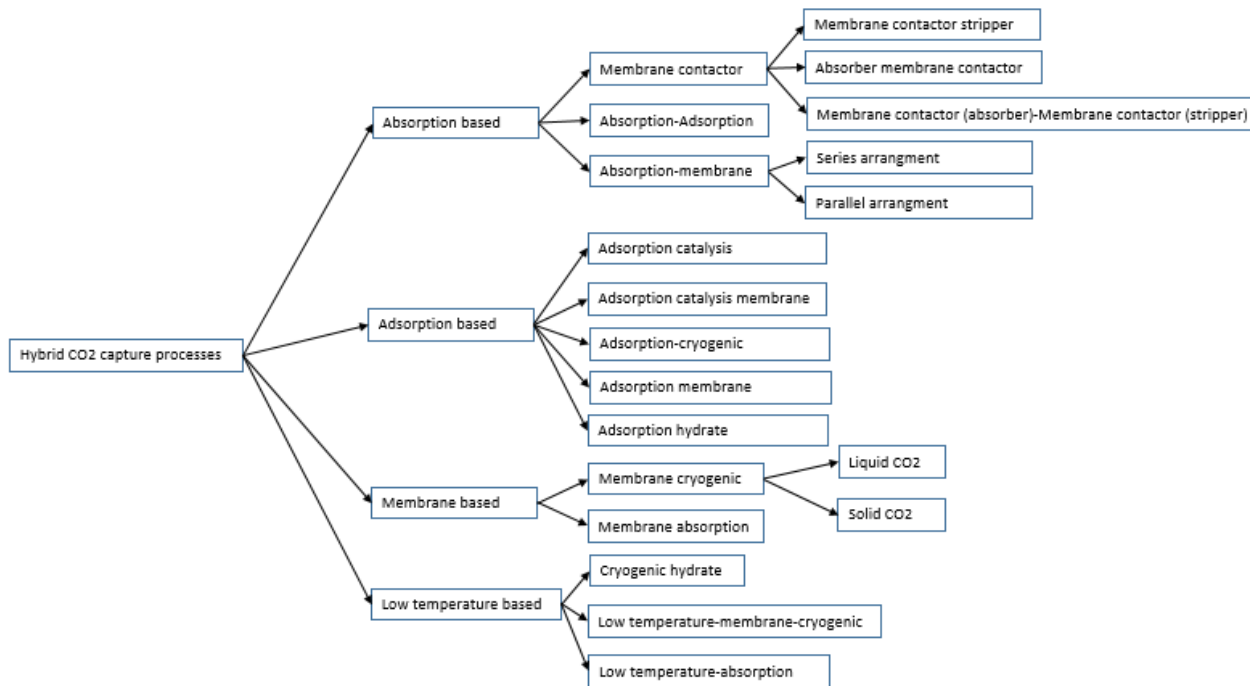


Figure 4 Existing hybrid CO₂ capture processes: absorption based, adsorption based, membrane based and low temperature based (Song et al., 2018, reproduced with permission number 4563280736814)

3.2 CO₂ utilization option

In addition to storage, CO₂ can be used and then valorized for:

- direct utilization;
- enhanced oil recovery, coal-bed methane recovery and similar, then CO₂ is used as injection fluid;
- conversion into valuable products;
- mineral carbonation;

CO₂ with a high purity is directly used in food and drink industry for carbonation, it is used in preservative production, as packing gas and solvent for flavors extraction and in decaffeination process. Also, CO₂ can be used in medical application or for drugs production (Cuellar-Franca and Azapagic, 2015).

In enhanced oil recovery (EOR) and enhance coal-bed methane (ECBM) CO₂ is used to take crude oil from an oil field or natural gas from coal deposit respectively. Enhance coal-bed methane actually is not yet developed, while EOR is widely used in USA in addition to recovery gas from natural reservoirs (Metz et al., 2005). CO₂ can be used also in enhanced shale gas recovery (ESGR), enhanced gas recovery (EGR) and enhanced material recovery (EMR). In this contest, CO₂ is used as injection agent due to a low cost and availability.

CO₂ can be used for conversion into chemicals and fuels, as in figure 5 where a detailed roadmap is suggested (Ampelli et al., 2015). It is possible to see how many products can be obtained as urea, polymers (polyurethane), methanol, syngas, dimethyl ether, algae, etc. even if actually most of them are at demonstration level and only in the future are commercially available.

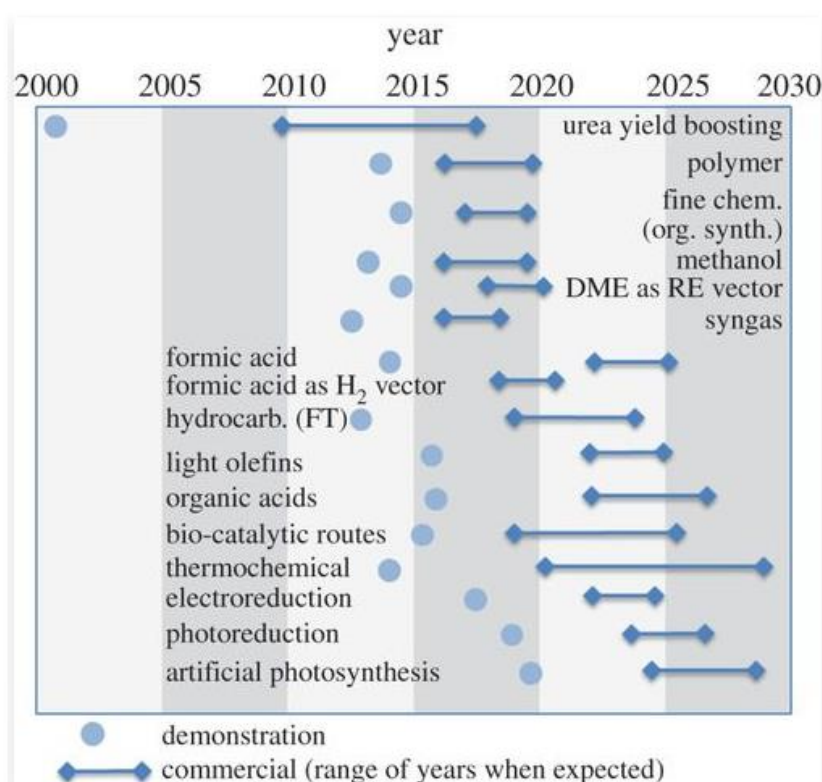


Figure 5 Road map for the commercialization of CO₂ utilization, showing if it is at demonstration or commercial scale (Ampelli et al., 2015).

A detailed analysis regarding possible fuels that could be produced from CO₂ is shown in figure 6: formic acid, ethanol, methanol, methane, dimethyl ether, syngas, hydrocarbons and hydrogen are obtained with the respective reactions.

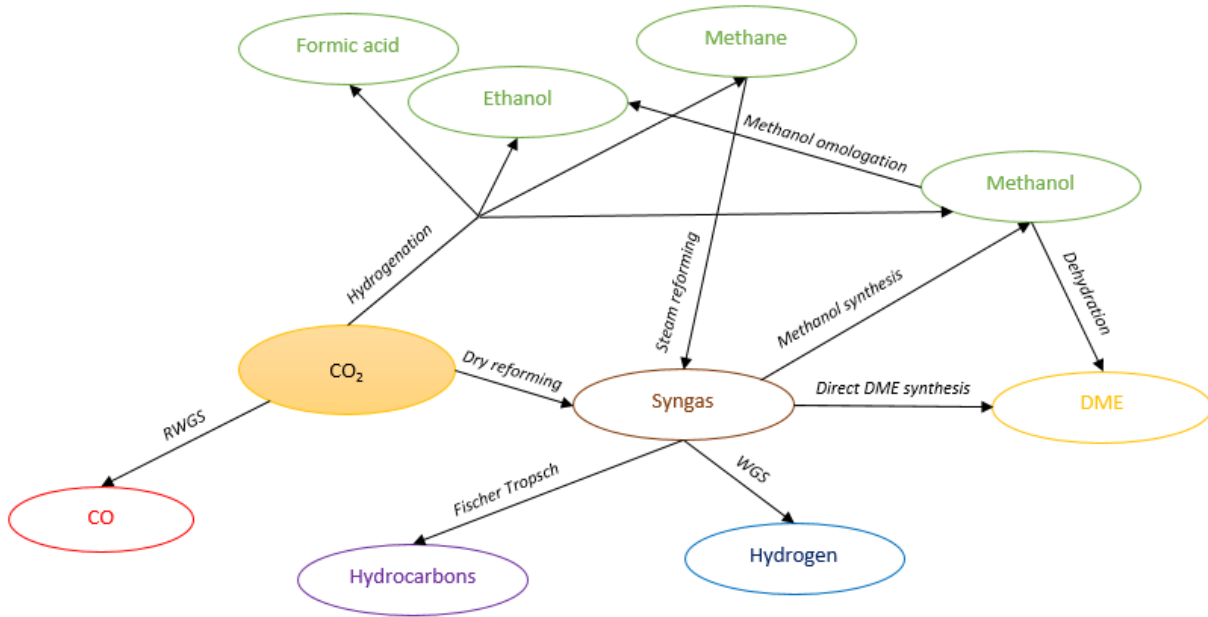


Figure 6 Different routes for CO₂ utilization: products that can be produced by CO₂ and respective reactions (Leonzio, 2018)

In mineral carbonation, CO₂ reacts with a metal oxide such as magnesium or calcium to produce carbonates. For example, steel slugs obtained by the extraction of alumina from bauxite are sources of metal oxides. However, actually, this route is not used at large scale and high costs are required. Related to mineralization, is the production of concrete, in particular concrete curing and concrete by red mud using CO₂ (Patricio et al., 2017).

A summary of different CO₂ utilization options is shown in figure 7, considering for each option potential application, economic aspects, energetic consumptions, the amount of required CO₂, the time of sequestration and environmental impact.

	already industrial			short term		medium term		long term				
	EOR	industrial use	organic synthesis	hydrogenation	algae-open p.	reforming HC	algae-reactor	mineralization	thermochem.	electroreduct.	photoelectrochem.	biocatal.
potential development	4	4	4	3	3	2	2	1	1	1	1	1
economic perspectives	4	4	3	3	3	not known	2	1	2	not known	not known	not known
external use of energy	3	3	2	2	4	1	4	1	4	2	4	4
potential vol. of CO ₂	2	2	3	4	4	4	4	3	4	4	4	4
time of sequestration	4	1.5	3	2	2	2	2	4	2	2	2	2
other impacts on environment	4	4	3	3	4	1	4	3	3	2	2	3

potential development: 1, more than 10 years → 4, industrial
 external use of energy: 1, difficult to decrease → 4, no need
 time of sequestration: 1, very short → 4, long term
 economic perspectives: 1, difficult to estimate → 4, available industrial data
 potential vol. of CO₂: 1, less than 10 Mton → 4, more than 500 Mton
 other impacts on env.: 1, significant → 4, low (solvents or toxic, metals resources)

Figure 7 Considerations about different CO₂ utilization: potential development, economic perspective, external use of energy, potential volume of CO₂, time of sequestration on other impact on environment (Ampelli et al., 2015)

3.3 CO₂ storage option

CO₂ can be stored into ground or ocean. In the first case, denominated as geological storage, CO₂ is injected into geological formations as depleted oil and gas reservoirs, deep saline aquifers, or for coal bed methane recovery and enhanced oil and gas recovery (they are both utilization and storage) at depths between 800 and 2000 m.

CO₂ is stored in “caprock” layers, that are impermeable trapping CO₂ (mudstones, clays, shales). According to the temperature and pressure of reservoir, CO₂ can be in different phase as gas, liquid or in supercritical conditions (31.1 °C and 73.8 bar) (Song et al., 2012). Deep saline aquifers have a storage capacity between 700-900 Gt CO₂ and can be offshore or onshore. Few information are present regarding coal bed methane recovery (Metz et al., 2005). On the other hand, a good knowledge is present about depleted oil and gas reservoirs. Figure 8 shows different geological storages.

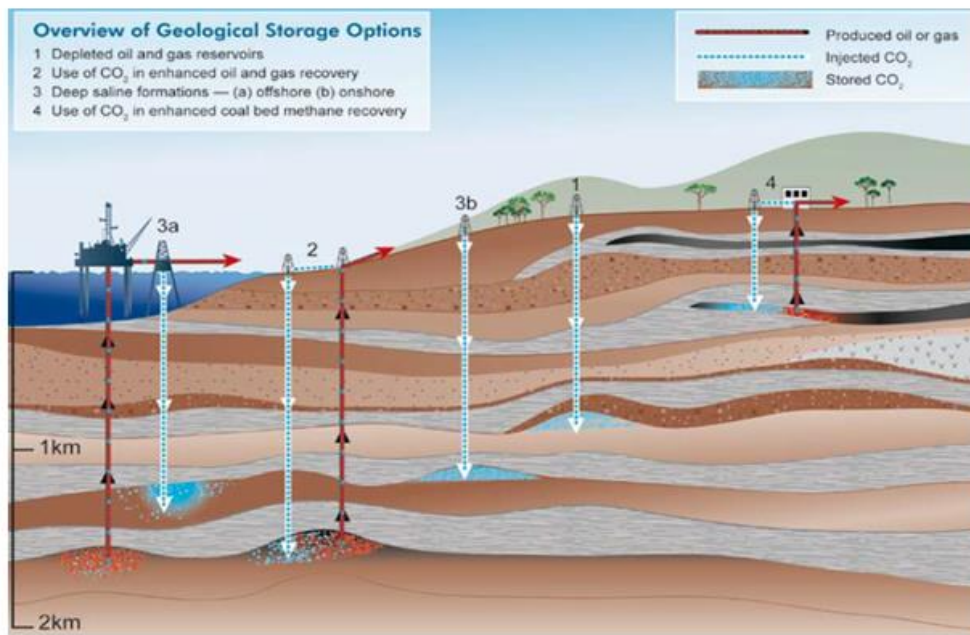


Figure 8 Geological storage of CO₂ in depleted oil and gas reservoirs, for enhanced oil and gas recovery, in deep saline formations (onshore and offshore), for enhanced coal bed methane recovery (Metz et al., 2005)

The geological storage of CO₂ then uses the same technologies used for oil and gas industry and it is not economically feasible for unminable coal beds being at demonstration phase. Ocean can storage a huge amount of CO₂ at great depth, but it is not tested at large scale yet and it is at research phase (Li et al., 2013). As shown in figure 9, two ocean storage options are present: the first consists on dissolving CO₂ into water at a deep below of 1000 meters, by using fixed pipeline or a moving ship; the second consists on putting CO₂ via fixed pipeline or an offshore platform at sea floor, at a deep below of 3000 m, producing a lake due to the higher density than water.

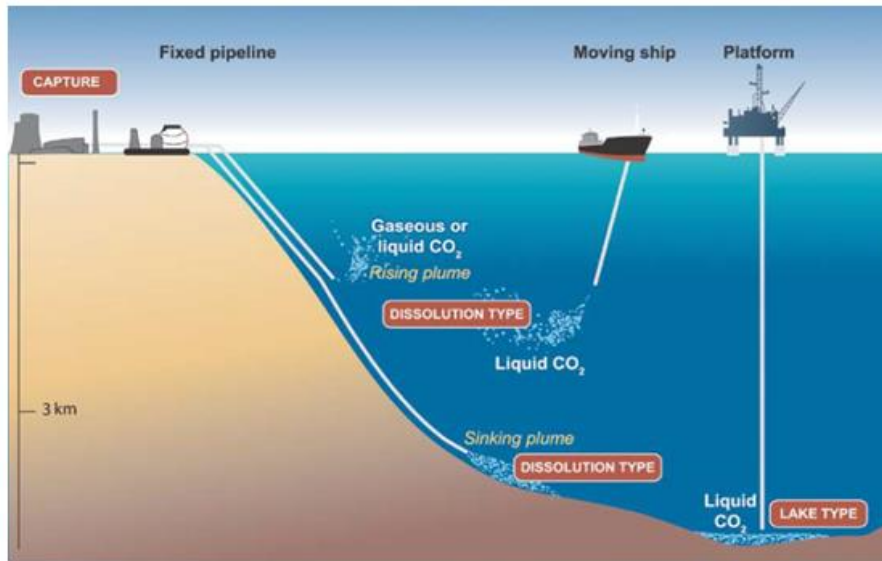


Figure 9 Ocean storage of CO₂ with fixed pipeline (lake type storage) and moving ship (dissolution type storage) (Metz et al., 2005)

CO₂ mineralization described in CO₂ utilization option can be also considered a CO₂ storage option.

4. Design and optimization of carbon capture utilization and storage supply chain

4.1 Methodology for the design

Through the design of carbon capture utilization and storage supply chain the volume of captured CO₂ from flue gases, the volume of utilized or stored CO₂, right sources, capture technologies/materials, utilization and storage sites are selected. Then, different CO₂ emissions, geographic sites, capture technologies, etc. are present in a carbon supply chain. Therefore, as shown in figure 10, carbon capture utilization and storage supply chain design is a multi-scale problem with different solutions at various length- and time-scales (Biegler et al., 2014; Hasan et al., 2014; 2015; Lucia, 2011). Overall costs are influenced by many factors, as materials, processes and supply chain level. At the material scale, materials for capture technologies are selected, considering their physical-chemical properties and disposability. At process scale, capture technologies are selected mainly according to their costs. At supply chain scale, the topology of carbon capture utilization and storage is selected. Carbon capture utilization and storage supply chain is then a complex and multi-scale system with performances depending on different factors.

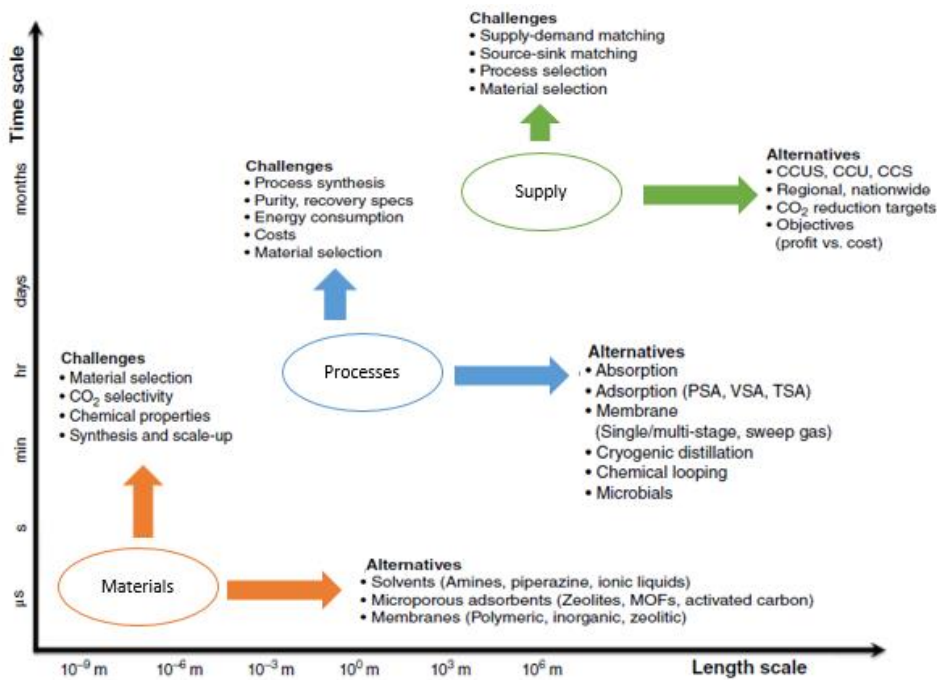


Figure 10 Different scale of carbon capture utilization and storage supply chain design: material, processes and supply chain scales with challenges and alternatives (Hasan, 2017)

According to process systems engineering, two different approaches can be used in the design and optimization of multi-scale carbon capture utilization and storage supply chain at multiple length and time scales: hierarchical and simultaneous, as in figure 11. In hierarchical approach, information flows in only one direction of length scale: from bottom to the top of length scale. Also, decisions are made only at each scale (micro scale for material, meter scale for technology selection, kilometer scale for supply chain topology and optimization), then there is a suboptimal decision at each level that is passed from one scale to another in increasing sequence.

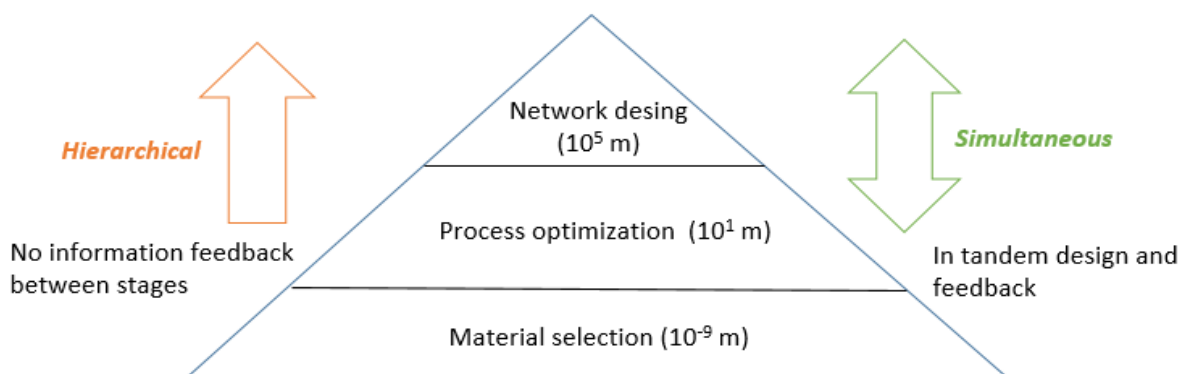


Figure 11 Design pyramid for carbon capture utilization and storage supply chain: comparison between hierarchical (from bottom to top: material selection, process optimization and network design) and simultaneous approaches (tandem design of material selection, process optimization and network design) (Hasan, 2017)

The following steps are identified by Hasan et al. (2015) as in figure 12: (i) materials screening, (ii) process optimization, (iii) process technology selection, (iv) materials screening and process optimization, (v) materials screening and process optimization and technology selection, and (vi) supply chain optimization. In this sequence, information of one step are used for the subsequent step that is in at first in micro-scale, then in meter-scale and at the end in kilometer scale.

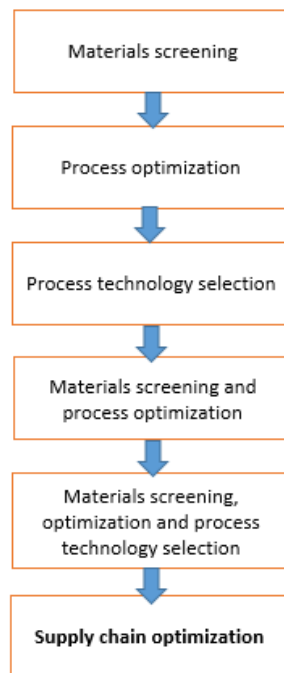


Figure 12 A hierarchical framework for carbon capture utilization and storage supply chain design: at first materials screening, followed by process optimization, process technology selection, materials screening and process optimization, materials screening optimization and process technology, supply chain optimization (Hasan et al., 2015)

In material screening step, the most appropriate capture material is selected according to its physical and chemical properties (First et al., 2011; 2013). In process optimization step, the best conditions are selected for the capture technology/material, chosen in the previous stage. These operating conditions are found in order to reduce capture and compression total costs also ensuring the specified purity and recovery. In process technology selection step, the capture technology is chosen by minimizing total costs. Generally, each capture technology can capture at least 90% of CO₂ that is compressed at 150 bar for utilization or storage. In material screening and process optimization step, the selection of capture materials and the optimization process that reduces total costs are developed in tandem, as in simultaneous way. In fact, carbon capture costs are influenced by CO₂ composition and flow rate and then, the choice found in the previous steps can be changed. It is important to optimize the system and to choose the best material simultaneously. In material screening, optimization and process technology selection step, different materials, processes and technologies are considered and optimized: the best technology is selected among other alternatives. The investment and operating costs of different capture technologies/materials are expressed by the relation of Hasan et al. (2012

a,b; 2014), as function of carbon composition, flue gas, and fixed parameters for each material/ technology. It is important to underline that no unique solution is present for the optimal solution of the process. Carbon flow rate and composition in the feed are important parameters in this context. Also, it is necessary to consider all configuration topology: all combination between CO₂ sources and capture technology must to be considered. The equation costs for carbon capture, expressed in following chapter, are an important link between process scale modeling and multiscale analysis of carbon capture utilization and storage supply chain network. In supply chain optimization step, the overall cost of supply chain is minimized. Total costs include CO₂ capture and compression costs, CO₂ transportation costs, CO₂ storage costs and CO₂ utilization costs (as the production costs of produced chemical compounds). In other cases, other economic parameters as net presentvalue, PayBack period, etc. can be considered for the optimization. Also, the objective function can describe an environmental parameter in order to maximize CO₂ reduction.

On the other hand, in simultaneous approach the design of supply chain is developed in tandem: the selection of material, process and supply chain is done in tandem, during the design of overall carbon capture utilization and storage supply chain. For this class of design, mixed integer linear programming (MILP) models are carried out and they are able to select the best supply chain among multiple capture materials/technologies, CO₂ sources, utilization sites and storage sites. This methodology is developed because it is important to evaluate the overall supply chain for optimization problem; in fact, it is possible to have an optimum capture cost that is lower than that related to CO₂ capture alone. To this purpose, the connection between CO₂ source, CO₂ utilization and CO₂ storage sites is critical. Hasan et al. (2014) suggest at first the simultaneous design of carbon capture utilization and storage supply chain for Texas, where CO₂ is used to enhanced oil recovery.

Considering the two methods, however, the design of carbon capture utilization and storage supply chain, as other supply chain, should be developed considering critical interdependent factors such as influencers, design decisions, building blocks as reported in figure 13 (Melnyk et al., 2013). Political environment, business models and the supply chain life cycle can be considered as influencers. These factors influence the supply chain in a significative way. Social aspects and the physical/structural design of carbon capture utilization and storage supply chain are related to design decisions. Building blocks are related to aspects that are necessary to realize carbon capture utilization and storage supply chain.

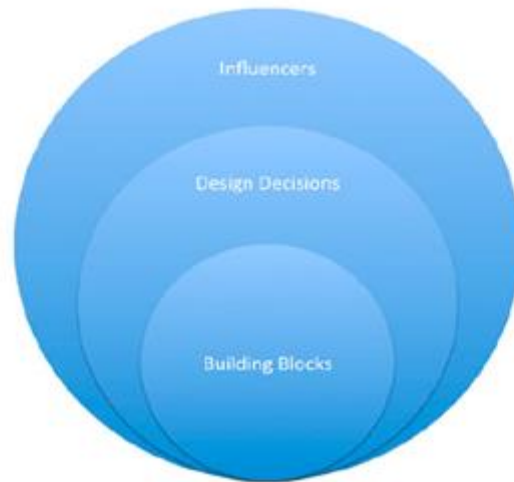


Figure 13 Factors influencing a CCUS supply chain design: building blocks, design decisions and influencers (Melnyk et al., 2013)

All these considerations, suggest as the design of carbon capture utilization and storage supply chain is critical, strategic and complex. For this reason, Fine et al. (1998) prefer the term “architecture” to design.

For the future, Melnyk et al. (2013) suggest some research area about the design of carbon capture utilization and storage supply chain: the dynamics design, the consideration of different outcomes, the stage of life cycle. It is important to consider not a static carbon capture utilization and storage supply chain but a dynamic one. Researchers should find and analyze factors that influence the dynamic process of supply chain. Melnyk et al. (2013), in their studies suggest that CCUS supply chain is increasingly dynamic and ‘extreme’. For the second point, a carbon capture utilization and storage supply chain can be design putting different objective in the outcomes as increasing responsiveness, driving innovation or improving sustainability. The designed supply chain obtained by minimizing total costs should be not appropriate for these suggested objectives. The study of supply chain at different outcomes is required and few works are present in literature. For the last point, the presence of supply chain life is recognized by several work (Van Wassenhove, 2006; Pettit and Beresford, 2005; Kovács and Spens, 2007), so it is possible analyzed and manage the transaction of one stage to next. As an important aspect a life cycle assessment analysis can be developed to verify that carbon dioxide loop is closed.

4.2 Development of optimization tool

To develop the design of carbon capture utilization and storage supply chain a tool for the optimization should be developed. Generally, A.I.M.M.S. (Advanced Interactive Multidimensional Modeling System) and G.A.M.S. (General Algebraic Modeling System) software are used. At first it is necessary to define a problem statement with:

- *assumptions*, that should be the following: capture plants are located at carbon dioxide sources, one to one coupling of source and capture node, carbon dioxide is transported via pipeline, the network is in

stationary or dynamic conditions, the production of chemical compounds is constant over time, the technology used to produce the selected chemical compounds, etc.;

- *given information*, for example, about carbon dioxide source sites, carbon dioxide capture and compression technologies/materials, utilization and storage sites, the national demand of chemical produced compounds, distances between different considered sites, etc.;
- *conditions that must to be respected*, for example, the efficiency of carbon dioxide capture technologies, the maximum storage capacity of storage sites, the target of CO₂ reduction, etc.;
- *what should be decided* as CO₂ source, utilization and storage sites, then the topology, the volume of captured CO₂ that should be sent to utilization or storage, the amount of chemical compounds that are produced, the capture technology that should be used for each source, the best way to transport CO₂;
- *objective function*, for example total costs that should be minimized or CO₂ capture that should be maximize (other objective functions relating to economic aspect and environmental analysis can be also considered).

After that, it is necessary to define:

- *set* with a defined index for CO₂ sources, utilization and storage sites, capture technologies, etc.;
- *parameters* to define particular values required by the model, as the minimum target of CO₂ reduction, maximum storage capacity, distance between different sites, CO₂ emissions for each source, flue gas flow rate and its CO₂ compositions, etc.;
- *variables*, binary (to select the combination between CO₂ source, capture technology/material and storage or utilization sites) or continues (to define the amount of CO₂ that is sent to utilization or storage, the amount of produced chemical compounds, etc.);
- *constraints* about the national demand of chemical produced compounds, the capacity of CO₂ storage sites, the selection of CO₂ capture technology/material, capture technology efficiency, the slitting of CO₂ sources, etc.
- *equations* for carbon dioxide capture and compression costs, transportation costs, storage costs, the production costs of different produced compounds in order to define the objective function.

Following these indications, a mathematical model of carbon capture utilization and storage supply chain should be developed and optimized due to the use of suggested software.

5. Cost analysis

Generally, the total costs of carbon capture utilization and storage supply chain includes total carbon capture and compression costs, total transportation costs, total storage costs and the production costs of considered and produced chemical compounds. The evaluation of total carbon capture and compression costs is suggested by Hasan et al. (2014) according to the following relation (see Eq. 3):

$$CC = CDC + CIC + COC \quad (3)$$

where CC are total capture and compression costs, CDC are de-hydrogenation costs, CIC are investment costs while COC are operating costs. The de-hydrogenation is carried out by using tri-ethylene glycol absorption with a cost of 9.28 € per ton of CO₂ (including capital and investment costs) (Kalayanarengan Ravi et al., 2017). Investment and operating costs (\$/year) are a function of CO₂ composition and flue gas flow are, respectively according to the following relations (see Eq. 4-5):

$$CIC = \alpha_i + (\beta_i \cdot x_{CO_2}^{n_i} + \gamma_i) \cdot F^{m_i} \quad (4)$$

$$COC = \alpha_o + (\beta_o \cdot x_{CO_2,i}^{n_o} + \gamma_o) \cdot F^{m_o} \quad (5)$$

where α_i , α_o , β_i , β_o , γ_i , γ_o , n_i , n_o , m_i , m_o are fixed parameters depending on used technology and material, as in table 3 (Zhang et al., 2018), x_{CO_2} is CO₂ composition in flue gas and F is flue gas flow rate in mol/s. A trend of these costs as a function of carbon dioxide composition and flue gas flow rate for different technologies as absorption, pressure swing adsorption (PSA), membrane and vacuum swing adsorption (VSA) and materials as monoethanolamine (MEA), piperazine (PZ), AHT zeolite, MVY zeolite, 13X zeolite, FSC fixed site carried, POE1 polymer and PO2 polymer is reported in figure 14 (Zhang et al., 2018).

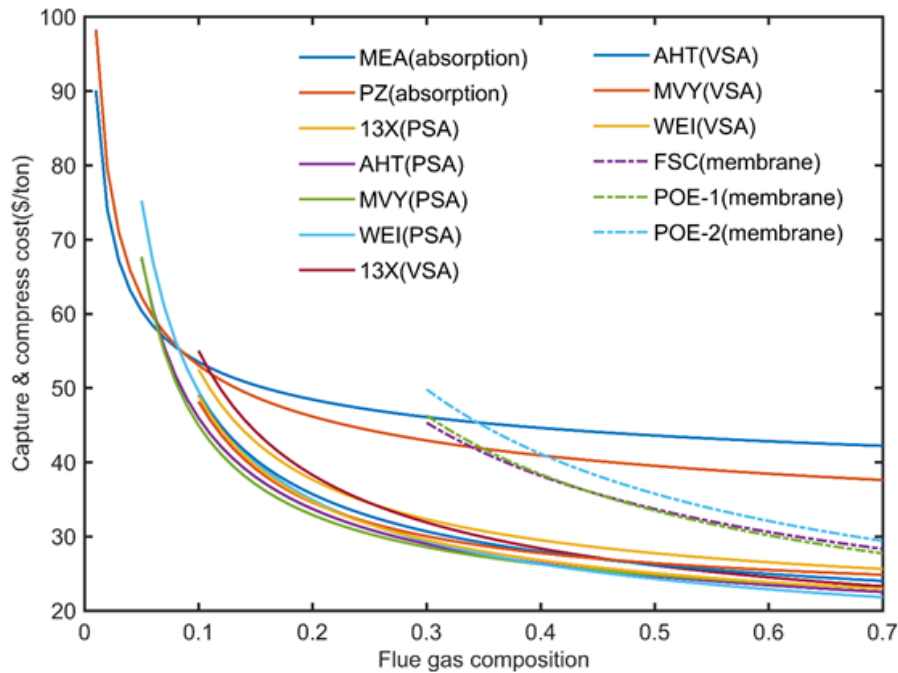


Figure 14 CO₂ capture and compression costs for different capture technologies/materials with flue gas flow rate of 10 kmol/s (MEA=monoethanolamine, PZ=piperazine, PSA=pressure swing adsorption, VSA=vacuum swing adsorption; 13X, AHT, MVY, WEI are the materials for PSA and VSA system; FSC, POE-1, POE-2 are the materials for membrane system) (Zhang et al., 2018, reproduced with permission number 4563301123383).

Table 3 Parameters of CO₂ capture and compression cost equations (investment and operation costs) (Zhang et al., 2018)

Process	Material	α	β	γ	n	m
Investment cost (\$/year)						
Absorption	Monoethanolamine	7719	67871	901.000	0.660	0.800
Absorption	Piperazine	0	59956	226.932	0.566	0.800
Pressure swing adsorption	13X	220462	26720	895.262	0.508	0.804
Pressure swing adsorption	AHT	214535	17833	4607.297	0.744	0.813
Pressure swing adsorption	MVY	162447	22468	6408.791	1.000	0.797
Pressure swing adsorption	WEI	142320	19332	6076.357	0.610	0.779
Vacuum swing adsorption	13X	91060	23096	7688.408	0.470	0.763
Vacuum swing adsorption	AHT	113969	24939	2659.383	0.468	0.786
Vacuum swing adsorption	MVY	119259	21652	8101.014	1.000	0.795
Vacuum swing adsorption	WEI	180953	15644	7751.257	0.874	0.802
Membrane	FSC PVAm	177500	16505	18912.000	0.880	0.770
Membrane	POE-1	568	19151	29669.274	0.778	0.735
Membrane	POE-2	53960	19967	28462.417	0.656	0.744
Operating cost (\$/year)						
Absorption	Monoethanolamine	0	24088	0	1.000	1.000
Absorption	Piperazine	0	26825	0	0.945	0.966
Pressure swing adsorption	13X	0	11352	3115.833	1.000	0.974
Pressure swing adsorption	AHT	0	7040	983.893	0.626	1.000
Pressure swing adsorption	MVY	0	7265	1328.677	0.756	1.000
Pressure swing adsorption	WEI	0	6398	1257.721	0.554	0.991
Vacuum swing adsorption	13X	0	8167	1580.419	0.590	0.985
Vacuum swing adsorption	AHT	0	8545	1725.654	0.842	0.996
Vacuum swing adsorption	MVY	0	9117	1839.193	1.000	1.000
Vacuum swing adsorption	WEI	0	7378	1493.500	0.753	1.000
Membrane	FSC PVAm	0	11619	0	0.210	1.000
Membrane	POE-1	0	12798	0	0.134	0.980
Membrane	POE-2	0	13556	0	0.135	0.984

For ionic liquid absorption, different correlations (\$/year) for investment and operative costs are respectively used, as the following equations (see Eq. 6-7) (Nguyen et al. 2017):

$$CIC = (\alpha_i \cdot F + \beta_i) \cdot x_{CO_2} + \gamma_i \cdot F^{m_i} \quad (6)$$

$$COC = (\alpha_o \cdot F + \beta_o) \cdot x_{CO_2,i} + \gamma_o F^{m_o} \quad (7)$$

where α_i , α_o , β_i , β_o , γ_i , γ_o , m_o , m_i are fixed parameters as in table 4 (considering 1-butyl-3-methylimidazolium acetate [bmim][Ac] ionic liquid), x_{CO_2} is carbon dioxide composition in flue gas, F is feed flow in mol/s.

Table 4 Parameters of CO₂ capture and compression cost equations with ionic liquid ([bmim][Ac]) absorption (investment and operation costs) (Nguyen et al. 2017)

Process	Material	α	β	γ	m
Investment costs (\$/year)					
Absorption	Ionic liquid	7.712	2654014	33546.87	0.67
Operating costs (\$/year)					
Absorption	Ionic liquid	33172.59	897224.4	187421.2	0.65

Total costs for carbon dioxide transportation in pipeline is provided by Sarpa et al. (2011) and Knoope et al. (2013): it is composed by investment and operating costs (€/year) as the following relation (See Eq. 8):

$$TC = TIC + TOC \quad (8)$$

where investment TIC (€/year) and operating costs TOC (€/year) are respectively (see Eq. 9 and 10):

$$TIC = (\alpha_t \cdot F_{CO_2} + \beta_t) \cdot F_T \cdot (D + F_c) \quad (9)$$

$$TOC = 4\% \cdot TIC \quad (10)$$

in the relations α_t is 0.019 and β_t is 0.533, D is distance between the considered sites and it is based on latitude and longitude (Kalayanarengan Ravi et al., 2017), F_T is a terrestrial factor (1.5 for mountain place, 2 for offshore, 1.4 for populated place, 1 for remote place) and generally an average value of 1.2 is considered (Broek et al., 2010), F_c is added to the distance to consider additional paths related to process (Dahowski et al., 2004), F_{CO_2} is the amount of carbon dioxide that is transported. Among other way of CO₂ transportation, pipeline is the favorite choice, being the most mature solution. Also, pipeline ensures the transportation of large volume of CO₂ at low costs. (Kalayanarengan Ravi et al., 2017).

Total carbon dioxide storage costs (CS) comprise investment costs (SIC) and operating costs (SOC), as in the following relation (Ochoa Bique, 2018) (see Eq. 11):

$$CS = SIC + SOC \quad (11)$$

where investment costs (€/year) are calculated as (Hendriks, 1994) (see Eq. 12):

$$SIC = (m \cdot d_{well} + b) \cdot N_{well}^{build} \quad (12)$$

where m and b are parameters respectively corresponding to $1.53 \cdot 10^6$ and $1.23 \cdot 10^6$ (Ochoa Bique, 2018), d_{well} is the depth of well storage and N_{well}^{build} is the number of wells built per year (Hasan et al., 2014) (see Eq. 13):

$$N_{well}^{build} = \frac{F_{s,CO_2}}{IC} \quad (13)$$

that is a function of stored carbon dioxide F_{s,CO_2} and injection capacity per well IC. Operating costs (€/year) are 4% of investment costs (see Eq. 14):

$$SOC = 4\% \cdot SIC \quad (14)$$

The production costs of each chemical compound can be found in literature.

6. Literature works about carbon capture utilization and storage supply chain

Carbon capture utilization and storage supply chain can be considered as a long-term CO₂ containment and despite its important role for the environment not many works are reported in literature about it.

O'Brien et al. (2017) suggest that carbon capture utilization and storage supply chains have a decisive role for the economic development. To this purpose can be useful to have a methodology to evaluate large scale capture options, to consider different CO₂ utilization options that are relevant for local economy and to establish a public-private partnership incentivizing carbon supply chains. Different models for the State of Illinois are presented. The work also suggests the actions required for the workforce development throughout the carbon supply chain.

Suggestions, recommendations and policies for the development of carbon capture utilization and storage supply chains in China as an important and strategic instrument to reduce CO₂ emissions and to ensure energy security can be found in the work of Zhang et al. (2013).

Considerations about carbon capture utilization and storage supply chain are reported by Floudas and Nye (2015) reducing up to 50% the total stationary CO₂ emissions. The authors underline as total costs vary with CO₂ capture materials/technologies, selected CO₂ sources, utilization and storage sites, CO₂ transportation, the amount of stored CO₂. Regarding this aspect, to understand the economy of CCUS supply chain, each component should be evaluated separately or integrated in all systems. Vikara et al. (2017) present tools, models, resources to this purpose.

Han and Lee (2012) propose a multi-period stochastic model for a carbon capture utilization and storage system in Korea to manage CO₂ emissions from 2011 to 2030. The model is a MILP and the uncertainty of price, costs and CO₂ emissions are considered. Results show that considering only the uncertainty of CO₂ emissions good results are obtained as those obtained considering all uncertainties. The work is subsequently improved in Han and Lee (2013) considering different aspects as techno-economic-, environmental- and risk.

The selection of right technology and respective CO₂ source is critical to develop a profitable carbon capture utilization and storage supply chain, as well as the selection of technologies and materials (Hasan et al., 2013a). Mohd Rudin et al. (2017) develop a new strategy suggesting the reduction of emissions from early stages. A methodology of carbon reducing, capture, utilization and storage known as CARCUS is proposed. Considering the reduction of CO₂ in the early stage, capture costs can be reduced because emissions are reduced earlier and smaller equipments for capture can be utilized. A mixed integer linear programming model is obtained and applied for Malaysia region. The best technologies that should be used are suggested.

CO₂ enhanced oil recovery is considered as a good option to use CO₂, then several carbon capture utilization and storage supply chains with CO₂ enhanced oil recovery are analyzed in literature. This solution can rise oil

recovery by 15% of original oil in place (OOIP) (National Energy Technology and Laboratory, 2010a). Kuuskraa et al. (2013), analyzing CO₂-EOR technology in the residual oil field in Texas, find that revenues obtained by the selling of captured CO₂ can hurry the application of this kind of carbon capture utilization and storage supply chain at a wide scale. CO₂ is tight stored: it is evident that CO₂ enhanced oil recovery will have an important role in worldwide carbon management strategy and in the related supply chain. A benefit-risk analysis of these systems for two stakeholders (power plant owner and oil field owner) is carried out by Zhu and Liu (2015): oil field has the main position in CO₂ utilization while contract designs have to get better the position of power plants. A model for carbon capture utilization and storage supply chains should be developed in order to gain insights for planning CO₂ utilization network.

Hasan et al. (2013b) optimize with a mixed integer programming (MIP) model a carbon capture utilization and storage supply chain for national and regional level in the United States. Total expenditure is minimized with a fixed CO₂ reduction target. The model is able to select source plants, capture systems (absorption, membrane, pressure swing adsorption and vacuum swing adsorption), capture materials (2 solvents, 4 zeolites, and 3 membranes), locations of utilization (oil and gas reservoirs) and storage sites. Results show that decreasing 50% of CO₂ emissions the cost is lower than 30\$ per ton of CO₂, an optimal value. It is underlined also as the choice of capture technology/material is crucial to be considered inside large-scale carbon capture utilization and storage design.

Hasan et al. (2014) suggest a carbon capture utilization and storage supply chain model that can be applied at national, regional and statewide level in the United State where CO₂ is used to enhanced oil recovery. It is the first model that considers the costs of CO₂ capture, compression, transportation, utilization and sequestration and at the same time choices CO₂ sources, capture materials, capture technologies, utilization and sequestration sites minimizing total costs. The authors, also, present several correlations to evaluate the capture costs of different capture systems, as a function of gas composition and flow rate. The authors find that the system is able to decrease 50–80% of CO₂ emissions with a total costs between \$58.1–106.6 billion, generating \$3.4–3.6 billion of revenues. The specific cost of carbon capture utilization and storage supply chain is \$35.63–43.44 per ton of captured CO₂.

Hasan et al. (2015) develop a strategy for the optimal design of supply chain minimizing total costs and reducing CO₂ emissions in the United States. In utilization section, CO₂ is used to recover oil. The overall framework includes the following steps: materials screening, process optimization, process technology selection, materials screening and process optimization, materials screening and process optimization and technology selection, and supply chain optimization. Information are passed by one previous step to another following step. The system is described by a mixed inter programming model. 444 sources for CO₂ capture, 76 oil and gas reservoirs for CO₂ utilization, 151 saline formations and 6 unmineable coalbeds for CO₂ sequestration are present in the analyzed system. For the capture, 13 technology-material pairs (monoethanolamine and piperazine for absorption; FSCPVAm, POE1 and POE2 for membrane; 13X, AHT, MVY and WEI for pressure swing adsorption; 13X, AHT, MVY and WEI for vacuum swing adsorption) are

considered. Authors suggest that the optimization of supply chain is a combinatorial problem where the optimal solutions are increasing with storage, utilization and source sites. The system is optimized minimizing total costs. 50% of CO₂ emission are reduced at \$35.63 per ton of captured CO₂. Results show that the cost of supply chain increases with minimum CO₂ reduction. In fact, reducing 60% and 80% CO₂, the costs of supply chain are equal to 36.93\$ and 43.44\$ respectively. In this analysis, the costs of dehydration, capture and compression have a higher influence on total costs, due to the high value these costs represent an impediment for the development of these technologies.

Tapia et al. (2016a) present a mixed integer linear programming model with discrete time optimization approach for carbon capture utilization and storage supply chain with CO₂ enhanced oil recovery as utilization. In the model, respect to other literature works, CO₂ allocation and scheduling issues are considered for EOR operation. Only one source is considered while more different reservoirs are present. In addition, two case studies are evaluated: one case study considers a fixed amount of CO₂, while in another case study CO₂ flow rate is varying during the considered period. The authors suggest to consider in future works several uncertainties as: oil price, reservoirs oil capacity and oil yield through Monte Carlo simulation or sensitivity analysis.

More sources are considered in Tapia et al. (2016b). Also, in this work a carbon capture utilization and storage supply chain with CO₂ enhanced oil recovery is considered, but compared to other literature works, three important considerations for the development of these kind of systems are underlined: scheduling of carbon capture utilization and storage operation, allocation of CO₂ supply for enhanced oil recovery operation and matching CO₂ source and geological sinks. Two mixed integer linear programming models are carried out: one for the design of an enhanced oil recovery system by using strip packing analogy (Castro and Grossmann, 2012) and another for source–sink matching in carbon capture storage systems. These two models are presented and described using a case study. Results for the first model show a direct proportionality between the amount of CO₂ in flue gas and profit. In the second model, results show that there is a no linear proportionality between the amount of captured and stored CO₂ and injectivity limits, but the a direct proportionality is present between the amount of capture and stored CO₂ and the total available capacities.

Middleton et al. (2015) develop an interesting carbon capture utilization and storage supply chain: ethylene plants are CO₂ sources and CO₂ is used to recover oil in the US Gulf Coast region and in near regions. This integration can increase the production cost in a lower measure than the case of CO₂ captured by fossil power plant: the increase of ethylene price ranges between 1-15%, while the increase of electricity price ranges between 50-100% with CO₂ captured by fossil fuel power plant. The network can reduce 50 MtCO₂/yr emissions producing 200 million bbl/yr of oil. Then system is economically feasible then can increase its social acceptance as a climate change mitigation technology.

Other mathematical models for carbon capture utilization and storage supply chain with enhanced oil recovery as CO₂ utilization are developed by Rahmawati et al. (2015) improving the work of Hassiba et al. (2016) by considering heat integration in the system.

Klokk et al. (2010) suggest a mathematical model for carbon capture utilization and storage supply chain with CO₂ enhanced oil recovery for Norwegian region with 14 oil fields, two aquifers and five CO₂ sources. Considering a fixed amount of CO₂ emissions, the system is optimized maximizing net present value, then selecting the best oil fields and geological storages. A parametric study is developed considering the most important factors. Results also suggest that the use of CO₂ for the analyzed scope can determine a profitable system in economic sense, even if expensive infrastructure is used.

Romanenko (2014) develop a system dynamic model for a carbon capture utilization and storage supply chain with enhanced oil recovery as CO₂ utilization, analyzing the influence of different policy designs. In this context, the Carbon Tax Credit policy determines several advantages on the system allowing its self-sustaining growth. This policy is defined as reinforcing mechanism.

Sun et al. (2017) analyze different carbon capture utilization and storage supply chain with CO₂ enhanced water recovery (CO₂-EWR), CO₂ enhanced oil recovery (CO₂-EOR) and CO₂ enhanced coalbed methane recovery (CO₂-ECBM) in China. Results show that in a short-period CO₂ enhanced oil recovery is the most favorable carbon capture utilization and storage technology while in a long term CO₂ enhanced water recovery is the best solution because saline aquifer has the largest storage capacity. The authors underline as for this kind of technology financial and political supports are required for their application in order to provide a great contribution to low carbon economy not only for China but for all the world.

A more detailed economic analysis for CO₂ enhanced oil recovery system is developed by Kwak and Kim (2017): net present value is optimized setting some constrain on dynamic CO₂ sources. A sensitivity analysis is developed in order to analyze the influence of oil and CO₂ price on total costs. Also, situations with a higher and lower amount of CO₂ compared to base case are evaluated. It is found that reducing CO₂ provision of 20%, overall oil production is decreased of 33.7%, otherwise increasing the CO₂ supply chain rate of 20%, overall oil production is increased of 5.6%.

Wu et al. (2015) provide an optimized model for carbon capture utilization and storage supply chain with enhanced oil recovery as CO₂ utilization under uncertainty about technical, economic and political aspects applied for China case. Results suggest that carbon price can have a political influence for the development of these technologies. Without a high cost of CO₂, it is difficult to realize this system in a short time.

Other utilization cases can be considered inside carbon capture utilization and storage supply chain. Yue and You (2015) develop a multi-scale multi-period mixed-integer nonlinear programming (MINLP) model for carbon capture utilization and storage supply chain in Texas where captured CO₂ is used by algae converting CO₂ into lipids, that are converted into renewable biofuels. Through Life Cycle Optimization (LCO) methodology the system is optimized minimizing CO₂ reduction costs and maximizing the amount of CO₂ avoided. A good reduction of CO₂ is achieved and equal to 80% producing 187 Mgal/year of renewable diesel. However, only the utilization of captured CO₂ is not able to obtain 80% of CO₂ reduction.

Ochoa Bique et al. (2018) study a carbon capture utilization and storage supply chain in Germany considering methanol production in the utilization site. CO₂ is captured from power plants while hydrogen for the reaction producing methanol is obtained by water electrolysis. The integration of CO₂ and H₂ supply chain is then evident. Results show that the system can be profitable if renewable hydrogen is distributed without paying.

Leonzio et al. (2018) suggest a methodology for the optimal design of carbon capture utilization and storage supply chain in Germany: the captured CO₂ is used to produce methanol via methane dry reforming. The supply chain is optimized minimizing total costs, using Advanced Interactive Multidimensional Modeling System (AIMMS) software. Results show that the system is economic feasible only considering economic incentives. Also, Germany will have, in the next future, an important role in world methanol market.

Other literature works pay attention on other aspects of carbon capture utilization and storage supply chain. Sun and Chen (2017) present a source-sink matching multi-stage programming model to design CO₂ pipeline layout using General Algebraic Modeling System (GAMS) software. It is, in particular, a mixed integer programming model minimizing net present value. Carbon capture utilization and storage supply chain is located in China and in particular in Jing-Jin-Ji region (Bohai Sea area). Results show that to transport 1620 Mt CO₂ during 2020-2050 period, 2200 km of pipeline are required with an investment cost of \$1.6 billion. The developed model is able to determine CO₂ transportation structure (number and length of pipeline), location and amount of captured CO₂. The authors suggest that in future works it is necessary to integrate an energy system optimization model to study a more realistic system.

From these literature works it is evident that mathematical programming is used in the planning of large-scale carbon capture utilization and storage supply chain, providing a flexible and high resolution. This is very important, because planning methods and tools are related to political decisions for carbon capture utilization and storage (Bryngelsson and Hansson, 2009; Tapia et al., 2018). Mathematical techniques are classified according to the method used for the design, in energy models, pipeline infrastructure design and source-sink matching (SSM). First models are related to the energy balance of carbon capture utilization and storage systems, considering power losses during capture phase (Tapia et al., 2018). Pipeline infrastructure design model is related to the economics of construction and management for CO₂ distribution networks. This aspect is very important, because the transportation cost of captured CO₂ contributes with 10% to total cost in carbon capture utilization and storage supply chain (Rubin et al., 2015). A good design of carbon capture utilization and storage pipeline network avoids the reconstruction or expansion after the realization that require a great investment. As also shown previously, single-stage and multi-stage models are carried out for carbon capture utilization and storage pipeline networks in China (Sun and Chen, 2015; 2017): pipeline network is optimized minimizing CO₂ transportation costs. Source-sink matching model is related to find CO₂ sources that should be matched with different utilization or storage options, without considering pipeline networks. In this model, source and sink are matched in terms of quality and continuity by optimizing (Tapia et al., 2016a; 2016b).

However, it is necessary to keep in mind and put more attention on the uncertainties of these models deriving by decades-long time horizons, as climatic and economic conditions, geophysical properties of storage

reservoirs and environmental policies. Uncertainties are due to the dynamic nature of supply chain as also reported by Ozkir and Basligil (2013). For this reason, in the future, more mathematical models considering uncertainty should be developed. A similar work is also developed already and in a more general way for green supply chain network by Rahmani and Mahoodian (2017) considering the uncertainty risk of some parameters (demand and facilities). These indicated risks are suggested by Hatefi and Jolai (2014). Then, these considerations can be more extended to carbon capture utilization and storage supply chains in the next researches in order to analyze a more realistic problem.

7. Conclusions

In this analysis an overview about carbon capture utilization and storage supply chain is proposed. In these systems CO₂ is captured, transported and sent to utilization and/or storage sites and it is the only system that can allow to achieve the objectives of environmental policy established in the Paris Climate Change Agreement. Several plants are present in the world, actually and others should be realized. For the important role of them, mathematical modellings with respective equations should be developed for optimization and design. Generally, a hierarchical and simultaneous methods can be used. A strategy for the modeling and optimization of carbon capture utilization and storage supply chain is also suggested minimizing total costs. The work presents, in addition, an overview about CO₂ capture technology, CO₂ storage and CO₂ utilization. CO₂ can be captured by chemical/physical absorption, adsorption, membrane, chemical looping combustion, cryogenic and hybrid technologies. Advantages and disadvantages are reported. CO₂ can be stored in geological storage or in ocean. CO₂ can be used directly, as injection fluid for oil or gas recovery, to produce different chemical compounds and fuels or for mineral carbonation. In literature many works are present about the modeling of carbon capture utilization and storage supply chains. However more studies should be done considering dynamic systems with uncertainties.

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