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Advances in CO_2 utilization technology: A patent landscape review

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ABSTRACT

There is rising concern on the increasing trend of global warming due to anthropogenic CO_2 emission which steers progress of carbon capture and storage (CCS) projects worldwide. However, due to high cost and uncertainties in long term geological storage, there is a growing inclination to include utilization, which re-use the CO_2, hence carbon capture utilization and storage (CCUS). Additionally, it is expected to generate income to offset the initial costs. This study methodically review patents on CO_2 utilization technologies for CCUS application published between year 1980–2017. It was conducted using the Derwent Innovation patent database and more than 3000 number of patents was identified. The patents identified are in the field of enhanced oil recovery (EOR) and enhanced coal-bed methane (ECBM), chemical and fuel, mineral carbonation, biological algae cultivation and enhanced geothermal system (EGS). Over 60% of these patents were published since the last 10 years, and a sharp increase in patents were seen in the last 5 years (~38%). The top major patent types are patents granted in the United States (US), China (CN) and Canada (CA) which makes of 3/5 of the overall patent type found. Recent patents published include enhancements to the state-of-the-art technologies and hybrid concepts such as in photo-bioreactor in algae cultivation, chemical reaction and EGS. From this study, it was found that further research for the best CO_2 utilization method which fulfil the need of an economic, safe, non-location dependent and environmentally friendly whilst efficiently mitigate the worldwide global warming issue is much needed.

1. Introduction

Limiting the increase of anthropogenic carbon dioxide (CO_2) emissions in the environment is a major challenge facing the world today. Hence, there is a vital need to assess the growing worldwide concern about global climate change. CO_2 generally originated from flue gas from fossil fuel combustion, biogas from anaerobic digestion, product of coal gasification and natural gas streams [1–4]. According to BP energy statistics, in the year 2016 there were 33,432.04MT of CO_2 emission worldwide [5]. An assessment conducted by The Intergovernmental Panel of Climate Change (IPCC), concluded that the CO_2 emissions should be decreased by at least 50% to limit the escalation of the global average temperature to 2 °C by 2050. International Energy Agency (IEA) presented models of technology mix which are essential to meet the 2 °C scenario. The model shows that in order to achieve the targeted scenario, CCUS will need to contribute at least one-sixth of global CO_2 emission reductions by 2050, as well as 14% of the cumulative emissions reductions from 2015 to 2050 as compared to a business-as-usual [6].

CCUS is a methodology to separate CO_2, then utilize CO_2 to produce valuable products and techniques to store produced CO_2, commonly from power generation, industrial processes and even high CO_2 gas fields. The IPCC report stated that without CCUS implementation, the overall cost required to mitigate global climate change may increase up to 138% and there is great challenge to achieve the targeted 2 °C scenario [7]. Various international agreements have been established to ensure that CCUS will play an important role for an economically sustainable route for CO_2 emissions cut required to limit the global climate change rise [8]. More recently, the Paris Agreement of 2016 was established to further accelerate the worldwide response to the threat of climate change by keeping a global temperature rise this century by limiting the temperature rise even further to 1.5 °C [9]. This effort requires even more effective actions to combat climate change, especially on the mitigation for CO_2 emission reduction worldwide. Therefore, new technologies are needed to be developed as one of the critical methods to mitigate the global warming issue [10]. Apart from international agreements, a global competition was introduced to combat CO_2 emission. NRG Canada's Oil Sands Innovation Alliance (COSIA)

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Carbon XPRIZE which began in September 2015 and will end in March 2020, is a US$ 20 Million international competition introduced to develop game-changing technologies that will convert CO_2 emissions from various sources into valuable product which will ultimately address climate change issue [11].

An extensive diversity of utilization techniques are being improved and developed, from technologies to make use of CO_2, increasing the design life of near depleted oil fields, working fluid in geothermal systems to energy storage. All these techniques are still under study or an early stage of development. The development stages of the CCUS technologies can be described using technology readiness level (TRL) scale classification from level 1 to level 9 [12]. Furthermore, selling captured CO_2 provides revenues to partly benefit and overcome the fairly high capital expenditure and financial risks associated with CCUS projects [8]. In addition, CCUS avoids the problems of high costs as well as public acceptance which previously hinders CCS implementation [13].

The CO_2 utilization potential should be of a scale proportionate with future CO_2 capture technology and requirements from large industrial sources and power generation [14]. In this paper, a patent landscape for CO_2 utilization technologies for CCUS application was investigated. A minimum limitation of 5 MTPA (million metric tonnes per year) of CO_2 utilization potential was applied in order to ensure CCUS to be successfully materialized and economically viable [15]. Potential CO_2 market demand and utilization method is presented in Table 1. Five (5) technologies have been shortlisted and identified as a potential CO_2 utilization method for CCUS application (Fig. 1).

In reference to Fig. 1, CO_2 utilization methods via food processing and beverage carbonation packaging was excluded from the listing although both methods have CO_2 demand of more than 5 MTPA. Since both methods are conventional industries with stable rate, the forecasted CO_2 demand growth is expected not to surpass 5 MTPA in the near future. Hence, both methods has been omitted from the CO_2 utilization methods for CCUS application listing.

2. Methodology for carbon utilization patent search

Worldwide, patents have been recognized as rich sources of data for competitive edge analysis, disruptive technology forecasting, and global management for invention portfolios. Due to high prospect of patents as key indicator of numerous technology development measurements and as economic scale, patent analysis is very important to corporate entities as well as significant to academic study [16].

This study utilizes the Derwent Innovation (formerly known as Thomson Innovation) (https://www.derwentinnovation.com/login/) [17] search and analytics platform to search for patents. Derwent Innovation offers over 23 million basic inventions and more than 51 million patents from major patent authorities, specific nations and proprietary sources exclusively with worldwide patent coverage and has access to patent records from over 50 patent issuing authorities, with English translations from 30 languages.

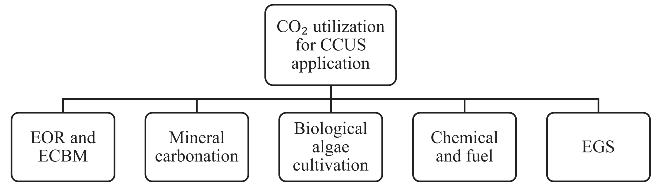

Fig. 1. CO_2 utilization methods for CCUS application.

Table 2
Search strategy in Derwent Innovation search and analytics platform.

CO_2 utilization methods	Keyword terms
EOR and ECBM	Search (CO_2 AND enhanced oil recovery (EOR)) and (enhanced coal-bed methane (ECBM)) [Title, Abstract, Claims]
Mineral carbonation	Search (CO_2 AND mineral carbonation AND carbonates OR concrete) [Title, Abstract, Claims]
Biofuels from microalgae	Search (CO_2 AND biofuels AND microalgae" [Title, Abstract, Claims]
Fuel and Chemical	Search (CO_2 AND conversion chemical/s) and (CO_2 AND fuel/s) [Title, Abstract, Claims]
EGS	Search "CO_2 AND enhanced geothermal system (EGS)" [Title, Abstract, Claims]

Using the Derwent Innovation search and analytics platform tool, an advanced patent search using keywords in patent titles, abstract or claims for CO_2 utilization options for CCUS application was performed. The search strategy for patents on CO_2 utilization method for CCUS application was carried out using specific keyword search terms (Table 2). Data were then extracted and analyzed using the Microsoft Office Excel 2013 software program (Microsoft Corporation, Redmond, Washington, USA). The extracted data were then tabulated into Microsoft Excel format spreadsheet and dashboard with data including; title of patents, applicant/s, inventor/s name, priority date of patents, International Patent Classification (IPC), abstract and claims. All listed patents details were then systematically reviewed and grouped into the corresponding category.

This systematic patent review process as illustrated in Fig. 2 was conducted based on the PRISMA statement [18]. A patent search was conducted in July 2017, and the patent abstracts or the full patents were carefully reviewed, grouped and analyzed. The search initially retrieved 10,200 patents with 6221 being excluded as duplicate patents. Then the title, claim abstract of each patent identified were evaluated to determine whether the patents should be considered for further analysis. Out of 3979 patents selected, 805 was excluded since it was not for CO_2 re-use and another 172 was excluded since it did not meet the eligibility criteria for CCUS application. A total of 3002 patents on CO_2 utilization method for CCUS application was finalized. After the evaluation, the full patent was screened in order to extract the

Table 1
Potential CO_2 market demand [15].

CO_2 utilization method	Potential CO_2 demand (MTPA)	CO_2 utilization method	Potential CO_2 demand (MTPA)
Enhanced oil recovery (EOR) & Enhanced coal bed methane (ECBM)	30-300	Horticulture	1-5
Mineralization	> 300	Pulp and paper processing	< 1
Fuel & Chemical including urea yield boosting	> 300	Inerting	< 1
Biofuel from algae	> 300	Steel manufacture	< 1
Enhanced geothermal system (EGS)	5-30	Metal working	< 1
Beverage carbonation	~14	Supercritical CO_2 as solvent	< 1
Food processing, packaging	~15	Electronics	< 1
Power generation – CO_2 as working fluid	< 1	Pneumatics	< 1
Water treatment	1-5	Welding	< 1
Wine making	< 1	Refrigerant gas	< 1
Coffee decaffeination	1-5	Fire suppression technology	< 1
Pharmaceutical processes	< 1		

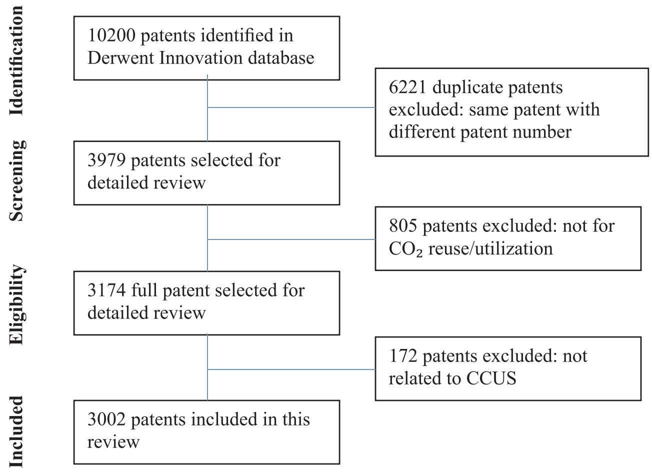

Fig. 2. Flowchart of selected process of patent. Adopted from PRISMA Statement [18].

relevant data. There are no patents with the same patent number and patents that were filed as different patent types and were considered as single patent.

2.1. Limitations

Patent search was conducted for patents from 1980 until July 2017. Patents that were unavailable in Derwent Innovation database were not included. Similarly, prospective associated patents that were not mentioned in the patent title and abstract keywords were also not included. Also, few non-English full patent were not accessible due to limitations of the database and data was based on the abstract and claims which were available in English language.

3. Carbon utilization patents

A total of 3002 patents on CO_2 utilization methods; fuel and chemical, mineral carbonation, enhanced oil recovery (EOR) and enhanced coal-bed methane (ECBM), biological algae cultivation and enhanced geothermal system (EGS) were shortlisted. There are approximately 53% (1592 patents) associated to fuel and chemical, EOR and ECBM has 25.8% (775 patents), biofuels from microalgae has 16.3% (488 patents), mineral carbonation has 3.4% (103 patents) and enhanced geothermal system (EGS) has 1.5% (44 patents) (Fig. 3). The most possible motivation that there were more patents on chemical and fuel compared to others is that there are many types of chemicals and fuels

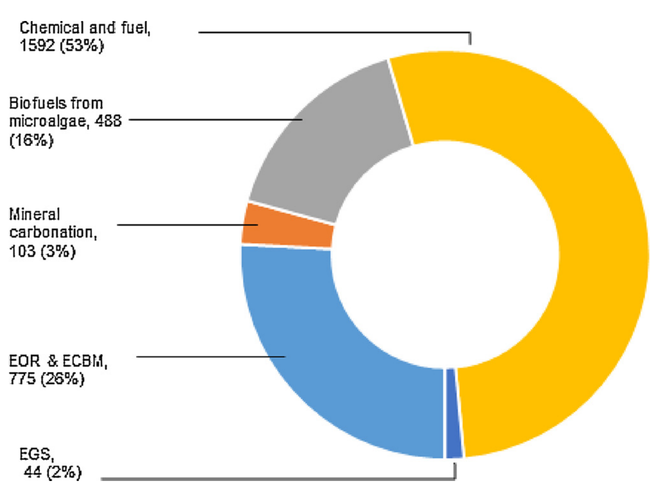

Fig. 3. Type of CO_2 utilization patents.

that could be developed utilizing CO_2. CO_2 can be transformed into useful chemical and fuels, for example, CO, syngas, hydrogen, methane, methanol, formic acid, dimethyl ether, formaldehyde, urea and others [19–24].

Based on the identified shortlisted patents, there were only 5 patents published in 1980 (Fig. 4). Since then, a slight increase in patent was found from 1981 and then remains almost constant onwards until late 1990 s. It was followed by a sharp increase whereby, every 5 years, the number of patents increased during 1998–2002, then with another increase during 2002–2007 (Fig. 4 inset). The increase may be related to the Kyoto Protocol of 1997, which is an international agreement that implemented mitigation measures and also numerous establishments generally through the catalyst of Carbon Credits which is a mechanism to reward organizations creating significant contribution to limit carbon emissions and penalizes those with high carbon footprint [25,26]. Afterwards, during 2008–2012, the figure increased rapidly up to more than 60% in 2013–2017 (data available until 1st July 2017) (Fig. 4 inset). The patent publication looks especially very promising in 2017, as while the patent data is only up to 1st July 2017 (half year), the number of patents has exceeded more than half the number of patents as compared to previous 2016. This is most likely due recent ratification of the Paris Agreement on November 2016. [9].

The top three patent type (country or organization where the patent was filed or granted) are US, CN and CA with approximately 62% (Fig. 5A) of total patents. Among them, US has 2250 patents, CN with 395 patents and CA with 253 patents (Fig. 5B). The highest number of patents in the US is in chemical and fuel with 643 patents followed by EOR and ECBM with 450 patents.

The number of types of CO_2 utilization patents by each year from 1980 until today are presented in Fig. 6(A–E). It is observed that there is a steady increment for most of the CO_2 utilization methods since 1980, which is then followed by a sharp increase from 1998 onwards. However, EOR and ECBM has ups and downs from 1980 to 2001 followed by a steep surge in 2002 with 149 patents in a single year. While for EGS, there is a significant void gap of patent publications during 1990–2003. This may be due to the fact that EGS requires specific suitable location to be deployed, same as in the case of EOR and ECBM. The overall patent increment trend can also be seen in Fig. 7, whereby there is a linear increase of the number of patents from 1980 to 1997 in every 5 years. This is followed by a sharp increase from 1998 onwards until today. This may be indirectly due to the Kyoto Protocol agreement signed in 1997 and the inception of its rules and implementations for greenhouse gas (GHG) emission reduction.

Based on these observations, the rapid CO_2 utilization research and development has commenced and most likely associated with the paradigm shift towards concerns on global warming, climate change, environmental issues, economics and uncertainties in CO_2 sequestration by countries worldwide.

3.1. EOR and ECBM

Enhanced oil recovery (EOR) and enhanced coal-bed methane (ECBM) are direct utilization of CO_2 whereby medium such as CO_2 is injected into depleted oil and natural gas field, respectively. The depleted field may be formed from clastic, carbonate, coal, or organic shale formations, and with the CO_2 injection, it will increase the reservoir internal pressure which ultimately lead to the increase of the productivity [13,27]. Also known as tertiary recovery, EOR is used to extract unrecoverable oil reserves by injecting different agents for example CO_2, natural gas, polymers and surfactant into the reservoirs to remove the trapped oil in the rocks. EOR could extract additional 30–60% of the oil originally available in the reservoir, as compared to primary and secondary extraction which only recovers 20–40%. CO_2 is commonly used as it naturally available and low cost. In CO_2-EOR process, CO_2 acts as a solvent to decrease the oil or gas viscosity, allowing it to flow to the production well. The CO_2 may potentially be

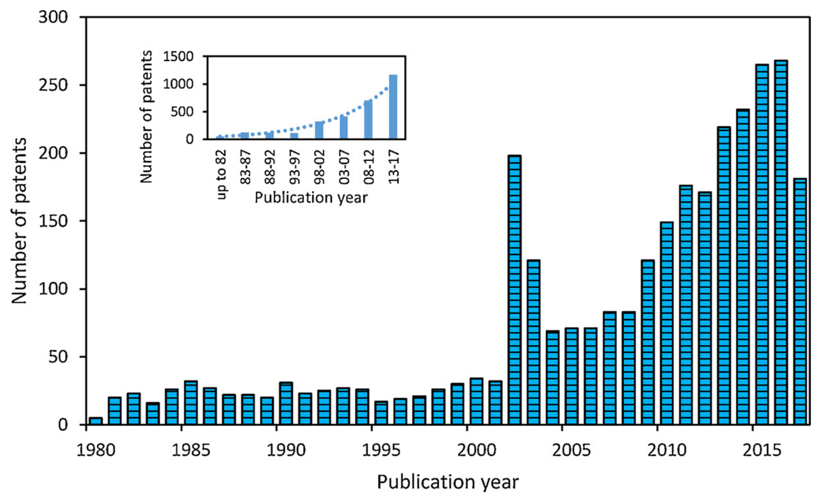

Fig. 4. Number of publications vs publication year.

then stored permanently in the same reservoir after production has completed [6].

One of the earlier EOR patents published in 1981, US4299286 [28] described CO_2 containing fluid is injected up-dip to displace oil downward, via gravity-stabilized displacement process for oil recovery from dipping reservoirs. Then, the CO_2 containing fluid is mixed with an inert gas such as nitrogen or methane to decrease its density adequately in order to increase the critical rate of the displacement process.

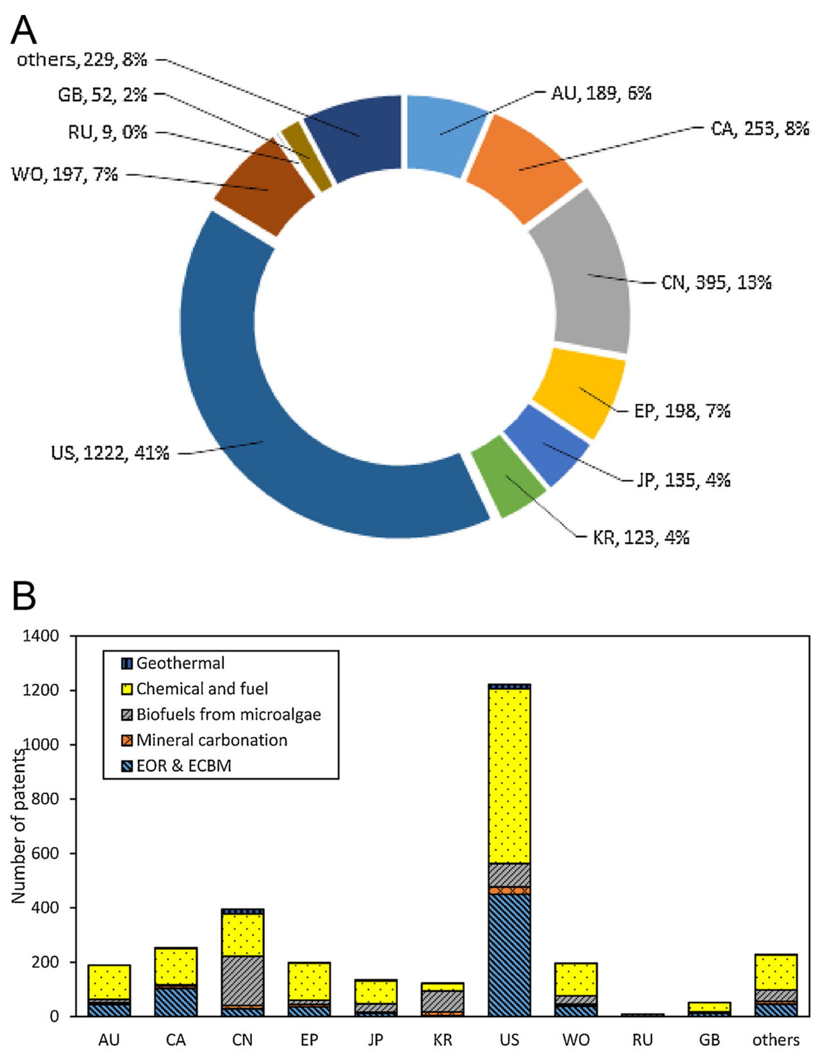

Fig. 5. A): Distribution of patent type Country codes: AU (Australia); CA (Canada); CN (China); EP (European Union Office); JP (Japan); KR (Korea); US (United States); WO (World Intellectual Property Organization, WIPO); RU (Russian Federation); GB (United Kingdom). **B):** Number of CO_2 utilization patents vs patent type.

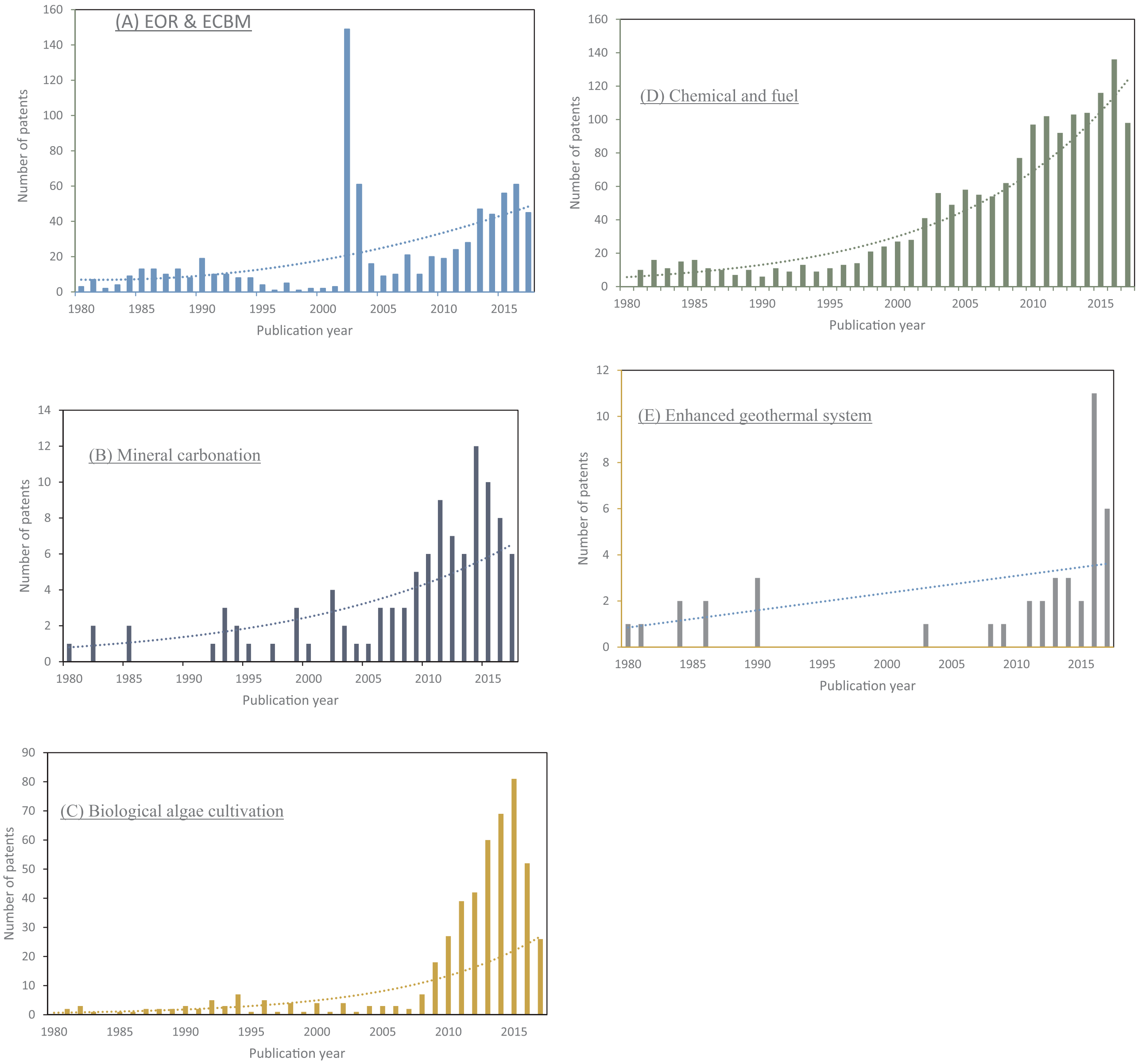

Fig. 6. A): Number of EOR and ECBM patents vs publication year. **B):** Number of mineral carbonation patents vs publication year. **C):** Number of biological algae cultivation patents vs publication year. **D):** Number of chemical and fuels patents vs publication year. **E):** Number of enhanced geothermal system (EGS) patents vs publication year.

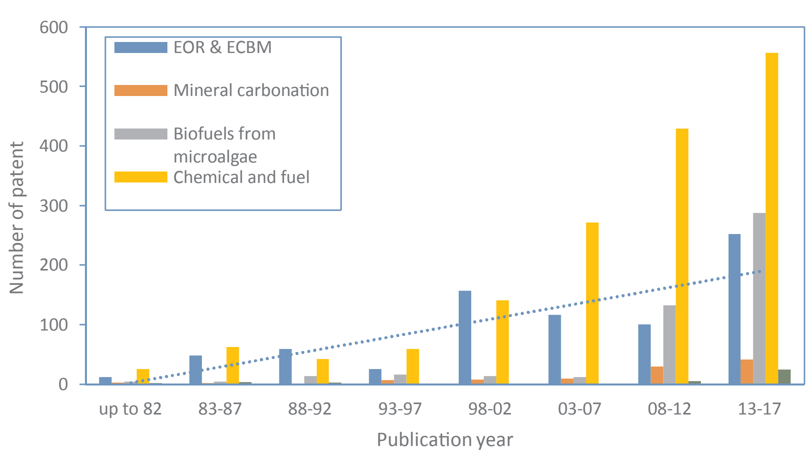

Fig. 7. Number of patents vs publication year – Distribution every 5 years.

With this process, the estimated design life of a reservoir is increased significantly. From thereafter, there were spikes of published patents in EOR utilizing CO_2, such as US20120138316 [29], US20140338903 [30], US 20170114269 [31], US4609043 [32], US4683948 [33], US4799551 [34], US8733459 [35] and CN103422838 [36] which generally described various systems and methods for EOR injection using CO_2 to displace the trapped oil contained in the unrecoverable oil reservoir rock. The EOR technology has been widely practiced in several oils producing countries for over 40 years and the patents are mostly published by oil producers, including Shell, ExxonMobil, British Petroleum, PetroChina, Chevron and Saudi Arabian Oil.

For EOR industrial application, there are several strategies for injecting CO_2 and recovering oil. The direct approach, known as cyclic stimulation or the "huff and puff" method whereby CO_2 is injected into a single well over a finite time, leave the CO_2 in the reservoir for days, weeks or even months (soak period) and then produce reservoir fluids using the same well. This is generally used only in small fields or pilot test. For large scale CO_2-EOR, WAG (Water Alternating Gas) method is usually employed to reduce the chance of early breakthrough and improve sweep. During this process, alternating slugs of water and CO_2 is injected into the well to maintain a more efficient sweep. This strategy has been deployed at the Weyburn field in Saskatchewan, Canada [37].

ECBM is a valuable source of energy and is progressively extracted and utilized to supplement conventional natural gas supply. Generally, coal seams are flooded and injected with CO_2, which then displaces methane upwards to the surface for capture and consumed as fuel.

Several patents on ECBM were published for production of methane by injecting CO_2 into un-mineable formation. WO1995033122 [38] described ECBM method in a semi-closed Brayton cycle power plant which involves generating and injecting a diluent gas mixture comprises of nitrogen and CO_2 into a coal bed to recover methane gas. CN104773709 [39] reported system and method for producing synthesis gas from CO_2 enhanced coal-bed methane. The system comprises a CO_2 trapping system which is connected to a reaction channel of methane catalytic reforming reactor and heating channel so that the efficient utilization of and coal-bed gas is achieved. CN104777269 [40] disclosed a supercritical CO_2 injection and coal-bed methane enhanced displacement simulation test method. The supercritical condition injection mixes well with the oil to decrease its viscosity thus assists the increase of extraction yields [6].[69] There is also patent specific for injection method, whereby US8794320 [41] described a system and method to inject water into a hydrocarbon bearing formation. ECBM pilot project has been implemented in San Juan Basin, New Mexico whereby CO_2 was injected into methane unmineable coal seam for methane recovery. As CO_2 was injected into the coal reservoir, it is adsorbed into the coal matrix, displacing the methane that exist in the space. The displaced methane then diffuses, migrates and is produced from nearby production well. However, significant coal permeability reduction was reported, and this compromised long term methane incremental recoveries and project economics [42].

As one of the major greenhouse gas (GHG) contributor, CO_2 application in EOR and ECBM has positive impact to the environment. Geological sequestration of CO_2 in oil and gas reservoirs is also one of the options to minimize the volume of CO_2 released to the environment [43]. However, uncertainty related to the long term underground behaviour of CO_2 is a concern for EOR, ECBM and geological sequestration [13].

3.2. Mineral carbonation

Since the first recognition of the potential of mineralization as CCUS route, extensive research has been made to accelerate the reaction, thermodynamically favourable but not kinetically interesting [13]. Mineral carbonation is a chemical process to convert CO_2 into solid inorganic carbonates when reacted with metal oxides e.g., calcium oxide (CaO) and magnesium oxide (MgO) [44].

During this process, CaO and MgO which are alkaline and alkaline-earth oxides, naturally exist in silicate rocks such as serpentine and olivine or in natural brines, are reacted chemically with CO_2 to produce magnesium carbonate ($MgCO_3$) and calcium carbonate ($CaCO_3$), generally known as limestone. This carbonation process is shown by the chemical reaction as below:

$$CaO + CO_2 \leftrightarrow CaCO_3 \Delta H = -179\ kJ/mol$$

$$MgO + CO_2 \leftrightarrow MgCO_3 \Delta H = -118\ kJ/mol$$

During the above exothermic carbonation, heat is released. In nature, however, calcium and magnesium are commonly found in silicate minerals. In typical calcium and magnesium containing silicate minerals, the reaction is still exothermic however, the heat released is less. The net reaction equation can be generalized as [45]:

$$(Mg,Ca)_xSi_yO_{x+2y+z}H_{2z}(s) + xCO_2 \rightarrow x(Mg, Ca)\ CO_3(s) + ySiO_2(s) + zH_2O \quad (1)$$

$(\Delta H = -64$ to $90\ kJ/mol)$

The main prospective minerals for carbonation are olivine, serpentine and wollastonite. The carbonation for each mineral are shown below [44]:

Serpentine:

$$Mg_3Si_2O_5(OH)_4 + 3CO_2 \rightarrow 3MgCO_3 + 2SiO_2 + 2H_2O + 64\ kJ/mol \quad (2)$$

Olivine:

$$MgSiO_4 + 2CO_2 \rightarrow 2MgCO_3 + SiO_2 + 90\ kJ/mol \quad (3)$$

Wollastonite:

$$CaSiO_3 + CO_2 \rightarrow CaCO_3 + SiO_2 + 90\ kJ/mol \quad (4)$$

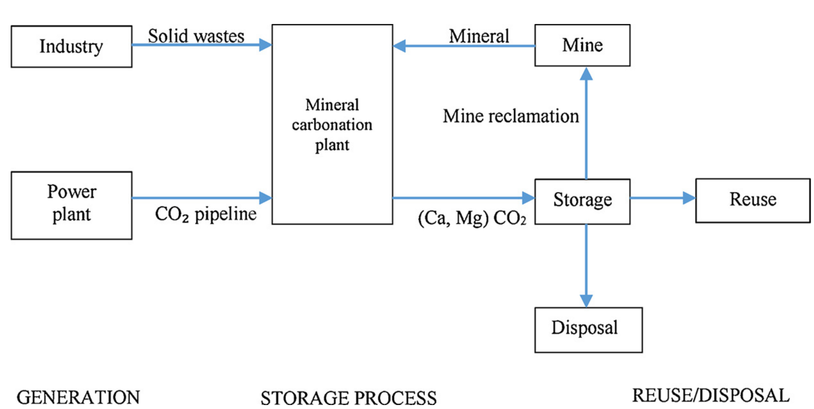

Fig. 8. Process flow diagram for mineral carbonation [15].

The mineral carbonation process flow diagram is shown in Fig. 8. The carbonates end product are very stable over a long period scale. Hence, it could be utilized at any time for construction, mine reclamation, or disposal without any strict requirement for monitoring or the concern of possible CO_2 leakage that could impose health, safety and environmental (HSE) risks. Current research and development in mineral carbonation are focused to achieve energy efficient reactions as well as reaction rates viable for storage using natural rock silicates or industrial waste such as fly ash.

Patents for CO_2 utilization includes using mineralization process, such as EP2532624 [46] which provided a process for the mineralization of CO_2 to form a magnesium carbonate compound, which process comprises contacting the CO_2 in the free form, or in the form of an alkali metal carbonate or bicarbonate, with an alkali metal magnesium silicate to produce the magnesium carbonate compound. Patent WO02085788 [47] described a process for mineral carbonation with CO_2 wherein CO_2 is reacted with a bivalent alkaline earth metal silicate, selected from the group of ortho-, di-, ring, and chain silicates and then immersed in an aqueous electrolyte solution. The invention further expands to the use of the mixture of carbonate and silica formed for the application in construction materials and production of calcium oxide. WO200608242 [48] presented the process for producing $CaCO_3$ or $MgCO_3$ from a feedstock comprising a Ca- or Mg- containing mixed metal oxide. KR2016019011 [49] presented the method for mineral carbonation of CO_2 by passing CO_2 into concentrated water containing sodium ions generated from desalination process, and removing precipitate from concentrated water. Patent US9440198 [50] presented the process and system to use serpentine which is a type of mining residue to produce $MgCO_3$ by contacting with industrial flue gas containing CO_2.

There are also patents focusing on the development of device/apparatus for mineral carbonation. Among them, CN102343199 [51] described a device for immobilizing CO_2 by enhancing mineral carbonation by transforming the CO_2 into HCO_3. CN202569936 [52] presented a device for reducing emission of CO_2 in flue gas generated by coal-fired power plant through adopting wet mineralization and sealing mode. CN104907010 [53] accomplished a reactor for mineralization fixation of CO_2 by fortified calcium-base solid wastes in ammonia medium system. CN105457461 [54] disclosed a CO_2 absorption and mineralization method device comprising a reactor and a three-phase separator. CN205495307 [55] presented a utility model relates to a CO_2 absorption including reactor and three-phase separator.

CO_2 from various sources are utilized to cure precast concrete products and then transformed into cement based material. The output material was found to be of equal material performance as compared to the traditional curing method. As a result, its potential use as a source material for CO_2 utilization has been suggested repeatedly by several researchers and organizations [56]. In KR1303622 [57] it described the method to produce a concrete admixture having self-healing property by reacting to water and CO_2 without using expensive expansion material and carbonation agents. US5935317 [58] accomplished accelerated curing of cement-based materials using CO_2 during pre-curing step. JP06199547 [59] disclosed method for the development of high strength cement composition using gaseous CO_2.

High operational expenditure (OPEX) of mineral carbonation which requires extreme operating conditions as well as feedstock mining and extraction, is a common hurdle for its implementation. However, an economic evaluation which leverages on the mining residue from Quebec has shown potential rational return and payback period. Nevertheless, the mineral carbonation implementation is very much dependent on the current demand and market sale value of $MgCO_3$ [60].

Recently, Mineral Carbonation International (MCI), an Australian based company is developing CCUS pilot plant in New South Wales to research CO_2 transformation into stable carbonates and silicates for application in building products such as cement, plasterboard and others. The pilot plant processes serpentinite from the nearby Orica Kooragang Island operation and permanently converting into solid carbonates [61]. Currently, the carbonation mechanism of cement-based materials has reached a sufficient level of understanding; however, knowledge on the inherent carbonation mechanism still needs to be summarized to address its uniqueness and difference compared other methods in terms of CO_2 utilization [62].

3.3. Biological algae cultivation

Algae is generally known as one of the oldest life form as well as the quickest growing plants. As phototrophic organisms, it needs energy sources such as sunlight, CO_2, inorganic salts (nitrogen, phosphorous, potassium), water with temperature of 20–30 °C for optimum growth. Algae able to utilize the CO_2 from the main three sources: atmosphere, soluble carbonates and discharged gases from heavy industry. Generally, different species of microalgae will produce different types of hydrocarbon, lipids, and other complex oil. Most algae species have oil content ranging from 20 to 50% (dry weight of biomass) while the lipid and fatty acid contents vary based on the culture conditions. [63]. The oil productivity rate (mass of oil produced per unit volume) depends on the algal growth rate and the oil content of the biomass. The algae will then be cultivated for the production of biofuels which generally involves the processes of flocculation, filtration, floatation, centrifugal sedimentation, extraction and purification [63–65]. Algal fuel (oilgae or 3rd generation biofuel) is a type of biofuel which is derived from algae. This is the right move for the production of biofuels as algae possess enormous potential (like low-input, high-yield prospect) for renewable energy applications [66,67]. In the perspective of eco-sustainable process productivity, biological algae cultivation are being considered as promising alternatives as compared to sequestration [68].

Algae cultivation is conducted in an open or closed systems and controlled by various precursors. The algae cultivation can be performed in several methods, including open raceway ponds and photobioreactors (tubular, flat plate and annular) [70,71]. All the specified methods requires energy sources as described earlier. The process flow for algae biological cultivation for biofuel production is presented in Fig. 9.

The efficiency of the biofuel production could be increased if high yielding algae species can be found, innovative production and harvesting techniques are adapted and advanced drying and oil extraction methods are implemented. Previously, the 1st generation of algae cultivation for biofuel production was based on feedstock which was also food commodities (maize, oilseed rape) and resources suitable for conventional agriculture. [66,67]. However, with the rapid progress in the microalgae technology, current microalgae cultivation does not represent a threat to the food market, however it still requires large land areas [72]. Unlike biofuels from crops, the current biofuels derived from algae has no impact on the environment and the food supply [91].

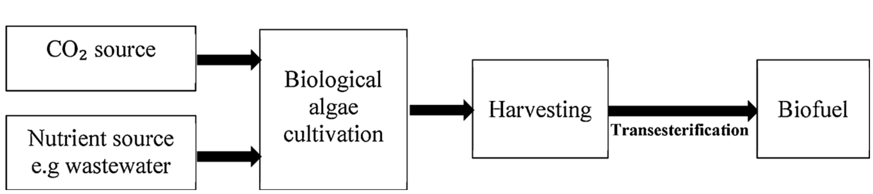

Fig. 9. Process flow for biological algae cultivation for producing biofuel [69].

Table 3
Algae cultivation methods; related patents, advantages and limitations [72–74].

Production system	Related Patents	Advantages	Limitations
Raceway ponds	[75–77]	Relatively cheap Easy to clean Utilises non-agricultural land Low energy input Easy maintenance	Poor biomass productivity Large area of land required Limited to few strains of algae Poor mixing, light and CO_2 utilisation Cultures are easily contaminated
Tubular photo-bioreactor	[78–83]	Large illumination surface area Suitable for outdoor cultures Relatively cheap Good biomass productivities	Some degree of wall growth Fouling Requires large land space Gradients of pH, dissolved oxygen and CO_2 along the tubes
Flat plate photo-bioreactor	[84–87]	High biomass productivities Easy to sterilize Low oxygen build-up Readily tempered Good light path Large illumination surface area Suitable for outdoor cultures	Difficult scale up Difficult temperature control Small degree of hydrodynamic stress Some degree of wall growth
Column photo-bioreactor	[88–90]	Compact High mass transfer Low energy consumption Good mixing with low shear stress Easy to sterilize Reduced photo-inhibition and photo-oxidation	Small illumination area Expensive compared to open pond Shear stress Sophisticated construction

Based on Table 3, biological algae cultivation has limitations in terms of algae species strain yield, production method and extraction process. If these challenges could be overcome, biofuel has high potential to offer true supplement to fossil fuel [70,92]. Toshiba Corporation has completed construction of CCUS at municipal waste plant in Saga, Japan capable of capturing CO_2 emitted from the flue gas of the incinerator. The captured CO_2 is utilized for algae cultivation for the production of biofuels and other commercial products.

3.4. Chemical and fuel

As active carbon source, CO_2 can be converted into synthesized fuel and chemical product that is able to enhance or replace current chemical feedstock in the chemical, pharmaceutical, polymer industries, and for automotive industry in the future. This can be attained through carboxylation reactions whereby CO_2 molecule is used as a precursor for organic compounds for example, polymers, acrylates and carbonates. Also during chemical reduction, the C=O bonds are broken in order to convert into chemicals products for instance, formic acid, methane, urea, syngas and others [6,93].

There are quite a number of patents for the utilization of CO_2 for the system and production of fuel and chemical that have been developed. Among them, US20060235091 [94] reported production process of formaldehyde, formic acid and methanol blends production from CO_2 through electrochemical reduction reaction. The produced formic acid can then become the source of carbon or hydrogen and converted further to form dimethyl ether, methanol and others. US20140093799 [95] described an electrochemical device to convert CO_2 into valuable products such as methanol, diphenyl carbonate, acrylic acid, organic acids as well as synthetic fuels. US2015034503 [96] disclosed systems and methods to effectively convert CO_2 to hydrocarbons (methanol, methane isopropanol, formic acid, formaldehyde, glyoxal, ethanol, butanol) by electrochemical and/or photoelectrochemical methods. WO2010118137 [97] provided a process to render petroleum oil as the source material. During which, CO_2 produced from petroleum oil combustion is captured, purified, combined with steam, minimal hydrocarbon elements or with hydrogen, and then reacted under specific conditions suitable to produce methanol and dimethyl ether. CA2813368 [98] disclosed method for recycling CO_2 by capturing the emission, sequester in an underground/undersea storage and converting them into carbon containing compounds such as methanol and dimethyl ether.

CO_2 also being converted into syngas as reported in EP2926904 [99] using multifunctional catalyst where adsorption and activation of CO which takes place in a two-phase reactor system. This invention may then be applied to enhance the energy rate of the syngas for the production of fuel, additives for fuel and also other chemicals from renewable resources. CO_2 can also convert into carbon fuel and urea as reported in US20120138860 [100] and WO2015184368 [101] using system utilizing heat and electric current.

In addition, CO_2 can also act as feedstock to produce fuels, for example using Fisher-Tropsch process [102,103]. Several patents such as WO201151902 [104] and WO200948685 [105] supported this claim whereby both invention described method to produce synthetic fuels and organic chemicals from CO_2 using the Fisher Tropsch process.

CO_2 could be synthesized into various value added products such as methanol through hydrogenation process using various catalysts. Based on theoretical and experimental setup using binary metal oxide, ZnO-ZrO_2 solid solution catalyst could achieve methanol selectivity of up to 86%–91% in a single-pass CO_2 conversion [106]. Using the same catalyst, conversion of CO_2 into lower olefin (e.g. ethylene and propylene) could also be achieved at different energy changes and temperatures stage [107]. Also, CO_2 hydrogenation could produce liquid fuel using bifunctional catalyst, such as indium oxides (In_2O_3) and zeolites. This could be achieved as the oxygen vacancies on the In_2O_3 surface activate CO_2 and hydrogen to form methanol and thus, C−C coupling will occur in the zeolite pores [108]. Another hydrogenation catalyst, Na-Fe_3O_4/HZSM-5 reported viability to produce liquid fuel with low H_2/CO_2 ratio, hence reduces hydrogen cost [103]. Gold nanocatalyst could also be used during hydrogenation due to its fast conversion properties. The Schiff-base-modified gold nanocatalyst has shown direct catalytic conversion of CO_2 into formate [109]. CO_2 hydrogenation into methane using noble metal ruthenium (Ru) catalyst which has low temperature (less than 200 °C) and high dispersion properties could achieve high yield of methane while increasing the duration of catalytic conversion [110].

German car manufacturer, Audi is also embarking in the development of “fuel of future” using catalytic chemical conversion of CO_2 into synthetic “e-diesel” and is currently in the midst of demonstration for high scale production [111]. For sustainable large-scale utilization of CO_2, the commodity products of CO_2 conversion processes should be economically viable and are in high demand. Unfortunately, the associated highly endothermic CO_2 conversions consume lots of energy [6,20].

Table 4
CO_2 utilization technology advantages and challenges.

CO_2 utilization technology	Advantages	Challenges
EOR and ECBM	• Mature technology • Permanent storage • Large potential use of CO_2 plus revenue stream that can offset the costs of carbon capture • Methane could replace more carbon-intensive fuel sources	• Facilitates additional fossil fuel use, producing more CO_2 • Long time to commercialization • Low methane price • Cost of transporting CO_2 • Location specific
Mineral carbonation	• Abundant materials (minerals or industrial waste) • Chemical free • CO_2 separation or compression is not required • Special CO_2 feed quality requirements is not necessary	• High energy use to accelerate the reaction • Requirement of large amount of reagent • High cost for mineral and processing
Biological algae cultivation	• Competitive source of biofuel • Can result in permanent storage • Efficient in low-concentration CO_2 sequestration • Non location specific	• Algae sensitive to impurities, pH • Cost of controlling growth and drying condition • Large area and sunny climate needed for ponds • High energy required for photobioreactors construction
Chemical and fuels	• Energy carrier could replace fossil fuels, reducing dependence on conventional fuel for transport and other uses	• Inefficient process, requires renewable or low emission energy to have CO_2 abatement benefit • Cost of purifying CO_2
EGS	• Good thermodynamic properties ensuring larger flow rates, reduction in circulating pumping power requirements, higher power output and efficiency increase • Carbon credits from the CO_2 storage will offset portion of the costs of drilling deep EGS wells • Limit water use	• High cost for access to CO_2, proximity of the EGS relative to the electricity grid, and access to cooling water supply • Long term commitment for the resultant reservoir which include the liability for possible future CO_2 leakage • Location specific

3.5. *Enhanced geothermal system (EGS)*

Geothermal energy is a type of conventional low-temperature heat resource which has been utilized to generate electricity for decades [112]. Current enhanced geothermal systems (EGS) is an innovative geothermal technology method whereby subsurface reservoirs which are not naturally fit for geothermal energy extraction can be performed using economically feasible engineering techniques. Formerly known as hot dry rocks (HDR) or hot fractured rocks (HFR), EGS is able to efficiently convert the huge resources supplied by geothermal energy into large scale electricity power for human utilization [113]. For a typical EGS, brine or water as heat exchange fluid flows in a continuous loop in the subsurface reservoir, usually found at about more than three kilometers below the Earth surface where heat is produced by leveraging on high temperature granites. Next, the heat exchange fluid medium extracts the high temperature heat from the granite which then raised to the surface. It is then removed to a secondary geothermal heat transfer fluid, and flowed into turbine generator for electricity power generation. CO_2 is deemed as a key alternative heat transfer fluid selection due to its advantageous properties in fluid dynamics and as heat transfer medium in comparison to water [114]. This is supported by one of the earliest patents EP36592 [115] which was published back in 1981, reported that geothermal energy can be efficiently utilized to generate electricity by using CO_2 as the heat transfer medium. JP2008248837 [116] presented method of acquiring geothermal energy for combining large scale discharge source of CO_2 involving injecting hot water into high temperature rock ground from injection well.

The current concept for this method is using supercritical CO_2, as it is circulated as the heat exchange fluid to retrieve the geothermal energy from the reservoir. This will directly generate power by using a supercritical CO_2 turbine before transferred back into the subsurface reservoir. This could be achieved as supercritical CO_2 has better thermodynamic properties over water and ambient CO_2 while simultaneously attain geological storage. This new approach is anticipated to considerably escalate the cycle efficiency for geothermal development associated with geological storage, hence achieve the double win of economic benefits and environmental protection [117,118]. Patent CN202125410 [119], TWM427450 [120], CN206219216 [121] and CN104791204 [122] presented various utility models for supercritical CO_2 gas turbine power generation system. An organic Rankine cycle system using supercritical CO_2 is reported to exhibit high energy conversion efficiency. This is due to the exceptional behavior of fluids properties in geothermal water temperature [123]. KR1683714 [124] described geothermal power generation system using a supercritical CO_2 Rankine cycle. The system has re-heating fluid path for guiding supercritical CO_2 coming-out from re-heater, and low-pressure steam fluid path for guiding condensed water and passing water to injection well. This is also supported by CA1273496 [125] and JP61244880 [126] which explained various system for utilizing the CO_2 as geothermal fluid for better efficiency power generation. JP2007211633 [127] described additional EGS benefit in a condenser using CO_2 to cool the turbine after driving process is over and converts the remaining geothermal steam into hot/cold water.

The application of EGS utilizing CO_2 rather than using water as heat transfer fluid, will also lower the water consumption and saving pump costs [128–130]. This EGS process will leave substantial amount of CO_2 stored in subsurface reservoir. Long term storage monitoring for possible subsurface leakage will be of key importance to be further researched in this field.

The CO_2-EGS has been applied at pilot scale of 1 MW power plant by Geodynamics Ltd at Habanero power plant in Australia. During the process, supercritical CO_2 was circulated as the heat exchange fluid, then directed to turbine to recover the geothermal heat from the reservoir for power generation. Supercritical CO_2 thermodynamic properties has advantages that could increase the cycle efficiency with favorable economics [15].

Table 4 summarizes the advantages and challenges of CO_2 utilization technologies. To overcome the challenges of CO_2 utilization technologies, significant improvements will have to be developed. For instance, in EGS, one unique approach is using hybrid power source as described in CN206064104 [131,101] whereby it combines renewable solar energy and geothermal power plant. For fuel and chemical, a hybrid concept was developed as described in WO2011139804 [132] via utilizing chemical and biological process that is able to capture and convert CO_2 into CO, methane, methanol, formic acid and syngas by setting the carbon sources into longer carbon chain organic chemicals. This is performed by using microorganisms as reaction catalyst during the oxyhydrogen and the autotrophic fixation of CO_2. Also, the emerging application of solar and nuclear energy has the potential to accelerate the production system [133]. In biological algae cultivation, the latest type of photo-bioreactor are using a unique approach of hybrid combination, whereby it maximizes the volume of work and the

Table 5
CCUS projects worldwide [137].

Type of CO_2 utilization	Location	Project name	Industry
EOR	US	Terrell natural gas processing plant	Natural gas processing
		Shute Creek gas processing plant	
		Century Plant	
		Lost Cabin gas plant	
		Core Energy/South Chester Gas processing plant	
		Coffeyville gasification plant	Fertilizer production
		Enid Fertilizer	
		Petra Nova carbon capture	Power generation
		Bonanza Bioenergy ethanol plant	Chemical production
		Air Product steam methane reformer	Hydrogen production
	UAE	Al-Reyadah CCS	Iron and Steel production
	Saudi Arabia	Uthmaniyah CO_2-EOR Demonstration	Natural gas processing
	China	CO_2-EOR Changling gas field	Natural gas processing
	Canada	Great Plain Syncfuels plant and Weyburn Midale	Synthetic natural gas
		Boundary Dam CCS	Power generation
	Brazil	Petrobras Santos basin pre-salt oil field CCS	Natural gas processing
ECBM	Japan	Yubari CO_2-ECBM pilot project	Gas processing
	China	Qinsui Basin pilot project	
	US	San Juan Basin pilot project	
Mineral carbonation	US	Searles Valley Minerals CO_2 capture plant	Industrial application
		Skyonic carbon capture and mineralization project	Cement production
	Australia	Australia mineral carbonation international	Construction
	Iceland	Carbfix Pilot plant	Power generation
	India	Tuticorin Carbon Clean Solutions	Power generation
Biological algae cultivation	Japan	Saga city waste incineration plant	Waste incineration
Chemical and fuels	Japan	Kansai Mitsubishi carbon dioxide recovery (KM DCR)®	Industrial application
	Saudi Arabia	SABIC carbon capture and utilization	Chemical production
EGS	Australia	Habanero enhanced geothermal system pilot project	Power generation

rate of photosynthesis of the system as reported in the patent WO201641028 [134] and WO2010138657 [135]. These out-of-the-box innovations are creating a paradigm shift for research in CO_2 utilization of CCUS application.

Based on the CCUS projects implementation worldwide, EOR is the most popular CO_2 utilization method with US having the highest number of active large scale CO_2-EOR projects and ranks first in terms of total oil production, accounting for approximately 80% of oil sourced globally from CO_2 injection [136]. While CO_2-EOR remains as key business driver, other CO_2 utilization methods are in development and some has already begun global operation for CCUS application as shown in Table 5.

Most of the countries that have implemented CCUS are developed countries. Substantial challenges are faced by developing countries to embark in CCUS project, due to the high investment cost and uncertainties. Chemical and fuel technology development may experience tremendous growth due to increasingly high CCUS investment by giant oil & gas producers, such as Shell and BP [138]. Extensive development in mineral carbonation is expected due to the potential growth in magnesium carbonate market in the Asia Pacific region during year 2017–2027 period [139]. With the increasing patents in CO_2 utilization technology, increasing research and development and increase in global market demand, it is hoped that CCUS will be more economical for developing countries, and ultimately achieve the emission reduction target.

4. Environmental and health concern

In general, CO_2 is usually considered as safe, non-toxic inert gas and also a natural part of the basic biological processes of all living organisms. However, elevated concentrations of CO_2 in atmosphere could lead to negative environmental impact, and exposure to high concentrations of CO_2 can cause death [4,140–142]. CO_2 utilization environmental and health impact is not yet well studied due to its immaturity of the technologies thus further studies are much needed. In EOR and ECBM, the injection of CO_2 underground is reported to be a well proven technology, achieved TRL-9, as petroleum industries in the US have been injecting CO_2 in geological formations for many years [143]. However, the added pollution from the process itself as well as potential CO_2 leakage and gradual migration of CO_2 back to the environment from the storage site have to be systematically assessed [143]. The uncertainty related to long term storage due to potential CO_2 leakage from the reservoir could happen through or around the CO_2 injection well and cap rock failure [13,144,145]. It has been projected that for current EOR projects, almost 10% of CO_2 injected will be released back to the environment. However, the leakage rate, which is considered “safe and acceptable” for the underground storage of CO_2 was estimated to be 0.01% per year, which may add up to, for a sequestration period of 500 years, a total of 5% leakage is expected [146]. The EGS environmental effect is caused by the drilling of geothermal wells during construction as well as potential leakage during storage [129]. These EOR, ECBM and EGS requires more study in measuring, monitoring and verification (MMV) to ensure no possible leakage from the long-term storage of CO_2 underground.

Microalgae cultivation is a potential water cleansing method which it is able to recover a variety of compounds from wastewater such as; fertilizer derivatives, heavy metals, pharmaceutical waste, oils/grease and polycyclic aromatic hydrocarbons (PAH) /polychlorinated biphenyls (PCB) [147]. However, there are environmental concerns to water, land use, biodiversity and greenhouse gas (GHG) emissions as the due to its toxic byproduct [148]. Furthermore, large scale uncontrolled cultivation could lead to blooms, disease or pest leading to population crashes and spills of cultured algae into natural ecosystems [149,150].

The application of mineral carbonation may offer the solution to the CO_2 emission concern without the slightest possibility for unintentional discharge as its process does not generate harmful byproducts and there are almost no emissions of CO_2 due to leakage [45]. However, there are concerns on the effect of ore preparation, huge scale-mining and waste product disposal which may lead to massive land clearing and highly likely pollution of soil, air and water in the surrounding environment [44,151].

5. Conclusions

This paper has analyzed the patent landscape for various CO_2 utilization methods for CCUS application, namely EOR and ECBM, mineral carbonation, biological algae cultivation, fuel and chemical and enhanced geothermal system. The most published patents on CO_2 utilization is on fuel and chemical products, followed by EOR and ECBM. The least published patent in on EGS. Overall, based on the patent trends, the patents published are increasing every year, especially during the last 5 years (2013–2017) whereby a sharp increase was observed.

Fuel and chemical are highly published by most countries, possibly due to its versatility on different types of fuel and chemical product and also it is not location dependent which could be implemented anywhere nearby the CO_2 source. The technologies utilizing CO_2 during fuel production may also deliver indirect impact as fossil fuels substitute. However, high investment cost is required for the CO_2 purification for the fuel and chemical production.

Countries like China, Korea, US and Japan have long embarked in extensive research background in algae cultivation for food industry, and also was found as the top contributor for biofuel produced from algae cultivation patent publication. The most apparent advantage of biological algae cultivation as well as mineral carbonation method for CO_2 utilization is that it can be performed at any location as long as it is nearby to CO_2 source, or if economics calculation permits to include transportation cost.

On the other hand, EOR and ECBM is very much dependent on location specific, whereby CO_2 sources and reservoir will determine its viability and economics. Based on the patent type published by which, US has the most publications due to its abundant EOR location sites. Not many patents on EGS was found, whereby it is also location specific and requires specific hot dry rock (HDR) site. There are also significant concerns that it is required to be fixed to utilize CO_2 as the working fluid in EGS which in the form of superior geochemistry supercritical CO_2.

Some of these technologies have undertaken development and in commercial application achieving technology readiness level (TRL) at scale of 9, however, others still remain at lower TRL. There are significant technical and economic challenges that have to be overcome before these technologies can be commercialized and applied in the open market. EOR is expected to remain as the dominant method for CO_2 utilization in the short to medium term as it is a mature technology and suitable for large scale CCUS. Mineral carbonation requires further technological improvement to reach the technical maturity for deployment at commercial scale. This utilization method may appeal to the interest in the Asia Pacific region especially by the emerging and developing economies such as China and India, where there are strong demand for construction materials. Magnesium carbonate market growth will likely influence increase in technological research and investments for mineral carbonation to offset the high capital expenditure (CAPEX) associated with CCUS projects at these developing countries. The development in chemical and fuel technology is expected to experience high growth due to the increasingly high CCUS investment by oil & gas producers. With forward-looking plans, some of today's oil & gas companies could become tomorrow's highly diversified energy companies offering wide array of zero emission energy sources and chemical products.

Further development in EGS leveraging the patented innovation of using hybrid power source, coupled with solar energy, which is a non-carbon energy is expected to reduce the CO_2 emission significantly. This new approach of integration with renewables could be adapted by other CO_2 utilization methods, to leverage the locally available renewable sources such as wind, solar, geothermal and tidal energy. A power system leveraging renewables complementing current system will provide uninterruptable power supply day and night. For instance, in biological algae cultivation, solar power could be harvested (if abundant solar available at site) to provide energy for the bioreactors. With further extensive research to cultivate resilient algae species strain yield, coupled with the renewables, it is foreseeable that if best approach of biological algae cultivation is implemented, large volume of CO_2 may be utilized, thus, one step closer to the emission reduction target. Also, the emerging nuclear assisted green chemical and fuel technology could also be adopted by other CO_2 utilization methods that requires high energy, such as in mineral carbonation processing and for photobioreactors in biological algae cultivation. However, further research in monitoring and maintenance has to be in place to ensure the nuclear system integrity.

Future technologies should focus on non-location dependent CO_2 utilization methods with the best potential economic solution. At current stage, as the options of CO_2 utilization are highly diverse, the potential economic benefit also requires much study as most of the technologies are still in the early to medium stage of development. Techno-economic analysis should be continuously updated and benchmarked to ensure viability and economics at every stage of the technology development, from its ideation, prototyping, demonstration until commercialization.

Based on the current trend of patent publications, it is highly likely that more patents will be published, and CCUS project as well as CO_2 utilization conversion projects will be materialized efficiently in the next coming years to come.

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