



Review Article

Multifaceted Perspectives and Advancements of CO₂ Capturing Switchable Polarity Solvents and Supercritical SolventsAnupama Sharma^a, Pinki Chakraborty^{a,*}, Sunny^b, Sandeep Kumar^c^a School of Basic and Applied Sciences, Galgotias University, Greater Noida, India^b School of Medical and Allied Sciences, Galgotias University, Greater Noida, India^c School of Pharmacy, Sharda University, Greater Noida, India

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ABSTRACT

Thus Carbon-dioxide Capture and Sequestration (CCS) has potentially emerged out to be a most effective way to lower down the atmospheric CO₂ levels as well as other related greenhouse emissions. This review article mainly focuses on the role and applications of one of the famous green-house gas carbon-di-oxide (CO₂). Being an environmental waste, CO₂ is one of the inexpensive and non-toxic triggers used to produce the Switchable Polarity Solvents (SPS). The present review highlights the utilization of SPS as an efficient and cost-effective technique for the sequestration of CO₂ and as an affable solvent for the production of bio-fuels. The other major focus of the review is on 'Chemical looping combustion (CLC)' which can be another promising technique for CO₂ sequestration. As per the review studies, the most common CO₂ capture methods includes pre-combustion, post combustion based on chemical absorption, chemical looping combustion and oxy-combustion are discussed in this paper. However, commercially available CO₂ capture technologies are not cost effective. In CLC method, the oxygen circulation is as essential as in human body for survival. The technique can be visualized as non-living 'RBCs' which can behave as an artificial oxygen carrier and can behave as an 'artificial lungs' responsible for organic matter conversion including combustion of hydrocarbons with reduced CO₂ emission into the atmosphere and inherent separation and storage of carbon dioxide. CLC has attracted the attention of many researchers as one of the stands out capture technique having maximum efficiency of CO₂ removal and utilization in power and heat generation transferring oxygen from the air to the fuel. This review also presents the role of supercritical (SC) CO₂ for bio-fuel production, yet another way to minimize atmospheric CO₂ levels. Finally, this review article will provide a new perspective to the researchers to attain ecological benefits thereby discovering new SPS for efficient CO₂ capture. The review also assesses present challenges and future considerations related to solvents and processes equipped for CCS to provide insights into future research and development demand.

1. Introduction

The greenhouse gases that are majorly responsible for global climate changes are carbon dioxide (CO₂), water vapors (H₂O), chlorofluorocarbons (CFCs), methane (CH₄), nitrous oxide (N₂O), and ozone (O₃) [1]. Among all, CO₂ is the significant prime source that embrace nearly to 76% with the average atmospheric lifetime of about thousands of years [2]. It has been reported that the concentration of CO₂ in atmosphere has already been escalated to more than 40% since the beginning of industrial era that is about 280 ppm to 406.42 ppm till February' 2017 [3]. As of now, none of the records has shown such a hike in CO₂ levels in

such a small duration of time, followed by the continuous fall in emissions due to COVID-19 situation in the long-haul everlasting graph. [2] For the same reason, the review of SPS and SC solvents have tried to attract the scientific community towards the way of capturing of environmental CO₂ sequestration in order to reduce the present global emission to pre- industrial levels. Thus Carbon-dioxide capture and sequestration (CCS) has potentially emerged out to be a most effective and efficient way to bring down the atmospheric CO₂ levels as well as the green-house emissions. Table 1.

According to Benson et al, Carbon-dioxide Capture and Sequestration technology (CCS) is an efficient cost-effective technology to minimize

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the emission of greenhouse gas [4,5]. Lee and Park, 2015 has revealed that the CCS technology often includes capture of CO₂, its transportation and effective storage among which the process of capture holds for a substantial cost of 80% of the total cost of CCS [6,7]. Phase transition solvents known as “switchable polarity solvents” (SPS) are supposed to be the most promising and potential solvents for CO₂ capture as they remarkably take the edge off the high energy consumption as well as possess high CO₂ absorption capacity [8]. In fact, SPS are combinations of solvents like primary and secondary amines and the solubilizing solvents such as tertiary amines/ alcohols/ water, etc of some specific ratio that can absorb CO₂. Hence, the presence of CO₂ rich aqueous phase makes the regeneration process simpler, cheaper and efficient as the energy consumption in regeneration of solvent has been reduced noticeably [9]. Raynal and his coworkers have reported that these energy consumptions can be further minimized to 0.22–0.25 kWh/kg of CO₂ by enabling phase transition solvent-based processes [10]. Chemical Looping Combustion (CLC), is a clean energy technology for carbon dioxide capture, storage and power utilization with an aim to minimize the emissions specially from coal and other solid and gaseous fuel based thermal power plants [11]. Some of the popularly used fuels for CLCs are gaseous fuels (syngas, NG and propane); liquid fuels (diesel, bitumen and heavy oils) and solid fuels (e.g., coal, biomass). In fact, this technique stands out to be an efficient way to cope with environmental CO₂ levels that are the major causes of the global warming [12]. In this technique, CLC can be visualized as an artificial oxygen carrier technique in which there is a chemical in the form of a metal/metal oxide (such as iron, manganese or copper) termed as an oxygen carrier (OC) that completes a cyclic loop between two reactors (an air and a fuel reactor) in the process and also helps in combustion of the fuel. The process of CLC avoids direct contact between the fuel and the air and this method of burning of carbon-based fuels is blessed with inherent sequestration of CO₂ that does not require any extra energy [13,14]. In the air reactor, oxidation of the metal particles takes place and there is formation of metal oxides followed by the flow of these metal oxides where these are reduced by combustion in the fuel reactor, emitting out CO₂ and H₂O. The CLC finally results in the condensation and formation of pure CO₂ which can be further utilized for a variety of useful purposes [15]. There are a variety of CO₂ capturing techniques, the conventional CO₂ capture technologies for large scale power plants are energy intensive resulting in a significant decrease of the overall efficiency and exorbitant price. In comparison, CLC could be proved to be a good alternative way with cost effective and high CO₂ capture technique. The most convincing feature of CLC is that it has low irreversibility in comparison to the conventional combustion techniques which saves it from excessive wastage [12].

Moreover, the use of Supercritical solvents for the extraction of biofuels from organic bio-masses is another efficient technique for CCS, where SC - CO₂ is involved as SC solvent. In fact, extraction of bio-oils from algae with supercritical carbon dioxide (SC-CO₂) is considered to be a well- grounded and a secure alternative technology for the production of bio-fuel [16]. In fact, in industry and the other stakeholders are aware of potential disadvantages of aqueous fluids such as water scarcity, environmental impact from constituent chemicals, and

sometimes the poor performance of solvent. To address these problems, the use supercritical CO₂ as a replacement working fluid is thought to be an excellent choice [17]. In this review the profuse roles and principles of CO₂ responsive SPS, CLC technique and SC solvents are outlined and the comprehensive advancements in the development of phase change solvents and their fundamentals are taken into consideration that can be a better alternative for CO₂ capture and storage.

2. Switchable polarity solvents and carbon dioxide (CO₂) sequestration

2.1. CO₂ triggered switchable polarity solvents

According to Jessop et al., SPS are “reversible ionic liquids” which can transform their polarity from low to high by the application of a trigger as shown in Figure 1. According to them, the stereo-typical switchable polarity solvents are composed of Amidine/alcohol mixtures, guanidine/alcohol mixtures, amidine/amine mixtures, secondary amines, diamines and guanidine/acidic alcohol mixtures [18].

One of the most primitive works in this direction was carried out Jessop and his co-workers. This was one of the marvelous works and was a revolution in the field of green chemistry as in this work a reversible and smart solvent which can switch itself from non-polar to polar nature was developed. In this work solvent made of the mixture of non-ionic component (made of 1:1 ratio of 1,8-diazabicyclo-[5.4.0]-undec-7-ene, DBU (a bicyclic amidine) and 1- hexanol mixture) and ionic component (a salt in liquid form) was developed which has this unique switchable polarity nature on exposure to carbon dioxide atmosphere possesses polar nature because of CO₂ capturing ability and then reverting back to non-polar state on removal of CO₂ and introduction of inert Ar or N₂ atmosphere at ambient temperature as represented in Figure 2. [18]. Thus, they concluded that both N₂ and CO₂ at one atm pressure acts as wonderful triggers by inducing non polarity and polarity respectively in the reaction mixture [19]. These “smart materials” are found really helpful in increasing the efficiency in chemical processes and thereby reduces the environmental impact [20]. In general, when the CO₂ reacts with amine components of SPS, they transform into carbamates and on reaction of amidine/guanidine with CO₂ forms alkyl carbonates thus these two can be used as efficient CO₂ capturing agents

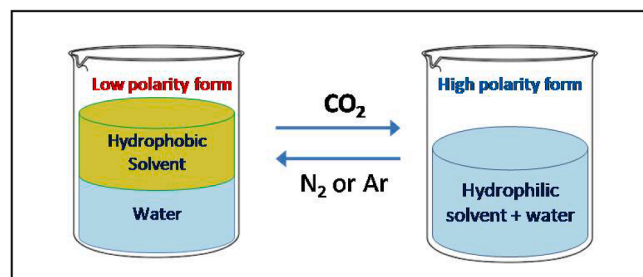


Figure 1. Illustrating the change in polarity of solvents on the addition and removal of CO₂ Click or tap here to enter text.

Table 1

Amount of CO₂ sequestered by various switchable polarity solvents

S. No	SPS for CO ₂ sequestration	Methods used	Amount of CO ₂ Sequestered(g)	Total Reactiontime (min)	Application	Reference No.
1.	1-cyclohexylpiperidine(CHP)	Electrochemical reduction of CO ₂	135.96	90	Production of Syngas	[23,29]
2.	Tris[2-(dimethylamino)ethyl]amine (Me ₆ TREN)	Precipitate formation and filtration	148.6	30	Removal of toxic catalyst (Cu) in ATRP	[30]
3.	1,8-Diazabicyclo[5.4.0]undec-7-ene (DBU)	Direct trans-esterification	143.25	28.65	Production of bio-diesel	[24,31-35]
4.	Ammonium pyrrolidine dithiocarbamate (APDC)	SPS based liquid phase Microextraction	400	120	Microextraction of Cd (II) Ion	[36]

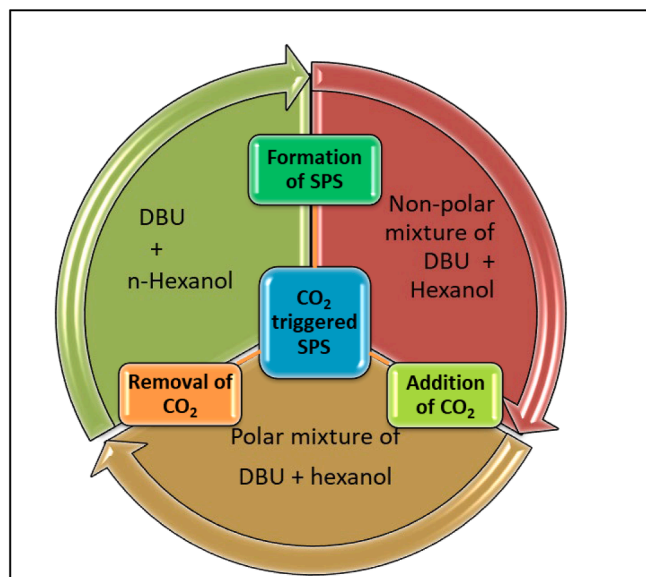


Figure 2. First ionic liquid mixture (DBU+ Hexan – 1 – ol in 1:1 ratio) studied by Jessop et al attains the polarity by the addition of CO₂ at 1 atm pressure.

from gas streams at low- pressure like flue gas [21]. However, the high cost of amidine and guanidine lowers down their feasibility for CO₂ capture processes. In fact, amines have a great practicability as they have this dual nature that is they can act as nucleophiles as well as proton donors and therefore can serve as an excellent cost-effective SPS with single-component for CO₂ capture. From past few decades, the CO₂ triggered materials have drawn much attention due to their excellent separating efficacy and smooth reversible recovery during the chemical processes. In 1986, Moore et al developed the first CO₂-responsive latex resin as one such switchable polymeric material by capturing CO₂ with an innovative mechanism of its own as shown in Figure 3. [22].

Moreover, in recent years, various types of CO₂-switchable materials have been developed by capturing environmental CO₂ and these CO₂ triggered switchable materials found to have a wide range of applications and proved to have versatile roles. They are useful for the production of syngas. 1-Cyclohexylpiperidine (CHP) one of the SPS is used as a capture-electrolyte media to trap CO₂ and shows polar to non-polar transition. As a result the captured CO₂ undergoes electrochemical reduction to produce syngas at low temperature and pressure [23]. 1,8-Diazabicyclo[5.4.0]undec-7-ene (DBU) is yet another switchable polarity solvent undergoes direct trans-esterification for the production of biodiesel. DBU is an environmentally friendly switchable solvent on mixing with an alcohol forms a non-polar DBU-alcohol mixture that can be used for the extraction of oil from biomass. When CO₂ is added to this mixture it becomes polar and extracted oil separates out of the DBU-alcohol mixture. Later on, the DBU can be recovered by the release of CO₂ [24]. Therefore, it can be concluded that environmental waste CO₂ is an efficient trigger for the switching or to create “smart materials” is

certainly an inexpensive, non-toxic, eco-friendly and green choice in comparison to other possible alternatives and these “smart materials” are proved to be potential agents for trapping the environmental CO₂ and thereby decreasing its levels in the atmosphere.

2.2. Mechanism of working of CO₂ triggered SPS

For preparation point of view of switchable solvents, the substituted amines which have got pH tunable structure and solubility features are utilized for inculcating the trigger effect in CO₂ triggered SPS as shown in Figure 4. With lower pH values, i.e. in acidic condition, at equilibrium, ionic form predominates over non-ionic form and forms a homogenous aqueous solution with high solubility. This acidic environment is obtained by passing excess of CO₂ which converts amines to quaternary ammonium cations which have high solubility in water and thereby shifting the equilibrium towards ionic form.

CO₂ acts as the best and eco-friendly trigger for such switching “on” or “off”. At first, an aqueous solution of amine having low ionic strength with higher pH value is acquired by dissolving in water. Later when this solution reacts with CO₂, it converts to a bicarbonate salt, as a result there is a considerable increase in ionic strength and the pH value decreases [25] as described in the below mentioned equations



In these equations, **B** is the nitrogenous base (amine) and **n** is the number of protons accepted by the base **B**.

In accordance to eq-2, if number of protons **n** accepted by the base **B** increases, the ionic strength can be potentially increased and thus the separating capability of an organic compound can be maximized [26]. When the pH value increases by adding concentrated alkali solutions, CO₂ is removed and amine gets deprotonated as a result, non-ionic form dominates which have low solubilities in aqueous media. This leads to the formation of Biphasic Systems as explained by Bazel et al [27]. Furthermore, the non-aqueous amine-alcohol solvents, CO₂ reacts either with primary or secondary amines by forming carbamic acid [28]. This carbamic acid is then de-protonated by the presence of excess of amine.

2.3. Principles and Techniques involved in CO₂ sequestration using SPS

The various CO₂ triggered switchable materials have been discussed here along with the principles and techniques involved in the CO₂ sequestration as discussed in Figure 5.

2.3.1. Syngas production using SPS capturing electrolytic media

From applicability purposes, Syngas, a mixture of H₂ and CO is an extremely valuable product which has got the tunable that can be tuned for the synthesis green fuels which can greatly substitute fossil fuels without disturbing the better physical and chemical changes. SPS has the potential to act as a good CO₂-capture-electrolytic media for the

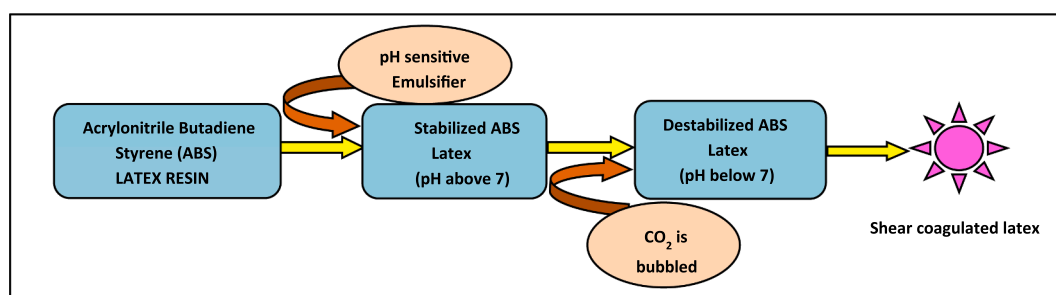


Figure 3. Scheme representing the first CO₂ responsive latex resin developed by Moore et al.

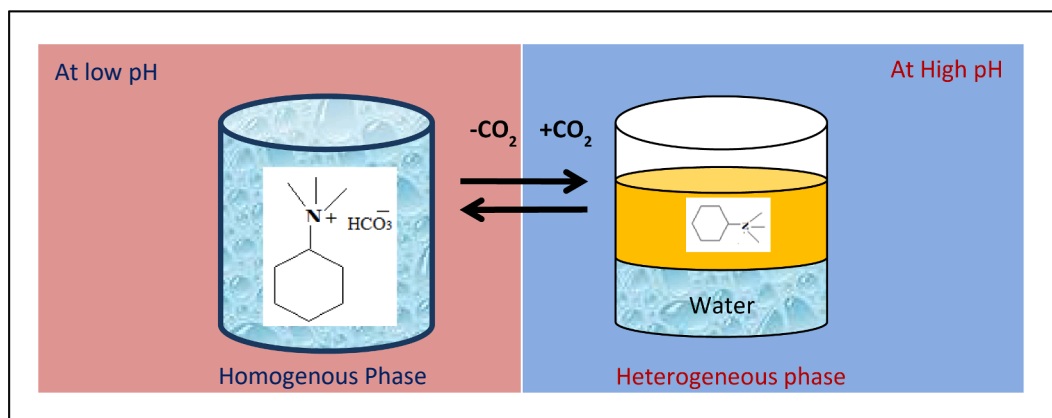


Figure 4. SPS are generally amines that show structural and solubility changes with the change in pH. At low pH amine changes to ammonium cations (ionic form) after passage of CO_2 . At high pH value amines (non-ionic form) regenerate after removal of CO_2 .

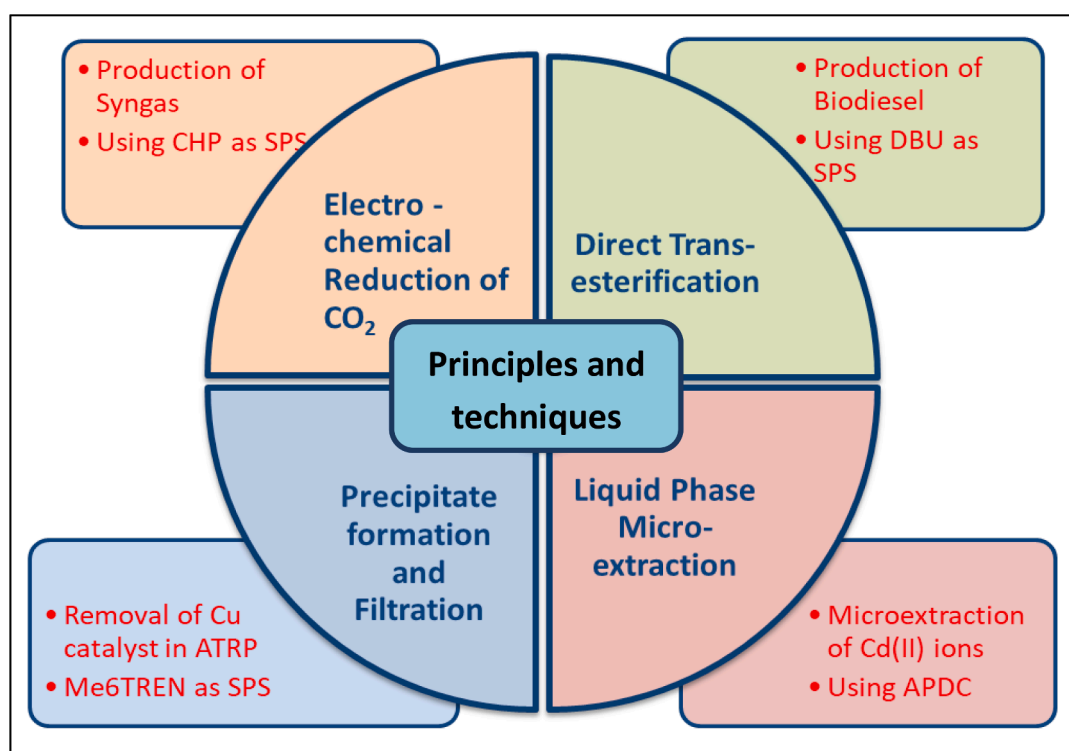


Figure 5. A brief outlines of various principles and techniques using of CO_2 triggered Switchable Polarity Solvents (SPS) for CO_2 sequestration.

electrochemical reduction of captured CO_2 . SPS or commonly known as SHS have emerged as an excellent versatile technical alternative material which have the capacity to shift their polarity depending on the concentration of CO_2 . It was tested first by Handford et al, in his work the 1-Cyclohexylpiperidine (CHP) was used as the switchable solvent for capturing of CO_2 followed by electrochemical reduction. The main highlighting point of the study that this particular SPS was found to be a wonderful low cost and compatible SPS in comparison to various other polymeric system [29]. And this study proposed the CHP to become a good non polar and water insoluble capture-electrolyte media that can be recovered again. Diaz and his coworkers experimentally proved that under low temperature and pressure conditions a non -diluted syngas was obtained.

2.3.1.1. Principle and technique. Diaz et al, 2018, tested CHP as SPS for CO_2 capture and its electrochemical reduction on the basis of its high

CO_2 absorption capacities (189.63 g L^{-1}) and probably low production cost. [36–38]. The electrochemical reduction and release of captured CO_2 was carried out in a buffer-layer-type electrochemical cell with a cation exchange as shown in figure 6. Oxidation of water takes place at anode of the electrochemical cell thereby releasing O_2 gas and H^+ . On the other hand, at cathode, so produced H^+ ions combine with the $[\text{HCO}_3^-]$ and thus releases CO_2 for electrochemical reduction near the electrocatalyst surface. This simple acid–base reaction allows CO_2 release to maintain a sufficient CO_2 concentration on the cathode surface. Thus, the release of CO_2 , switches the polarity of CHP back to water insoluble form to facilitate the recovery and re-utilization of the electrolyte capture media for CO_2 sequestration.

This process developed by Diaz et al was very effective, as the electrochemical reduction of captured CO_2 to CO occurs in a single electrochemical cell and also there is no need to add supplemental CO_2 gas to the electrochemical cell. According to Diaz et al, the Figure 7. shows

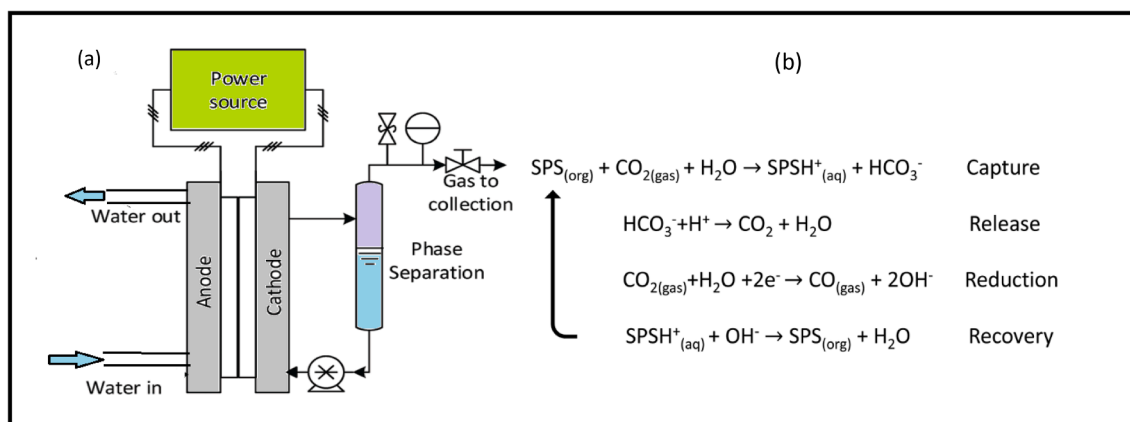


Figure 6. (a) Electro - chemical reduction of captured CO₂ (b) CO₂ sequestration cycle

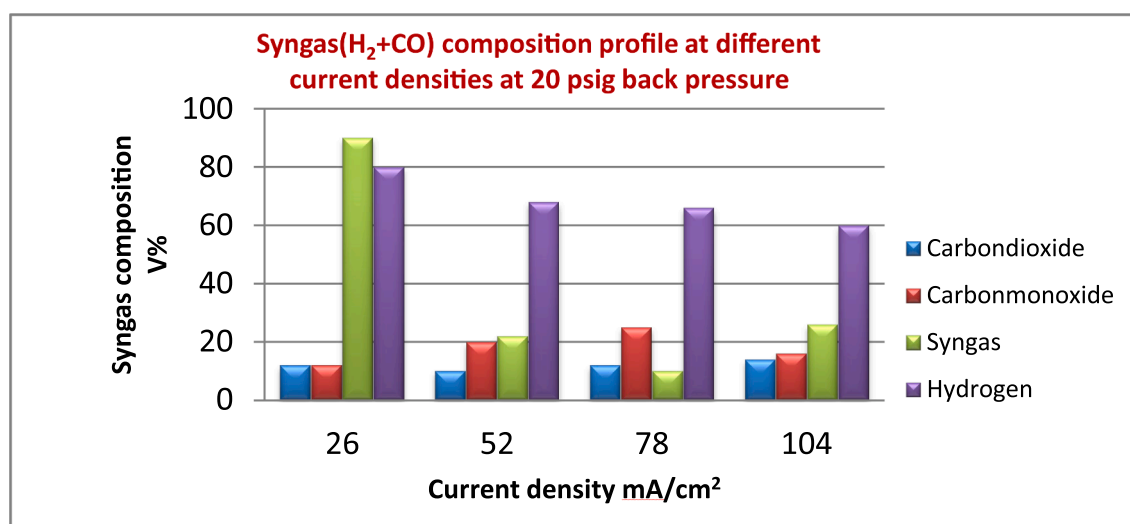


Figure 7. Represents composition profile and H₂ : CO ratio for the syngas obtained at different current densities and at 20 psig back pressure

the various gaseous compositions obtained during the electrochemical reduction of captured CO₂ for the synthesis of syngas at 25 °C along with 20 psig back pressure and 26 to 104 mA cm⁻² as current densities. It is worthy to note that the maximum concentration of CO was obtained at 78 mA cm⁻² and with increase in the current there is an increase in the amount of CO₂ evolved out from the CHP-H₂CO₃ solution[23].

2.3.2. Application of SPS as catalyst for biodiesel production

Phan et al identified that, 1,8-Diazabicyclo[5.4.0]undec-7-ene (DBU), as a switchable solvent, helps in efficient oil extraction from the biomass when treated with an alcohol [21,31] by the utilization of captured CO₂ that act as a trigger. Figure 8. gives a representation that by the induction of CO₂ it converts to polar form as a result DBU-alcohol

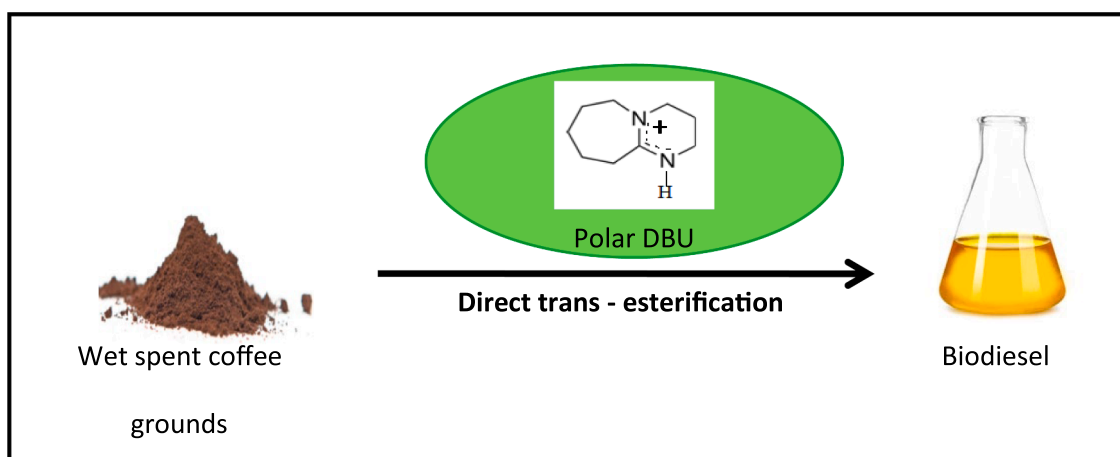


Figure 8. Shows the role of DBU as solvent and catalyst in direct trans-esterification of wet spent coffee grounds for the production of biodiesel.

solvent separates out from the extracted oil and the obtained CO₂ produces makes it a recyclable and reusable SPS [24].

Thus, the use of DBU in as probable catalyst and solvent in direct trans-esterification of wet Spent Coffee Ground's (SCG's) is really an efficacious and potential process for biodiesel manufacturing. In fact, the SCGs obtained from a coffee industry actually possess greater water content (> 70%) therefore, there is a need for the direct trans-esterification of wet SCGs so as to minimize the energy and time [32]. According to Nguyen et al, to predict the reusability of DBU, the direct trans-esterification of wet SCGs was conducted under optimal conditions. Later, the reaction mixture was bubbled with CO₂ with a rate of 5 mL/min for nearly half an hour at 25 °C and then accompanied by centrifugation for 10 min (approx) at 6000 rpm. After centrifugation, the Biodiesel was obtained in the upper layer and the remaining layer of the polar methanol-DBU mixture separates out. This methanol-DBU mixture was then heated to 90 °C and N₂ (5 mL/min) gas was introduced for nearly one hour in order to switch the DBU to its original non-polar form. Subsequently, this re-covered DBU can be added again to a reaction vessel containing fresh methanol and wet SCGs to instigate a new direct trans-esterification reaction.

2.3.2.1. Principle and technique. DBU is a polarity-switchable solvent with its hydrophobicity and hydrophilicity that can be regulated reversibly. This reversibly switchable property enables the phase separation of the biodiesel product and DBU, allowing a simple process for product purification and making DBU potentially reusable. In the present study, DBU reusability was examined by conducting the direct transesterification of wet SCGs under optimized conditions. A homogeneous solution was found before CO₂ was introduced into the reaction mixture. However, after induction by CO₂, the solution was clearly separated into two phases, namely biodiesel and the methanol-DBU solvent, indicating the formation of the polar DBU. Before reusing DBU for a new direct transesterification reaction, the polar DBU was switched to its hydrophobic form by heating at 90 °C and bubbling N₂ through it. As indicated by the results, DBU could be repeatedly used for at least 10 cycles without a dramatic reduction in the biodiesel yield (97.07%). This finding suggested that DBU can be reused efficiently in direct transesterification, where DBU acts as both the catalyst and solvent, rendering the process to be cost-effective and efficient for biodiesel production. In fact, the yield biodiesel obtained for each reaction cycle was monitored. Thus, by using Response Surface Methodology the reaction takes 28.65 min and produces the maximum 97.18% of biodiesel when methanol amount taken as 6.25mL/g, DBU amount is 14.46mL/g of wet SCG's at 60.2°C [24]. This suggests that the direct transesterification of wet SCG's is really efficient, inexpensive and environmentally beneficial method for the production of biodiesel [33].

2.3.3. Role of SPS as a ligand for catalyst removal in ATRPs

Su et al in 2018, had made appreciable efforts in order to remove the residual catalyst from the polymers prepared by using Atom Transfer Radical Polymerization (ATRP) technique. ATRP, promotes the polymerization by using a small amount \approx 25 ppm of copper as a catalyst [30,37]. Innumerable approaches have been put forwarded for the removal of toxic copper catalyst from ATRP but it was found that each development was encountering with an additional purification step. This leads to the generation of supplementary waste as well as reduces cost-effectiveness of the prepared polymer. According to Su et al, the use of CO₂-switchable technology, for the removal of copper catalyst and ligand and also for the purification of synthesized polymers by ATRP is a cost-effective and an efficacious route. Here, Su et al had used N,N-dicyclohexyl-methylamine (Cy₂NMe) as a switchable solvent. The selection of Cy₂NMe was based on the fact that it can switch between a non-polar form that is sparingly soluble in water and a polar form that is more soluble in water. In Atom Transfer Radical Polymerisation (ATRP), Cy₂NMe as a switchable solvent, 2-bromoisobutyrate (EBiB) was used as

an initiator, CuBr as catalyst, and tris[2-(dimethylamino)ethyl]amine Me₆TREN as the major CO₂-switchable ligand. In this study, there was aerial oxidation of Cu(I) to Cu(II) followed by the inclusion of CO₂ and water. Polystyrene polymer was found to precipitate out which was filtered off and the soluble salts like CuBr₂, Cy₂NMe and Me₆TREN remained in the solution. Figure 9. shows how after the removal of CO₂, there is conversion of Cy₂NMe to non-protonated form [30].

2.3.3.1. Principle and involved. Su and his coworkers had used Cy₂NMe as the switchable solvent and Me₆TREN as the switchable ligand. In order to initiate the process of polymerization, initiator EBiB was added into the reaction mixture in absence of oxygen. The round-bottom flask containing 0.14 g of CuBr along with a dry magnetic stir bar was stoppered and made deoxygenated by using argon. Later, 20.0 g Cy₂NMe, 20 g styrene and 0.70 g of Me₆TREN were mixed together in flask to start polymerization followed by subsequent heating of flask up to 80 °C with continuous stirring. Then the polymerization has initiated by adding 0.19 g of EBiB as initiator with argon at 80 °C. Subsequent to polymerization, to oxidize Cu(I) to Cu (II) the air was bubbled into the reaction mixture for 30 min followed by addition of CO₂ in the reaction mixture for 30 min to precipitate out the synthesized polymer. Thereafter, Su et al added NaCl to the filtrate after the removal of polymer, to separate out the ligand Me₆TREN from water phase that can be used in the next reaction cycle. The method adopted by Su et al proved to be a viable method for the removal of copper from polymer in ATRP process. Furthermore, the use CO₂ as a switch makes the ATRP process much cost effective and economical by recovering and recycling the CO₂-switchable ligand. After the removal of CO₂ the Cy₂NMe converts to non-protonated form along with non-protonated Me₆TREN can be used for cycle of ATRP process [30].

3. Supercritical Solvents and Bio-fuel Extraction

Super-critical fluids are being reported as wonderful solvents for the extraction of bio-fuels from the various available biomasses due to their low viscosity and manageable solvent power [38-41]. Moreover, they are also considered as "Green Solvents" as they are non-toxic, cheap, recyclable, eco-friendly and non-hazardous and thus these creates an opportunity for sustainable chemical processes [42-45].

3.1. SC-CO₂ in extraction of algal bio-oil.

Algal biomass is actually considered as an unrealized potent feed-stock for the extraction of bio-oil for the production of bio-fuel due to their expeditious growth, high yield, larger stock of bio-oil and an exceptional property to minimize CO₂ concentration in atmosphere [46,47]. In fact, extraction of bio-oils from algae with supercritical carbon dioxide (SC-CO₂) is considered to be a well-grounded and a secure alternative technology for the production of bio-fuel as shown in Figure 10. According to Patil et al, SC-CO₂ is non-flammable, cost effective, eco-friendly and often regarded as safe solvent with standard critical constants i.e. T_c = 31°C and P_c = 7.38MPa. SC-CO₂, peculiarly capable for the dissolution of even non-polar compounds when the desired molecule is not soluble [42,43]. The extraction of algal bio-oil using SC-CO₂ with azeotropic mixture of co-solvents (Hexane + Ethanol) beholds the higher purity rate, no extra residual solvent, selective fractional distillation and rapid and easy separation. Previously, the co-solvents such as dichloromethane, ethanol, hexane, methanol were also investigated for algal bio-oil extraction with SC-CO₂ before the selection of (hexane and ethanol) azeotropic mixture as a co-solvent and it was found that the results were surprisingly different.

The investigation shows that SC-CO₂ with dichloromethane, methanol, hexane and ethanol produced nearly to 10-12%, 12-15%, 13-15% and 18-20% of total extracted algal bio-oil respectively. On the other hand, azeotropic mixture (hexane + ethanol in 1:1 ratio) under same

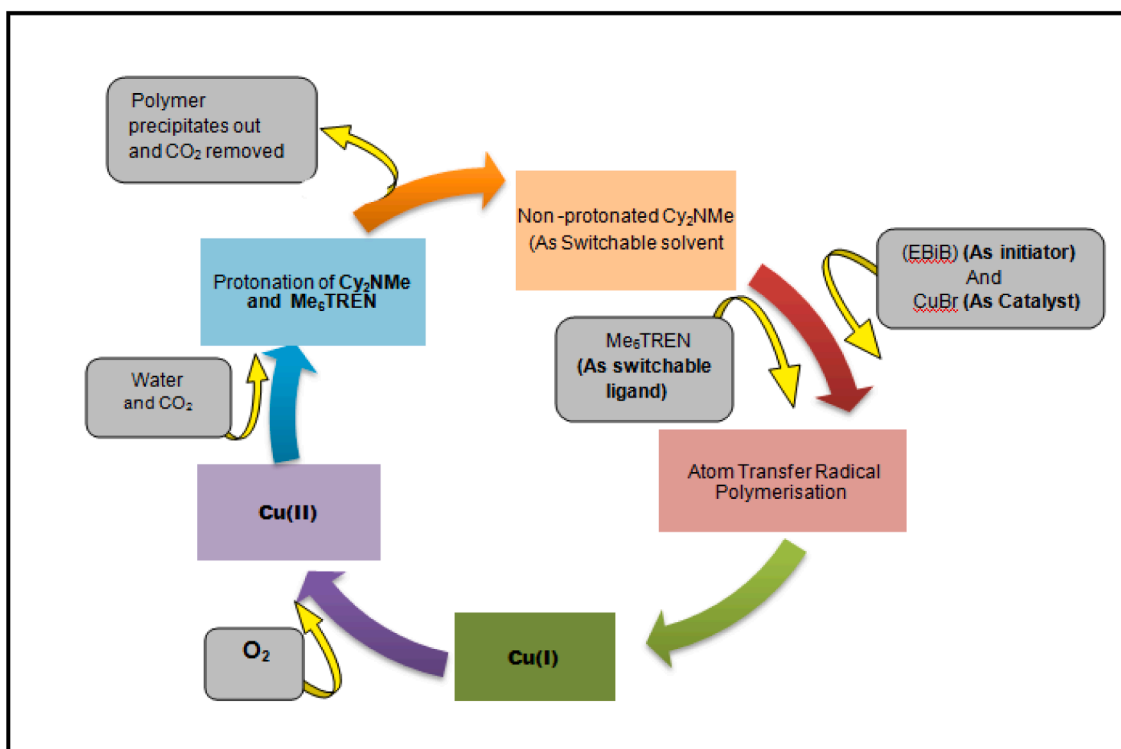


Figure 9. Outlines the use of a CO₂-switchable solvent (Cy₂NMe) N, N-dicyclohexylmethylamine for the Atom Transfer Reaction Polymerization (ATRP). Following polymerization, addition of water and CO₂ sparging result in the ligand (Me₆TREN) and copper salt.

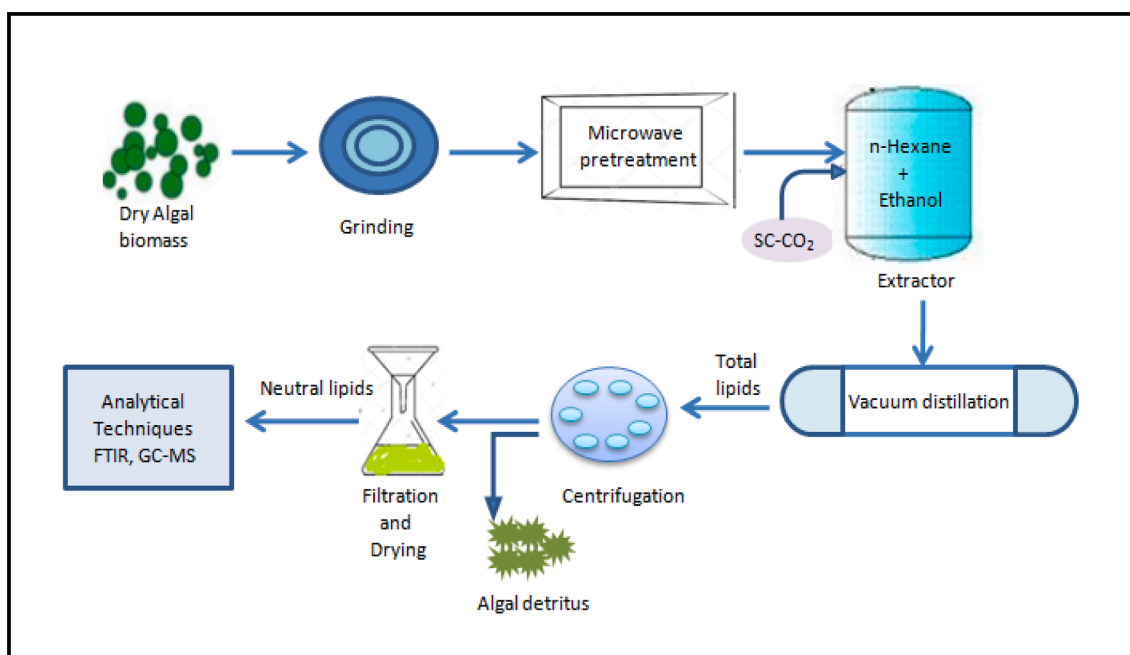


Figure 10. Schematic diagram to show the extraction of algal bio-oil using SC-CO₂ and 1:1 mixture of n-hexane and ethanol.

conditions produced about 25-30% on total extracted algal bio-oil [42-47].

4. Chemical Looping Combustion (CLC) technique for CO₂ sequestration

CLC has emerged out to be a most promising combustion technology

for CO₂ capture. According to Mukherjee et al, CLC technique has showed $\approx 100\%$ CO₂ capture when compared with other pre-combustion methods having much lesser ($\approx 94.8\%$) CO₂ capture rate. Even more, the results of energy penalties from various methods such as CLC, pre-combustion and oxy-fuel combustion (4.5%, 7.1%, 9.1%) has proved that CLC is most promising among all [48]. According to Nareja et al, CLC is a greener technology for capturing CO₂. This technique is able to

sequester enough CO_2 streams produced due to flameless combustion of fuel by utilizing periodical oxidation and reduction of an oxygen carrier (OC) [11]. OC are fine metal particles which usually transfers oxygen from the air reactor (AR) to the fuel reactor (FR) for the combustion of fuel. Hence, oxidized OC after the supply of oxygen to FR undergoes reduction and reduced to metal. Thereafter, the reduced OC again moves to the AR so as to get back to its original oxidized form. This sets a continual combustion loop between AR and FR. For the same reason, the gases evolved will be free from N_2 and majorly contains CO_2 and H_2O . Therefore, the condensation of steam is easy as well as CO_2 can be sequestered. [14,49]

4.0.0.1. Principle and involved

According to Nandy et al, CLC included metal/metal oxide often called as OC that has helped in completing the cyclic loop between the two reactors involved in this technique. In fact, OC was involved in the transfer of oxygen from AR to FR for the combustion of fuel by keeping away the contact between air and the fuel. Nandy et al had used CLC process, that includes two reactors namely air reactor (AR) and fuel reactor (FR) and these were interconnected. As per the technique, FR was carrying the fuel and the OC was used for the oxidation of fuel. The stream of gas exiting from the FR mainly contains CO_2 and H_2O . Thereafter, the pure CO_2 was separated out at low energy cost followed by condensation of water as shown in figure 11.

In fact, in the AR, air was introduced and the OC particles were oxidised. These oxidised OCs were then transported to the FR. These OCs were then reacted with the gaseous fuel available in FR. After the reaction, the fuel was oxidized and the OC was reduced. The reduced OCs (metal oxide particles) were then again returned to the AR so that they can re-oxidize by the stream of air so that they can enter into next cycle. Thus, a cyclic loop was set between the AR and the FR to avoid direct mixing of gases between the AR and FR. Hence, the main aim of this technique was to transfer oxygen from the AR to the FR without nitrogen contaminants [12]

5. Cost effective parameters of SPS over other techniques for CO_2 capture

According to the recent studies, SPS have gained much attention of researchers due to their immense potential to reduce energy penalties and cost of equipment required for CO_2 capture when compared with other methods of CCS [50-54]. In fact, Zhuang and his coworkers has

presented a review of ten years of research that centralizes the role of SPS for CO_2 capture [55]. SPS are bi-phasic solvents, usually in single phase before addition of CO_2 and after absorption of CO_2 they shift towards a two- phase system. In these SPS, only the two- phase system or CO_2 rich phase is required for regeneration of solvent. This eventually leads to the decrease in the mass of the solvent that is to be regenerated [9,56,57]. As a consequence, the heat required for the regeneration of solvent (sensible heat) is greatly reduced. Therefore, these solvents are considered to be **energy harvesters** for CO_2 capture process. Moreover, according to the concept of phase equilibrium, higher concentration of CO_2 in CO_2 rich phase elevates the partial pressure of CO_2 and thus reduces the stripping heat (utilization of heat energy associated with the vaporization of water from CO_2 rich phase) as well as reduces the costs of involved equipment. Hence, these SPS tends to minimize all the energy parameters associated with solvent regeneration. Conventionally, energy penalties of any process are responsible for increasing the cost and making it expensive. That being a case, definitely, SPS are thought to be cost-effective solvents for CO_2 capture. Zhang et al and Raynal et al, has reported that the energy penalties corresponding to the SPS involved in CCS can be minimized to 0.22–0.25 kWh/kg of CO_2 . [58-60]. On the other hand, the use of super-critical solvents is definitely an efficient technology to sequester large-scale availability of CO_2 but this technology has certain constraints that more conspicuous. In SFE, the super-critical solvent needs to be maintained in its super-critical state, hence, high pressure conditions are required [61]. Hence, the use of SPS for the CCS technology is definitely a more efficient and cost-effective technique over SFE technology because SFE utilizes solvents at high pressure that increases the cost of technology for sequestering CO_2 . Nevertheless, SPS composed of organic or non-aqueous solvents are advantageous over traditional aqueous solvents due to their low heat capacity, minimal stripping heat and reaction heat, those are certainly beneficial to minimize other energy penalties [62-64]. Conversely, the CLC technique is also having great potential insights for capturing CO_2 and for power generation. But there are certain perspectives that need to be considered while opting for more greener and low-cost technology. In this technique, both the reactor systems AR and FR are maintained under controlled pressure conditions. These operative pressurized conditions are again an obligation while attaining a low-cost technique for CO_2 capture [65]. However, such obligations are restricted for CO_2 capture via SPS as no controlled conditions are required. Moreover, SPS composed of the organic solvents are really cost-effective as they reduce the risk of equipment corrosion. However, a true estimation for cost and efficiency of SPS for CO_2 capture is not fully assessed as per the available

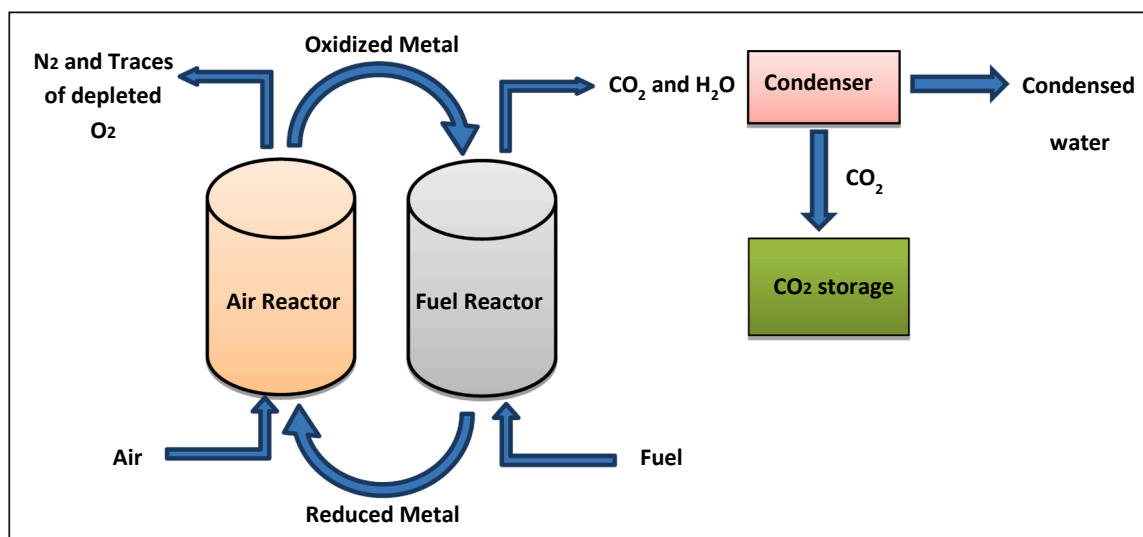


Figure 11. Illustration to show the CO_2 Sequestration using CLC technique.

reported literature.

6. Challenges and future Considerations

The switchable polarity solvents assumed to be promising solvents for CO₂ gas capture. However, when practical aspect is taken into consideration it is found that industrial waste, accidental spills and waste obtained due to solvent degradation are found to be toxic and tend to produce serious concerns to health of human beings and on the environment as well [66,67]. The gas also contains impurities such as HCl, NH₃ etc therefore the efficient absorption of the gas now becomes a matter of concern. This fact has drawn the attention of the researchers towards amine containing switchable polarity solvents in recent years. Particularly, the evolution of nitrosamines and nitramines from these solvents is a matter of great concern [68,69]. Moreover, Thitakamol and his coworkers has even reported certain inherent toxins evolved from the classical CO₂ capturing solvents with their probable implications on humans and environment after investigating their toxicological aspects that were collected from Material Safety Data Sheets [70,71]. As SPS also possess these amine-based materials similar to classical single-phase solvents for CO₂ sequestration hence they may be significantly similar in their toxicity levels as well. However, SPS come into the light with great possibilities hence by acquiring a cognizance related to their toxicological aspects will be of great help for framing new solvents for capturing CO₂ with less adverse effects on environment and bio-diversity [72]. In fact, it has been reported that their thermal and oxidative degradation rates increases with the temperature and the extent of CO₂ loading [73]. Even more, revelation of the fact that the primary and secondary amines of SPS can degrade at very minimal temperature (100 – 130 °C) as they form cyclic oxazolidinones and their carbamates forms urea. However, tertiary amines without methyl groups are much stable at elevated temperatures [74]. Hence their oxidative stability depends upon various factors such as CO₂ loading, concentration of amine, temperature etc which needs a consideration before their use [75]. Moreover, the SPS designed from amidine/guanidine and CO₂ are found to be very effective for CO₂ sequestration. Yet, practically the use of amidine and guanidine for CO₂ capture is still controversial as these are very expensive. Nevertheless, in a recent study, Mantripragada and his co-workers had estimated the approximate cost (\$43–73/ton) of capturing CO₂ from 90% of the CO₂ emissions of a power plant using SPS [76]. Even more, Mumford et al, had mentioned that Boundary Dam power plant, Canada and Petra Nova power plant, U.S. had used these amine-based solvents to capture 90% of the CO₂ that obtained due to combustion of coal [77].

Even, supercritical fluids especially SC-CO₂ is found to be promising solvents for Supercritical Fluid Extraction (SFE) technology, thereby also can be another possible way to sequester the CO₂. As the large feedstocks of bio-masses are available for the extraction of bio-fuels, they are the solvents of great help for the ease extraction and separation of bio-oils [41,77]. They are often called as “green solvents” due to their environmental benefits and specifically low energy penalties. The use of SC-CO₂ for the extraction of bio-oils is efficient method to utilize and reduce the large-scale availability of environmental CO₂. In fact, it is a solvent with versatile applications as it is non-cancerous, possesses low toxicity, cost-effective, available on large-scale and thermodynamically stable. Supercritical fluids are usually used in nation - wide chemical industries for the extraction processes. Yet they have a limitation i.e SFE must be employed at the high pressure so as to maintain the solvent in its supercritical state and therefore it requires higher costs [78]. Moreover, the some of the organic extracts (bio-oils) are temperature sensitive and may have a possibility to decompose at very high temperature; hence supercritical fluid extraction cannot be useful in that situation and thus need to be considered while using this SFE.

Moreover, CLC technique has emerged up as a most potential technology to be at service for power generation as well as CO₂ capture. This technique is found to be most promising when ecological issues are kept

in mind as it is environmentally safe, cost-effective and often includes low energy penalties [79–81]. In last few decades, it has come to light as a greener technology for the generation of power on a commercial scale. Therefore, with little amendments and developments in the technology give this CLC technique a futuristic potential insight. Yet there are certain perspectives to be kept in mind before its large-scale commercialization. In CLC, the reactor systems are usually operated under atmospheric pressure. Thus, pressurized operational conditions is a big challenge to be met with. Even, substantial studies over OC had been conducted over the period of time has shown up that if the OC are prepared by lab-based procedures, then energy penalties are of great concern [82,83]. However, OC synthesized from naturally occurring minerals are found to have better environmental performances [84,85]. Thus, in order to improve and enhance their application researchers may focus more on the better design and new advancements that can be made in solvents and techniques for effective CO₂ sequestration with less implications on the environment and thus helps in reducing atmospheric CO₂ levels in a better way.

7. Conclusion

The environmental and greenhouse gas CO₂ is a low cost, eco-friendly and non-toxic trigger which is used to synthesize switchable polarity solvents. These solvents often switch their polarity from lower to higher on the application of CO₂ trigger. These switchable solvents found have many roles and applications. It is really practicable to apply them in various fields such as waste water treatment, Gas capture media, Syngas production, Biodiesel formation and many more. So, these supposed to be the promising materials with great future scopes. Still there are many applications being yet to be discovered and great advancements yet to be made with these “Smart Materials”. In fact, the renewable energy is supposed to be a dynamic area research that also includes bio-masses which are considered as feedstock for production of bio-fuels such as bio-diesel, biogas, etc. Therefore, the principles of green chemistry must be integrated with the consumption of renewable resources to generate eco-sustainable generation of bio-energy. Supercritical fluid extraction follows these principles and thus allows non-toxic and non-carcinogenic solvent and catalyst utilization for generation of bio-fuel. In fact, more efficient and potential techniques are to be intended in order to utilize the available feedstock of bio-masses as a source of renewable and bio-energy. Presently, Carbon capture and its sequestration is a major challenge posed by activities that cause climate change. CLC is definitely a defensible approach towards maintaining the current ecological imbalance in carbon cycle across the globe. Nevertheless, the feasibility of the proposed technique and futuristic researches of the detailed oxidation and reduction kinetics, choice of OC, types of fuel etc of the CLC technique are currently under way.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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