

# Environmental management of industrial decarbonization with focus on chemical sectors: A review

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## ABSTRACT

A considerable portion of fossil CO<sub>2</sub> emissions comes from the energy sector for production of heat and electricity. The industrial sector has the second order in emission in which the main parts are released from energy-intensive industries, namely metallurgy, building materials, chemicals, and manufacturing. The decarbonization of industrial wastes contemplates the classic decarbonization through optimization of conventional processes as well as utilization of renewable energy and resources. The upgrading of existing processes and integration of the methodologies with a focus on efficiency improvement and reduction of energy consumption and the environment is the main focus of this review. The implementation of renewable energy and feedstocks, green electrification, energy conversion methodologies, carbon capture, and utilization, and storage are also covered. The main objectives of this review are towards chemical industries by introducing the potential technology enhancement at different subsectors. For this purpose, state-of-the-art roadmaps and pathways from the literature findings are presented. Both common and innovative renewable attempts are needed to reach out both short- and long-term deep decarbonization targets. Even though all of the innovative solutions are not economically viable at the industrial scale, they play a crucial role during and after the energy transition interval.

## 1. Introduction

Mitigation of greenhouse gas emissions is one of the most important challenges ahead of humankind in the current century. In order to reduce the climate change impact, CO<sub>2</sub> emissions should decrease considerably at all the steps of our life. A decrease in primary energy demand such as allowable fossil fuel consumption over time, energy optimization, and economically feasible efficiency improvements are noticeable in all sustainable scenarios (Kanchiralla et al., 2021; Pittel, 2019; Srivastava et al., 2021; Sweygers et al., 2021). The target of the European Union is drastic reduction of carbon footprint up to 80–95% in industrial and residential sectors by 2050 (Ávila et al., 2018; Geden et al., 2019; Pittel, 2019). In the past decade, 45% of global CO<sub>2</sub>

emissions was originated from the energy sectors including electricity and heat production, while, industrial sectors metals contribute to 23% of CO<sub>2</sub> emissions (Peters et al., 2019). The share of industrial subsectors on a total CO<sub>2</sub> emission based on the European ETS in 2018 includes 6.21% from the petro-/chemical and refineries, 5.06% from iron and steel, 4.14% from cement, 1.15 from fertilizers, 0.92% from lime and plasters, 0.92% from paper and pulp, 0.46% from inorganic chemicals and 4.14% from the other sub-sectors (Bruyn et al., 2020). Transportation contributes to 22.5% of the emissions, while the remaining emissions arise from other sectors, mainly buildings and agriculture (Peters et al., 2019).

Over the past decades, industrial sectors have implemented optimized systems for the reduction of costs and energy demands, which

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have significantly reduced the consumption of fossil fuels, while the focus was on the improvement of main processes, but not on the replacement of technologies, raw material or energy resources. A circular economy via looping of products and implementation of novel techniques for the reduction of energy consumption can help further the emission reduction at the process level. Moreover, the current debates on carbon footprint are more on the replacement of fossil fuels with renewable resources, development of cutting edge technologies, low-temperature heat management, electrification with green energies, and other economic abatement options that could reduce the carbon intensity in industrial processes (Chao et al., 2020; Luderer et al., 2019). The emission in the greenhouse gas (GHG) category includes CH<sub>4</sub> and N<sub>2</sub>O in addition to CO<sub>2</sub> and fluorinated gases mostly from the ceramics industry, while CH<sub>4</sub> and N<sub>2</sub>O are the essential releases from agro-industrial sectors and fiber production (Baeyens et al., 2015; Bretas et al., 2020; Kang et al., 2015; Van der Weerden et al., 2017).

Current chemical products are fossil fuel-driven worldwide, including oil and natural gas as they emit CO<sub>2</sub> after they are burnt [9]. Emission from natural gas is 25% less than oil, but it can be a considerable hazard to the ecosystem and environment due to the possible leakages of methane (CH<sub>4</sub>) at both extraction sites and distribution networks. At equal rates of emitted GHG gases, CH<sub>4</sub> has a 20 to 23-times higher effect on global warming in comparison to CO<sub>2</sub> [9], and hence, utilization of renewable energies instead of fossil fuels increases progressively. This transition requires novel chemical reaction technologies and essential changes in the petrochemical processes (Centi et al., 2019; Dupont and Oberthür, 2015). Moreover, to reach the target of net-zero GHG emission, innovative approaches, models, and technologies are needed. For example, hydrogen systems are one of the predominant pathways for future industrial development and grid stabilization, which require new and economically viable infrastructures for implementing the regional green supply (Lieshout et al., 2018). Additionally, switching to non-fossil feedstocks such as biomass and pyrolysis or catalytic depolymerization of plastic wastes, besides electricity-based heat generation at industrial scales are some of the alternative replacements for conventional fossil fuels (Deng et al., 2021; Pous et al., 2019; Reddy et al., 2020c; Vispute et al., 2010).

Walsh et al. (2017), introduced several scenarios for reducing the fossil fuel consumption with emission reduction to less than 25% by about 2100 at the primary energy supply and they suggested to drop further allowable fossil fuel consumption rate to reach the global negative emissions. Economical CO<sub>2</sub> removal from the atmosphere, smart and adequate infrastructure that guarantees interconnection, sectoral symbiosis, cross-border and regional activities, digitalization, electrification, further integration of relevant sectors, smart electricity grids, and hydrogen pipelines are the surpass techniques to pioneer energy transition to reap the benefits of a modernized and transformed European economy (Iora et al., 2016; Luderer et al., 2019; Spurgeon and Kumar, 2018). The industrial symbiosis is where the companies and sectors cooperate to optimize their feedstock supply, energy and waste flows to cooperate with other sectors such as agriculture, food, energy, and building utilities. Hence, the synergies of industries play an important role in GHG emission reduction. For instance, waste gas from steel manufacturers can be captured and utilized to produce high value-added chemicals (Fresta and Costa, 2017; Usubharatana et al., 2006).

To reach the highest degree of decarbonization, carbon capture and storage (CCS) is a promising technology that requires more development and implementation in the industrial sectors (Pous et al., 2019; Sharma et al., 2020b, 2020c). This technology suggests CO<sub>2</sub> capturing via the gas separation processes from industrial flue gases before emission into the atmosphere (Deng et al., 2021; Usubharatana et al., 2006). Furthermore, in the case of fossil-based syngases as feedstocks for a process, considerable amounts of CO and CO<sub>2</sub> are available. Hence, the advanced capturing of CO<sub>2</sub> has more advantages due to its higher pressures and richer concentration (Hajilary and Rezakazemi, 2018; Zhou et al.,

2021b). Different capture and separation technologies via the several methodologies exist, but their installation and operational costs depend on CO<sub>2</sub> amount, CO<sub>2</sub> concentration, partial pressure as well as concentrations of contaminants such as nitrogen (Abdelkareem et al., 2021; Imteyaz et al., 2021). Capture technologies are typically categorized as pre-combustion, oxy-fuel combustion, and post-combustion processes (Shah et al., 2021; Younas et al., 2020b). The post-, pre-, and oxy-fuel combustion carbon capture technologies make use of various materials and separation methods depending on the need and demand (Shamsabadi et al., 2021).

Pre-combustion capture is applicable in gasification at high temperatures to produce CO and H<sub>2</sub> to form the synthetic gas. Oxygen is separated from air in the initial steps, which is utilized for the gasification of fuel. While in the post-combustion capture, air is utilized as the conventional plants, and CO<sub>2</sub> is separated from the flue gas. Moreover, in oxy-fuel combustion technology, fuel is burnt by utilizing oxygen rather than air. The resulting end-stage mixture contains CO<sub>2</sub> and condensable water vapor in which water can be separated from CO<sub>2</sub> during the compression process (Abdelkareem et al., 2021; Younas et al., 2020a). The post-combustion route is the most mature technology, which is the widely used approach among the other three carbon capture and storage technologies (Araújo and de Medeiros, 2021). However, due to the presence of nitrogen in air, CO<sub>2</sub> is diluted and is has lesser partial pressure and hence, electricity generation costs are high by approximately 60–70% for a new infrastructure (Osman et al., 2021).

The CCS can be combined with combustion of sustainable biomass or other processes as well and the captured CO<sub>2</sub> can be permanently stored or used as a feedstock at different industries such as plastic and building materials production (CCU) (Solano Rodriguez et al., 2017). De Luna et al. (De Luna et al., 2019), investigated the CO<sub>2</sub> conversion into valuable hydrocarbons such as syngas, ethylene, and ethanol through electrochemical conversion. This research emphasized that coupling CO<sub>2</sub> reduction with renewable electricity resources or biomass power plants will lead to a negative slope on the net carbon emissions footprint (Ricke et al., 2017). Furthermore, to achieve the goals of the energy transition, European countries took major political decisions on reliable, affordable, and clean energy sources (Bosman et al., 2014; Forster et al., 2020). Therefore, CO<sub>2</sub> pricing structures are going to change by taking the social fair steps assisted with the governmental supports (Sharma et al., 2020a). This review provides the essential contributions on the existing and under developmental technologies facing the energy transition and carbon mitigation. Various areas of research that can improve the environmental effects of industrial sectors as well as energy-saving and greening of the process plants are discussed. Besides a thorough exploration of the renewable energy and feedstock resources, disruptive technologies are introduced for both the integrable technologies to the existing plants and for the new production routes.

## 2. Energy-intensive industry

The energy-intensive industry (EII), which has an important involvement in GHG emissions, requires thorough development and upgrades at all the energy, feedstock, and technology levels. The EII includes CO<sub>2</sub> intensive subsectors, namely construction, metal, iron, and steel production, petrochemicals, refineries, cement and ceramics, paper/pulp, food and drinks that require high-temperature processes, and the heat provided by high calorific value fossil fuels (Alshammari, 2021; Besier, 2021; Scalbi et al., 2021; Williams et al.,). Moreover, majority of these industries are conservative towards the changes (Ávila et al., 2018). Hence, allocating competitive technologies in EIIs and implementation of state-of-the-art techniques are essential for pushing of EIIs towards emission reduction. However, new unproven technologies with high risks on costs, payback periods, possible economic damages, and the level of maturity will face stiff competition in the long run (Ávila et al., 2018).

Different EU countries are following various pathways and

technologies to reach carbon-neutral industries by about 2050. Germany is focusing on syngas and  $H_2$  production by adjusting the flexibility of different sectors to utilize the periodic excess renewable electricity (Srivastava et al., 2020a, b). Dutch and Swedish regions concentrate on a low carbon economy by electrification of industry, while the approaches by UK and US are slightly different by considering deep decarbonization pathways, which greatly depend on the natural gas (Ávila et al., 2018; Chassein et al., 2017). Overall, multiple energy-intensive industries (EIIs) in the EU have a share of 60% in industrial  $CO_2$  emissions, which makes them an important target for emission reduction approaches. Considering all the leading-edge renewable sources at the current technical level, high-temperature process heat requirements (over 250 °C) of EIIs can only be fulfilled economically by biomass and biogas (Chassein et al., 2017; Miryahaie et al., 2020).

The burning of biomass or products from the gasification process with high-pressure air can produce high-temperature heat for the industrial processes. Other advantages of biomass to fuel industries are that the emitted carbon dioxide from the firing process is in balance with the amount absorbed during the growth of biomass. Moreover, abundant and homogeneous distribution of biomass worldwide improves the importance of these renewable resources (Giglio et al., 2021; Henry et al., 2021). However, on the restrictions side, bio-based fuels have some fundamental limitations on providing higher temperatures, namely the combustion purity and the need for precise temperature control, which make it inadequate for some industrial processes (Samimi et al., 2020). Moreover, bio-based resources for bioenergy supply should tackle high uncertainty on the non-climate ecosystem damages, mainly due to the land requirements (Luderer et al., 2019). Therefore, decarbonization of low-grade heat through key cross-sectoral technologies is the most important and feasible target in the close future. These segmental technologies include the implementation of membranes in petrochemical industries and refineries, advanced electrochemical processes, development of electrolysis processes, electrified heat generation, hydrogen-assisted production pathways, carbon capture, and storage as well as carbon-neutral steel making (Bernardo et al., 2020; Iulianelli and Drioli, 2020; Lu and Jiao, 2016; Parvasi et al., 2020). The fulfillment of these technologies is quite limited due to the lack of scientific background, appropriate adoption of the already installed processes to the new techniques surplus to the facility, and infrastructure requirements (Ávila et al., 2018).

Economic feasibility and different approaches have been implemented in various studies for the GHG mitigation, namely top-down and technological bottom-up models. The focus of the top-down approach is market interactions of the energy sector without focusing on technical and economic feasibility. In contrast, the bottom-up approach focuses on energy technologies and relative costs (Allen, 2014; Froemelt et al., 2021; Tennison et al., 2021). These approaches follow the roadmaps published by the European subsector associations such as iron and steel, cement, lime, or ceramic industry decarbonization (Ávila et al., 2018; Fennell et al., 2021; Gielen et al., 2020; Kaljuvee et al., 2001).

### 3. Development of classic decarbonization solutions

In efforts to reach the determined average global temperature by 2050, which is at the maximum of 2 °C higher than its value before the industrial revolution, the global greenhouse gas (GHG) emissions should diminish very fast and emissions from the industries require to be mitigated by about 80–90% compared to 1990 (Xu and Ramanathan, 2017). The severe issue that industries face for this huge emission reduction is that production processes require very high temperatures, which cannot be achieved with the current technologies sufficiently. Although some industrial subsectors such as washing and drying processes in food processing companies operate below 150 °C, the distillation processes, boilers, and reactors in chemical industries require heat with temperatures  $\geq 250$ –750 °C; iron and steel production processes need even higher temperatures. These temperature requirements of

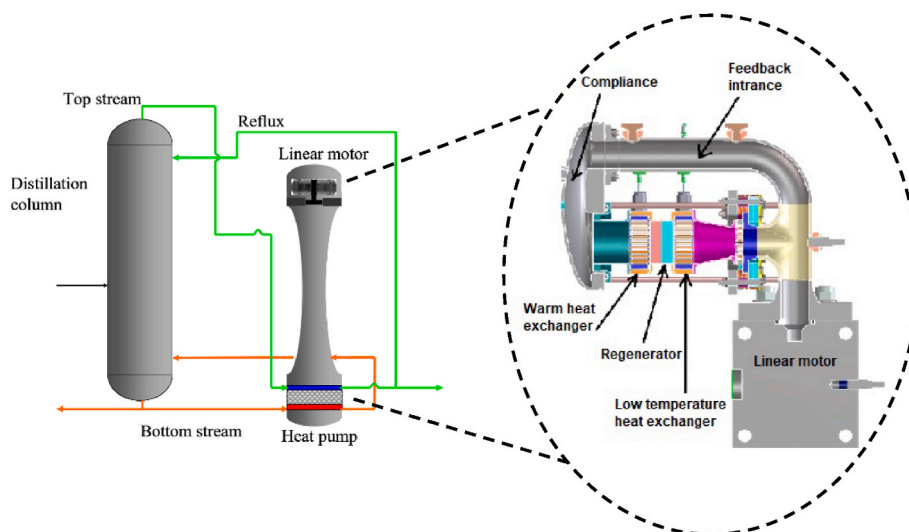
different sectors are the best examples for the assortment of new and combined technologies aiming at energy and emission reduction at the industrial level. In this review, detailed discussions of the technologies for upgrading a selection of processes are discussed and the potential improvements for optimization of the already installed plants are illustrated by introducing innovative techniques and state-of-the-art technologies. For example, retrofitting of the existing plants via the hydrogen and biofuels generation, novel hybrid systems, and enhancing the flexibility of the existing power plants, are within the framework of industrial carbon mitigation (Anniwaer et al., 2021; Daraei et al., 2021; Davarazar et al., 2019; Hameed et al., 2021; Kamali et al., 2019c; Piazzi et al., 2021).

#### 3.1. Stretching the operating boundaries

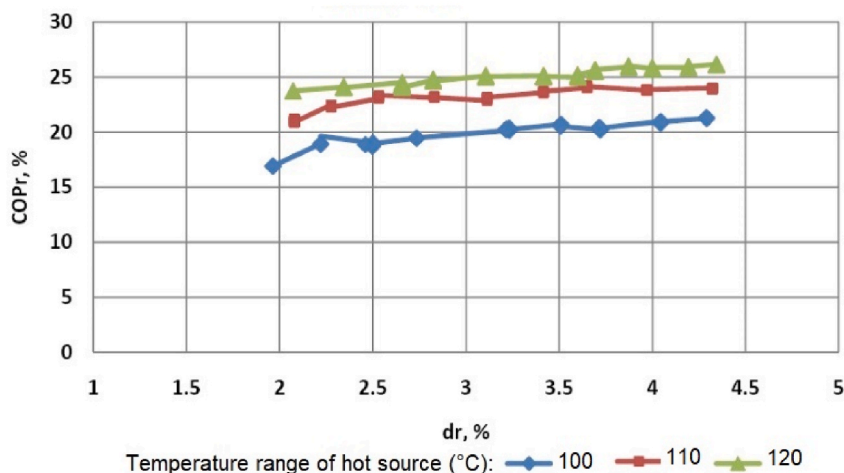
Conventional technologies and processes are already running based on the defined operating boundaries such as optimized temperature and pressure, which are compatible with the fossil-driven energy resources. Therefore, one important innovation towards decarbonization and electrification is the extension of operating conditions by introducing more flexible processes, equipment, and energy resources. Enlarging the process equipment at energy-intensive plants, making parallel plants, developing flexible control systems, generating new heat networks, which involve different types of energy buffers, and solving other related issues ahead of industries can enable the energy transition of EIIs (Iora et al., 2016; van Kranenburg et al., 2016). For instance, electrical-driven heat pumps, which are highly efficient, can upgrade the low-grade heat temperatures up to 250 °C. New working media, compressors, and turbines will bring more flexibility to the unit operation and industrial processes. For instance, an electrically driven thermo-acoustic heat pump can enhance the industrial residual heat to higher grades and circulate the energy internally to diminish the external utility requirements of the plant. This technology upgrades heat temperatures from 50 to 120 to 100–200 °C (van Kranenburg et al., 2016). The thermoacoustic heat pump is equipped with a helium-filled acoustic resonator and driver to create acoustic waves as a force for circulating the working media of heat pump between low- and high-temperature heat exchangers, which is insensitive to temperature fluctuations of the heat source. Working at a large range of temperatures and the possibility of swapping hot and cold streams simultaneously, a thermoacoustic heat pump can be implemented in a distillation process. The cold sink of such heat pump is the condenser on top of the distillation tower and the heat sink is the reboiler heat requirements at the bottom of the tower as depicted in Fig. 1a. Tijani et al., [38–40] tested the already designed heat pump at temperature intervals between 10 and 80 °C and elevated them between 50 and 150 °C. Their results show the maximum relative coefficient of performance (COP) equal to 27% for temperatures between 50 and 120 °C, as shown in Fig. 1b. The COP was calculated from the ratio of heat to input power, which was further extended relative to the Carnot value. By the installation of this heat pump, low-temperature heat at 50–80 °C available from the condenser at the top of the column was utilized for the reboiler side of the column providing temperatures up to 100–150 °C (Spoelstra and Tijani, 2005; Tijani et al., 2011, 2016; Xu et al., 2022). This technology significantly reduces the required energy for cooling on top and heating at the bottom of the distillation column. However, the consequence of fewer energy requirements is the considerable reduction of fuel consumption and emissions.

#### 3.2. Improved electrochemical system

Electrochemical processes to produce hydrocarbons from  $CO_2$  and water are the widely explored electrochemistry concepts that can improve reaction efficiency, activity, and selectivity. The concept is to provide required electrons for the process from green sources such as solar and wind power and reduce  $CO_2$  into high-value-added chemicals



(a)



(b)

**Fig. 1.** (a) Integration-of thermoacoustic and distillation column, the CAD-illustration of the heat pump cross-section, (b)  $COP_r$  as a function of the drive ratio at different temperatures (Tijani et al., 2011).

such as methane, methanol, ethylene, and formic acid (Pappijn et al., 2020; van Kranenburg et al., 2016). Overall, the high energy efficiency and flexible electrochemical systems that can be combined with other systems can reduce the operating process costs. Improved electrocatalysts, the decline of processing steps, and *in-situ* product separation are some of the other techniques to reduce the capital investments, making the whole system economically viable and thereby, improving the business. Accordingly, the focus on novel electro-catalysts should be on the performance increment and the development of more stable materials (Sodeifian et al., 2019; van Kranenburg et al., 2016). However, one approach is to find new alloys for bimetallic catalysts production in which the target is to affect the electronic nature and function of the materials. For example, see the production of nanostructured copper foam with a high electrocatalytic surface area as shown in Fig. 2a. Furthermore, modification of catalyst nanostructure can affect its performance.

Enhancing the nanoparticles in a path that each dimension of the catalyst becomes selective for different reactions is another field of investigation for elevating the electrochemical system performance (van Kranenburg et al., 2016). Alternatively, innovative photo-electrochemical  $CO_2$  reduction process is useful towards green-fuel production by the direct sunbeams. The covalent attachment of molecular  $CO_2$  to the surface of reduction catalysts such as  $TiO_2$ -protected  $Cu_2O$  photocathodes occurs by the phosphonate linkers as shown in Fig. 2a. One of the produced molecules is  $CO$ , which incorporates between phosphonate and bipyridyl moieties to adjust the electronic structure of the catalyst. A technique for the preparation of  $Cu_2O$  photocathodes is electrodeposition, which can be followed by the atomic layer deposition of Al-doped zinc-oxide (ZnO) and functionalized  $TiO_2$  nanoparticles (Schreier et al., 2016). Different catalysts were investigated for the Sunlight-driven  $CO_2$  reduction to achieve the high value-added hydrocarbons. Even though several challenging studies on



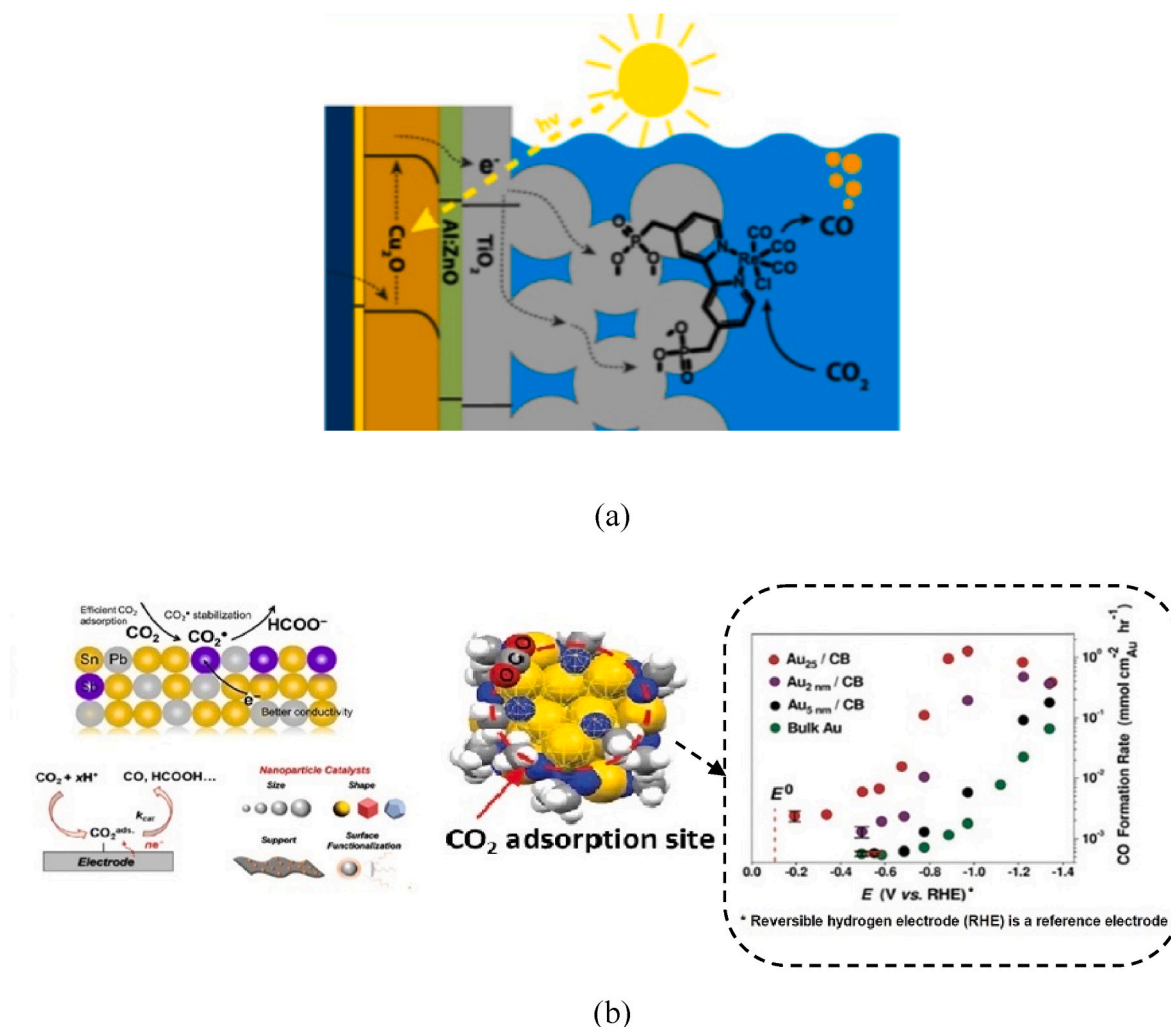


Fig. 2. (a) Schematic Sunlight-driven CO<sub>2</sub> reduction (Schreier et al., 2016), (b) CO<sub>2</sub> reduction on catalyst surface (Franco et al., 2020; Rasul et al., 2019).

CO<sub>2</sub> reduction have demonstrated a high achievement, still more efforts are needed for the scale-up to make them commercially viable. The particle size of the catalyst and its shape is important in CO<sub>2</sub> reduction on their surfaces by creating adsorption for electron exchange sites (Franco et al., 2020; Mayer, 2020).

Franco et al. (2020), investigated the electrochemical reduction of CO<sub>2</sub> using organometallics and molecular catalysis, which opened new research frontiers for designing and production of the selective and heterogeneous catalysts for CO<sub>2</sub> reduction. This research discussed the application mechanism of catalysts for CO<sub>2</sub> conversion to CO; a summary of these effects and the mechanisms are illustrated in Fig. 2b.

### 3.3. Maximized process optimization by standardized equipment

Equipments required for EIs such as furnaces, kilns, distillation columns, and drying can be used for the production of basic materials (Ávila et al., 2018). In contrast, the standardized equipment such as heat exchangers, heat pumps, or (hybrid)-boilers in which novel designs can replace them to reduce carbon footprint. Even though new technologies on waste reduction, heat provision, and process control cannot decarbonize the industrial emissions completely, improvement of these techniques can considerably decrease the emission (Ávila et al., 2018; Rajabloo et al., 2016, 2017). The hybrid operation mode assisted by the membrane-based separation technologies provides additional energy savings as well as the overall cost reduction. For example, hybrid fermentation-distillation mode can reduce the inhibition risk of the

fermenter ethanol and consequently the heat. The other novel technologies to optimize the existing processes such as ethanol production plants are direct membrane distillation and air gap membrane distillation processes coupled with fermentation as well as very high gravity fermentation methodologies (Baeyens et al., 2015). Furthermore, de-dusting of hot gases, especially in advanced power generation systems and petro-/chemical processes can improve the dew points and energy recovery at higher temperatures. Moreover, dust removal from hot gas protects the downstream heat recovery equipment from fouling or erosion, which can simplify the overall process. Additional benefits are the mitigation of power consumption and simultaneously capturing the gaseous pollutants (Li et al., 2021a).

### 3.4. Furnaces

Furnaces can provide high-temperature requirements of all the EII subsectors that are vital for hydro-metallurgy and pyro-metallurgy as well as for non-metallic and composite materials such as reinforced carbon fiber plastics (Ávila et al., 2018; Nuhiji et al., 2020). The laboratory-scale tests have proved that microwave-supported heating decreased the emissions from these processes by >50% (Ávila et al., 2018). Moreover, the advancing of air-assisted industrial combustion by the reduction of equipment size, providing uniform thermal distribution on the entire combustion zone at the furnaces, which burn fossil fuels to produce high-temperature heat have led to emission reduction, which is estimated to save nearly 180 Billion tons/year of CO<sub>2</sub> by about 2030

(Weber et al., 2020). In the ceramic sector, several applicable methods of energy-efficient technologies have been investigated to improve furnaces as well as variable frequency inverters, single-stage pressing-glazing, airless drying, implementation of sophisticated sensors and control systems (Agrafiotis and Tsoutsos, 2001; Branca et al., 2021; Luberti et al., 2022; Salomão et al., 2021). Furthermore, full electrification of furnaces in glass industries, besides the plasma melting technologies have been proved to be feasible and requires scale-up studies (Ávila et al., 2018).

### 3.5. Heat pumps and process heat recovery

Since all the EIs entail process heat efficiency improvement, heat circularity and management are unavoidable for emission reduction. In addition, industrial subsectors with multiple process steps such as food, drinks, refineries, and petrochemicals are more sensitive to process stability and safety issues. Hence, more flexible and compatible technologies are lacking to boost the heat circularity to efficiently improve the emission abatements (Cooper et al., 2019; Damasceno et al., 2020; Koufos and Retsina, 2001; Lerdlattaporn et al., 2021).

Heat pumps are the well-established technologies that are based on the primary studies that have shown their abilities for electro-thermal technology-based heat production. Heat sources for heat pumps can be supplied from various sources like air, lake, seawater, river, ground heat, or waste heat. Heat pumps intake one unit of electricity and produces 2–6 units of thermal energy depending on the heat sink temperature (Gerres et al., 2019; Mateu-Royo et al., 2020). A small number of heat pumps are installed that are operating in industries mainly for space heating and cooling. Refrigeration, low-grade steam production, drying, simultaneous heating and cooling, evaporation, cleaning, and distillation processes are the other areas that require heat pumps. Therefore, it is necessary to increase the heat pump installations to consider the market and economic models, which can reduce the fuel consumption by more than 40% (Gerres et al., 2019; Zhang et al., 2016b). However, waste heat recovery is currently developed at some stable and high-temperature sectors, but they lack technologies for the integration with non-steady processes (Compernelle et al., 2011).

### 3.6. Catalytic processes and membrane separations

In petrochemical industries, nearly 50% of process emissions come from the separation and cracking processes due to their high-temperature functions and consequently their high fuel demand. Current technologies are utilizing the catalysts assisted liquid distillation, but these are to be replaced by the membrane-assisted catalytic processes for a significant emission reduction. Implementation of membranes can reduce the temperature levels, but other alternative separation processes from thermal driven paths to mechanical aspects where the energy is used in the form of pressure instead of heat. It was estimated that membrane-based separations require 90% less energy in comparison to thermal separation processes (Alexis Michael Bazzanella and Ausfelder, 2017; Alrashed et al., 2021a, 2021b). Nanocomposite membranes phase may essentially help the decarbonization technologies once the commercial scales have emerged. Furthermore, membrane distillation (MD), which is a combination of membrane and distillation technology is crucial in petrochemical subsectors (Jyothi et al., 2019; Kamali et al., 2019a, 2019b, 2019c; Mosleh et al., 2017; Zandi et al., 2019). This hybrid distillation technology can achieve near to the ideal separation efficiencies to save energy by about 30%. Membrane-assisted technologies can also assist the separation processes in food and drinks industries as well as for the carbon capture and sequestration. The majority of novel membranes include carbon molecular sieves, polymers, and organic microporous membranes that their implementation at different industrial subsectors can reduce emissions between 5 and 45% depending on the nature of the sectors (Ahmed et al., 2020; Anyanwu et al., 2022; Hussin and Aroua, 2020; Li et al., 2022a; Rezakazemi et al.,

2018; Rozyyev et al., 2021; Shah et al., 2020; Yang et al., 2020).

## 4. Renewable energy and resources

Renewable energy and resources are the most essential elements towards the decarbonization due to flexibilities in feedstock and carbon-based fuel replacements. In this respect and hybrid renewable energy integrated systems are under the active investigations to extend their deployment. However, these techniques suffer from the drawbacks of low and inadequate density of the renewable resources and growing demand of the energy requirements (Mbungu et al., 2020). Since the temperature requirements of different industries vary over a wide range, the enhancement of green energy, direct utilization, and combination of both are indispensable in many industrial plants (Biencinto et al., 2021). However, the main recognized renewable energy and resources are solar thermal, wind power, geothermal heat, and biomass. Moreover, electrolysis using renewable energies and production of the chemicals by developing alternative carbon sources can be categorized as a renewable molecule production (Lonis et al., 2021).

### 4.1. Solar thermal

Solar thermal technologies are quite suitable for the generation of low and medium-temperature process heat. As the main representative, food and beverage industries utilize solar thermal technologies for washing, drying, and pasteurizing processes, while solar heat can assist textile sectors in washing and bleaching processes. The solar heat is directly used in the above-mentioned processes or is utilized for the generation of steam, which can be inserted into various processes. Moreover, chemical, petrochemical, pulp, and paper sectors are the other industries that can benefit from the solar heat. In 2019, the worldwide installed solar thermal plants could save 41.9 million tons of oil and consequently, 135.1 million tons of CO<sub>2</sub> in all the sectors. Reaching high temperatures of around 400 °C by concentrating solar thermal panels increases the industrial implementation of this technology. However, the main share of the industrial market requires temperature ranges between 180 and 250 °C (Schoeneberger et al., 2020). To achieve high-temperature heat for processes, concentrating solar panels including parabolic trough concentrators, vacuum tube collectors with aggregated parabolic concentrators or parabolic dishes have been installed (Afrin et al., 2021; Carolus et al., 2019; IRENA, 2014; Lizana et al., 2020). Concentrated solar power is a promising technology for high-temperature electrolysis systems as well (Mastropasqua et al., 2020). In addition, 80% of the reached radiation on the surface of photovoltaic (PV) panels can be converted into heat, which harms electrical efficiencies. Hence, researchers have investigated the combination of PV with thermal collectors to upgrade the efficiency of the system, while generating heat and electricity simultaneously (Zhang et al., 2014; Zhou et al., 2021a).

### 4.2. Geothermal

When the distance between a geothermal heat source and an industrial plant is close enough, direct utilization of this green heat is possible. For example, the direct utilization of geothermal heat in Iceland and Greece has been the drying of fish and tomatoes, respectively (IRENA, 2014). In the United States, geothermal deep is directly utilized for heating, cooling, and thermal energy storage (Beckers et al., 2021). Research efforts have shown that geothermal resources in the USA can provide a cost-competitive, low-carbon, and flexible energy that can replace the existing coal and combined-cycle gas turbine to provide a significant long-term greenhouse gas mitigation (Ball, 2021; Hamm et al., 2021). Moreover, many geothermal fields in Chile are under development, but some are facing the expansion (Letelier et al., 2021; Maldonado et al., 2021; Maza et al., 2021; Montecinos-Cuadros et al., 2021). Geothermal heat can be converted into electricity via steam

power or the organic Rankine cycle (Gunnlaugsson, 2021; Jolie et al., 2021; Rajabloo, 2017; Rajabloo et al., 2016; Sánchez-Pastor et al., 2021). Moreover, this kind of heat source can be managed for the cogeneration of heat and power, especially for local utilization (Eyerer et al., 2020).

#### 4.3. Biomass

Biomass can grow in a rather short time, which is considered a valuable renewable resource. Once it is combined with emission-free handling and transport, biomass can be contemplated as a near-zero-emission source in the long-term because of recapturing of CO<sub>2</sub> for their growth and returning of carbon into the biosphere. Hence, the emitted CO<sub>2</sub> from the biomass processing and combustion can be circulated, while emission from fossil fuel combustion cannot be naturally recaptured (Ávila et al., 2018; Patel et al., 2016; Sedjo, 2011).

Biomass represents both a medium to high process heat production and the potential feedstock for the chemicals and polymers (Centi et al., 2019; Gómez-Marín and Bridgwater, 2020; Patel et al., 2016). As for heat generation, biomass resources such as wood, bark, charcoal, and rice husk can feed the steam boilers and small-scale blast furnaces (IRENA, 2014). Conversion of biomass to bioproducts via the thermo-chemical conversion process such as pyrolysis (torrefaction), hydro-thermal treatment, gasification, and combustion has been investigated (Aliyu et al., 2021; Bridgwater and Boocock, 2013; Park et al., 2022; Seo et al., 2021). Moreover, lingo-cellulosic biomass can be utilized for the production of pyrolysis oils or bio-oils, which are considered as cheap liquid biofuels (Vispute et al., 2010). For high-temperature heat production, gasification of biomass is required. However, steam generation through the direct burning of biomass has around 75–90% efficiency, which is less than the burning of fossil fuels with an efficiency of 85–90% (Adams et al., 2018; IRENA, 2014; Reddy et al., 2020a; Reddy et al., 2020b).

Bio-based fuels as an important primary and carbon-neutral renewable energy source have some advantages and disadvantages as well (Nguyen et al., 2021). The advantages of biofuels are biodegradability and production from the renewable biomass resources such as crops, municipal waste, sewage from animals, and forest residues. Biofuels as non-toxic fuels can be utilized in transportation as well as the generation of cleaner and affordable electricity, since it is harmless to the surrounding environment. Moreover, biofuels can integrate with other energy resources such as coal and solar PV for hybrid applications (Sivabalan et al., 2021).

On the contrary, the disadvantages for biofuels are higher production costs in comparison to fossil fuel alternatives, the required pretreatment of biomass for biofuel applications such as evaporation of water existing in the raw materials, the technology gaps especially for algae included biomass sources, decentralized production besides the complexity of production, low heat value, transportation, harvesting and pretreatment before biofuel production, and the policy gaps to overcome these challenges (Banu et al., 2021; Kargbo et al., 2021; Karka et al., 2021; Sivabalan et al., 2021; Wu et al., 2021a; Yang et al., 2021). The biofuels can be obtained from various biomass resources in which carbon to hydrogen (C/H) ratio is not always high enough. The low C/H ratio leads to less heating value and aggregated quality of the syngas. Therefore, supplementary actions such as co-pyrolysis of several biomass feedstocks with coal and/or plastic waste are needed (Ge et al., 2019a; Kawale and Kishore, 2020; Meier et al., 2013).

Hydrocarbons with more than eight carbon atoms in their molecules (C<sub>8+</sub>) oxygenates are the highly attractive fuel compounds, since they significantly reduce the soot emissions and minimize the nitrogen-oxide (NO<sub>x</sub>) production. Biofuels include biodiesel, alcohols, and polyoxymethylene dimethyl ethers (PODE) that are mainly produced from the bio-based resources via transesterification, fermentation, and the Fischer-Tropsch process. The other drawback of biofuels is the presence of unsaturated oxygenates, which are the predominant coke precursors

because they can interact with the catalytic surface (Dimitriadis et al., 2021; Meyers et al., 2019; Wu et al., 2021b).

About the production of chemicals, biomass can be valorized through electrocatalytic technologies and coupled redox reactions for the production of bio-based molecules such as aliphatic dicarboxylic acids (Centi et al., 2019). Moreover, the laboratory-scale process of oxidative coupling of methane (OCM) process is a shred of good evidence for improvement of the technology to reach commercial sizes that can be installed as distributed by the small size plants (Wang et al., 2015). Distributed processes are interesting for better local integration of the resources as well as improvement of the local economics and circularity (Corma et al., 2017; Mousa et al., 2016).

#### 4.4. Feedstock for chemicals and polymers

Previous decades of converting fossil hydrocarbons into basic chemicals have generated raw materials to feed the chemicals and polymer factories. The conventional technology for the production of main chemicals such as ethylene, propylene, butadiene, and aromatics is steam cracking, which utilizes large amounts of naphtha and ethane/propane worldwide. Moreover, feedstock for the production of ammonia and methanol is natural gas and coal. As for the carbon black and carbides, oil and petroleum coke are utilized, respectively. Currently, the share of biomass on feedstock supply for petro-/chemical sectors is very small. The increasing share of biomass in the chain of raw materials for polymers and fibers production is expected to increase up to 90%. These technologies include the utilization of natural polymers directly or the conversion of biomass via thermo-chemical processes (IRENA, 2014). Metabolically engineered microbes can also participate in the production of different chemicals and fuels. Therefore, waste to chemicals or energy nexus is considered an alternative carbon source that can play an important role in manifold carbon resources for the production of chemicals. Food crops and pure carbohydrates such as glucose or other lignocelluloses are easy to grow, which can be metabolized by the microbes (Zhao et al., 2019). As another case in point, microalgae-based CO<sub>2</sub> fixation is possible through the harvesting of algal biomass to produce bio-fuels and bio-products such as food and fine chemicals (Hajilary et al., 2019; Zhou et al., 2017).

Global demand for plastics has increased in recent decades due to their specific properties such as low cost, high versatility, and lightness. Therefore, more research is being carried out on the improvement of the plastic sector and processes. Green-PVC is also getting more attention, which can be originated from the fully recycling industrial waste as well as the renewable resources. As a case in point, Correa et al. (2019) investigated reusing of PVC- pipes for developing this new recyclable and green source. They addressed that conventional plastics can be reused not depending on their sources which can be either fossil-based feedstock or renewable sources. Indeed, utilization of recyclable resources decreases GHG emission as well as the dependency on petroleum and its products. As an example of green feedstock for the plastic sector, bioethanol from sugarcane is converted successfully into polyethylene. In addition, chemical recycling of waste plastics and polymers can be the assisting resources conservation, which leads to less dependency on the feedstocks, especially the fossil-based ones (Dimitris and Achilias, 2014; Qureshi et al., 2020; Ragaert et al., 2020). In this way, a combination of different technologies is required to cover the recycling of various plastic waste stream types (Pohjakallio et al., 2020; Vollmer et al., 2020).

#### 4.5. Developing alternative carbon sources for industries

In the industrial sectors, GHGs are emitted from the products and processes in addition to heat production. This makes the decarbonization of industrial sectors more challenging and complex in comparison to other sectors such as building and transportation (Vine and Ye, 2018). Moreover, some industrial sectors such as metal industries



necessitate high-temperature heat in their processes that can diminish the implementation of renewable energies (Mekhilef et al., 2011). Being dependent on fossil fuels, more than 95% of the current petrochemistry requires further attention on the implementation of green resources. Direct electrification of EIs with green electricity is one of the best options for both process- and non-process-emission reduction. However, current technologies and green electricity production rates cannot fulfill the requirements of EI subsectors. Therefore, the development of diverse green feedstocks, CO<sub>2</sub> capturing, promote rural production based on local resources, partial integration of renewable energy, and implementation of novel technologies are the most important steps in close future. However, this multi-aspect approach requires considerable research efforts and investments for the minimization of emissions from the petrochemical sector (Centi et al., 2019; Mekhilef et al., 2011; Songolzadeh et al., 2014).

Bio-based processes, fuel cells, and hydrogen storage are the other structures for the integration of green hydrogen into the power system. Combining the above-mentioned technologies with green electrolysis can effectively play an important role in industrial decarbonization as well (Yue et al., 2021). Electrolysis is an electrochemical separation technique that does not require excessive thermal energy and can be utilized for hydrogen production. Hence, carbon-neutral hydrogen could replace the current hydrogen from natural gas using the existing natural gas transport infrastructure. However, the production of hydrogen via carbon-neutral electrolysis is high energy-intensive with electricity requirements of around 270–300 kJ/m<sup>3</sup> (Centi et al., 2019). The current scientific studies are investigating affordable green hydrogen production at higher capacities (Minke et al., 2021).

Hydrogen is promising toward decarbonization of industrial sectors and accelerating the energy transition. Industries can benefit from partial replacement of utilized fossil fuel for heat generation with hydrogen. (Li et al., 2020; Yue et al., 2021). Due to the resilient nature of renewable electricity production and considering daily pick demand periods of electricity demand, the production of hydrogen from electrolysis is one of the solutions for satisfying the grid stability. Hydrogen as molecular storage can assist the capacity of other types of electrical storage especially in the case of onshore production technologies (Chen et al., 2021; d'Amore-Domenech and Leo, 2019; Drespe et al., 2019).

## 5. Industrial decarbonization

The newborn state-of-the-art technologies are built on the applicability and operating assumptions for future industrial-scale implementations. Therefore, the range of minimum and maximum decarbonization probability has a huge effect on their realization and installation (Ávila et al., 2018). Apart from this uncertainty, GHG abatement could require external infrastructure for both inter- and cross-sectional emission reduction. These technological and economic issues are more significant for the existing process equipment of EIs because they are designed and manufactured for long-term working. Hence, replacement and update of them by new technologies is highly dependent on the start of installation and their remaining lifetime as well as the operational costs and prices of the expected technologies. Therefore, new technologies, which can assist functioning industries with emission reduction such as waste heat recovery and recirculation, CCS/U, altering feedstock to bio-based and recyclable resources are crucial for deep decarbonization in the near future. In parallel, maturing of the novel processes can also end up with the energy transition (Ávila et al., 2018; Galik, 2019; Rajabloo, 2019).

### 5.1. Green chemicals via renewable resources

In contrast to other industrial sectors, the full decarbonization of the chemical sector is not applicable due to the carbon-based nature of the feedstocks and the main products. The more viable option is to utilize green resources and raw materials to decrease the carbon footprint. For

example, a combination of large-scale bio-based raw materials and green electricity is a sustainable and climate-friendly solution, which is called “bio-refinery”. Chemicals via CO<sub>2</sub> routes are also in the same category, but more advanced technologies are required to make them viable at large scales. This new technology implements the direct routes of CO<sub>2</sub> methanation such as thermo-catalytic hydrogenation of CO<sub>2</sub> to synthetic methane via plasma technology and the Sabatier process, which is the direct catalytic conversion of H<sub>2</sub> and CO<sub>2</sub>. The process can be followed by converting the final methane into olefins, aromatics, and polymers (Engelbrecht et al., 2020; Ješić et al., 2020; Olah, 2013; Sun et al., 2017; Vogt et al., 2019). Yet as a key chemical product, methanol plays an important role in chemical industry feedstock for the production of chemical intermediates such as formaldehyde and acetic acid, which in turn can be used to produce daily items like paint, adhesives, and plastics (Hatti-Kaul et al., 2020; International, 2019; Vu et al., 2020).

Methanol was traditionally produced via destructive distillation of wood, giving it the name “wood alcohol”, but current routes used for methanol production rely on natural gas, oil, or coal as the feedstocks (International, 2019). On the other hand, both methanol and high added value chemicals can be obtained by the modern green-based technologies with green H<sub>2</sub> and CO<sub>2</sub> as initiatives to replace the fossil fuel-based hydrocarbons and refining technologies (Wang et al., 2015). Furthermore, regional strategies such as circular economy, flexible production units, which can vary in volume or type of final products, integration of energy storages, capture and storage of CO<sub>2</sub> (Duraccio et al., 2015; Espie et al., 2021; Ros et al., 2014), and utilization of innovative technologies, especially purification and separation methods (Centi et al., 2019; Grasso et al., 2019) are important aspects to support decarbonization of the chemical sector.

### 5.2. Carbon capture and utilization (CCS/U)

Although optimization of the current industrial processes has the lowest cost, it is not sufficient for emission reduction. The current processes are well matured following the current economical rules to get the highest benefits. Moreover, technologies are developed based on fossil fuel feedstocks and energies. Hence, innovative technologies and strategies which consider emission reduction as one of the important parameters toward optimization are required in industrial sectors. Furthermore, most of the chemical products contain carbons which make the carbon-neutrality impossible to achieve and the emission can release at feedstock preparation, the processing steps, and even from the final commodities. Therefore, carbon capture and storage (CCS) besides the electrolysis by green electricity, alternative feedstock, and novel membranes are essential for the industry, which can offer the highest emission reduction potentials for the current technologies (Gholami et al., 2017; Rezakazemi et al., 2019; Zhang et al., 2021). Accordingly, these inventive approaches can support flexible energy networks and improve the local energy roadmaps. Although the above-mentioned abatement options are not expected to reach the market before 2030, the concept of CO<sub>2</sub> storage systems is under development through different studies.

The CCS is one of the most striking technologies in the near future to decarbonize the industry and is also essential for reducing the CO<sub>2</sub> emissions of EIs, especially the petrochemical sub-sectors in which CO<sub>2</sub> emission is unavoidable (Duraccio et al., 2015). CCS focuses on the filtration of CO<sub>2</sub> from flue gasses or streams such as syngas before entering into the process at various parts of the chemical production units. However, specific characteristics of the industrial exhaust and flue streams determine the applicability of CCS. Various technologies used for CO<sub>2</sub> capture have been investigated and the leaping of the knowledge to enhance capturing and storage processes as well as commercialization of the well-studied techniques was well-realized (Gale et al., 2009; Galvez-Martos et al., 2018; Meng et al., 2018). However, the main challenges ahead of CCS technology are cost issues and the overall



cost-effectiveness at both sides of direct capturing from the air and the storage (De Luna et al., 2019; Harker Steele et al., 2021; Regufe et al., 2021). The other challenges ahead of CCS are transporting and storage capacity of CO<sub>2</sub> which has massive volume, the liability of CO<sub>2</sub> release both during transport and storage, and the long-term ownership of CO<sub>2</sub> sinks.

The storage of captured carbon requires high investments, so utilization of the captured CO<sub>2</sub> is to be done in parallel. Moreover, carbon capture and utilization (CCU) as a replacement of fossil-based feedstocks can provide business, support the economy and markets as well as can effectively help the stabilization of electricity grids by moderating their dependency on the fluctuating renewable electricity (Mennicken et al., 2016; Van Dael, 2018). Once the CCU technology matures, recycling of CO<sub>2</sub> at a large scale can shift the emission curves to negative slopes in shorter times by bringing the waste streams into recirculation and altering the fossil feed-stocks (Ješić et al., 2020; Koytsoumpa et al., 2018).

### 5.3. Implementation of CCS/U in the chemical industry

Even though chemicals and petrochemicals are strategic for the global economy, they have the highest intensity regarding the energy requirements by a worldwide demand share of 14%. Supplying 90% of the energy requirements at these sectors from oil and gas, these are responsible for 5% of global CO<sub>2</sub> emissions into the atmosphere, which is equal to 1.5 billion tons every year. To surge the international oil demand and provide environmentally benign feed-stocks, immediate actions are necessary for petrochemical sectors (Capocelli et al., 2019; Güleç et al., 2019; Mikulčić et al., 2019; Tan et al., 2021).

The common chemical processes such as ethylene and ammonium oxidation involve high purity CO<sub>2</sub> emission and are the low hanging fruits for carbon capture and storage. Similarly, other chemical sectors need to be investigated for their GHG level and their purity levels, which illustrate the hierarchal order of the sub-sectors towards emission reduction. Five commercial-scale CCS projects are demonstrating the possibility of industrial carbon capture worldwide. As a case in point, the Sleipner and Snøhvit (Norway), and Salah (Algeria) have investigated the stripping of CO<sub>2</sub> from high-CO<sub>2</sub> content natural gas to achieve the sales-grade quality of the natural gas. The striped and collected CO<sub>2</sub> is stored securely in deployed wells and underground geological formations. As another case, the Rangely project (United States) uses CO<sub>2</sub> captured from the natural gas processing at ExxonMobil LaBarge gas plant in Wyoming to enhance the oil recovery, and stores some part of the captured CO<sub>2</sub> at the Rangely field in Colorado (Hajilary et al., 2020; Jia et al., 2019; Karacan, 2020; Lake et al., 2019; Lee et al., 2019; Pandey et al., 2022; Zakkour and Cook, 2010).

#### 5.3.1. Reduction of CO<sub>2</sub> to higher value-added chemicals

Apart from the quickest utilization of CO<sub>2</sub> in oil extraction wells and production processes, direct reduction of CO<sub>2</sub> by the heterogeneous electrochemical techniques into high-added-value chemicals such as methane, ethylene, oxygenates, methanol, alcohols, olefins, and formic acid can be the other achievements of CCU studies. It was proved to convert CO<sub>2</sub> directly into C<sub>2</sub> molecules by changing the parameters of the processes such as pH or pressure in an electrochemical reactor using plasma technology (van Kranenburg et al., 2016). These molecules, which can respond as E-Molecules as well as the energy carriers are important chemical commodities that can be burnt as fuels. Thus, the CO<sub>2</sub> conversion assisted with the green hydrogen, but it requires renewable electricity or other clean resources such as nuclear to fulfill emission-neutral requirements. Lack of green electrical resources can add even more to CO<sub>2</sub> emission into the atmosphere during the production of electricity (Hoppe et al., 2018; Whipple and Kenis, 2010).

Plasma technology is appropriate for gas conversion applications and is an innovative route for the conversion of CO<sub>2</sub> into value-added molecules (Ješić et al., 2020; Lu et al., 2020; Olah, 2013). The methanation

reaction occurs via the catalyst illumination of CO<sub>2</sub> in a photothermal or plasmon-driven method, wherein the local temperature increases by light absorption, which can initiate the reaction with the excitation of electrons (Fresno et al., 2020; Gao et al., 2020; Khatun et al., 2019; Ulmer et al., 2019). The efficiency of photo-catalysis together with the separation efficiency of the photo-generated charges are the main parameters that can control the plasmon-driven CO<sub>2</sub> methanation process and reaction rate onto the surface of the catalyst (Xie et al., 2020).

#### 5.3.2. e-Methanol production and its utilization in chemical industry

Over the past decade, the production of methanol from CO<sub>2</sub> in combination with renewable energy has started at the demonstration phase to prove industrial-scale applications. The CO<sub>2</sub> is converted into the value-added chemicals and fuels such as methane (CH<sub>4</sub>), methanol, and carbon monoxide (CO) in which methanol (MeOH) is the most obtained product (Adnan et al., 2021; Sahoo et al., 2022). Between these products, MeOH has a high energy density as well as the highest CO<sub>2</sub> sequestration potential. Moreover, MeOH, which is a liquid at room temperature has the large demand as both a fuel and a basic feedstock chemical (Sarp et al., 2020; Vo et al., 2021). The pioneer to convert CO<sub>2</sub> into MeOH is theCRI company with a pilot plant installation in Iceland for methanol production in which CO<sub>2</sub> comes from flue gases of the geothermal power plant and H<sub>2</sub> was generated via the renewable electricity-assisted water electrolysis (Al-Qahtani et al., 2020; Bos et al., 2020; Crivellari et al., 2019; International, 2019; Lonis et al., 2019; Nami et al., 2019). Fuel production from CO<sub>2</sub> and green powers was considered as an energy storage medium to improve the flexibility of the energy system (Adnan et al., 2021; van Kranenburg et al., 2016).

The conventional production of methanol led to the emission at resource extraction, processing, and production stages that was equal to 0.7 t of CO<sub>2</sub> per 1 ton of produced methanol based on natural gas reforming (Ingham, 2017) and 3 tons CO<sub>2</sub> for the coal gasification process (Qin et al., 2016). Emission values were considerable by contrasting the emission reduction through industrial CCU, which utilized more than 1.3 tons of CO<sub>2</sub> for 1 ton of methanol production (International, 2019). Furthermore, e-Methanol offered an alternative feedstock for the methanol-to-olefins (MTO) process, which is currently fossil fuel-driven. e-Methanol can be further converted into more complex intermediates or solvents such as benzene, toluene, and xylene, which are traditionally produced from the oil (Ahmadipouya et al., 2021; International, 2019; Muradov, 2014; Ouda et al., 2019; Soroush et al., 2018).

### 5.4. CO<sub>2</sub> storage for decarbonization systems

#### 5.4.1. CO<sub>2</sub> storage via carbonation of minerals

An advanced methodology has shown the possibility of CO<sub>2</sub> injection into the concrete. The pressurized CO<sub>2</sub> liquid is then delivered into the wet concrete during the mixing step in the concrete-curing process. By this, the quality of the concrete remains the same or better than those of the conventional products. The absorption rate of the injected CO<sub>2</sub> which is converted permanently into a solid mineral was 3.5 kg of CO<sub>2</sub> per one cubic meter of the concrete (Zhan et al., 2016; Zhu, 2019). The other CO<sub>2</sub> storing possibility is the natural process that has trapped CO<sub>2</sub>, oil, and gas for millions of years. Both oil and gas fields, as well as deep saline aquifers, are suitable underground candidates because they have the required geological features for CO<sub>2</sub> storage. The porous rock layer absorbs the liquid CO<sub>2</sub> while it is sealed by the impermeable layer of the caprock (He et al., 2011; Shabani et al., 2020). One of the existing CO<sub>2</sub> infrastructures in Europe is located in the North Sea (Alcalde et al., 2021; ML Veloso et al., 2021). The first four European countries regarding the capacity of CO<sub>2</sub> storage in deep saline aquifers and hydrocarbon reservoirs are listed as Norway, Germany, United Kingdom, and Spain (Abdelaal and Zeidouni, 2022; ML Veloso et al., 2021; Sun et al., 2021).

#### 5.4.2. Copolymerization of CO<sub>2</sub>

By utilizing appropriate catalysts, CO<sub>2</sub> can be stored inside of some polyols during the polymerization of epoxides, resulting in polycarbonate polyols. Although the final product was changed in their properties such as increased viscosity, they have the new properties as an advantage, which can be suitable for other applications. As a case in point, CO<sub>2</sub>-absorbed polyols for polyurethane production can be utilized as foams in car seats and mattresses. The homogenous catalyst system for the absorption of CO<sub>2</sub> inside the polymers is developed by Eonic Technologies in the United Kingdom (Zhu, 2019). This innovative technology allows waste CO<sub>2</sub> to be used as a feedstock in polymer manufacture, replacing up to 50% of traditional oil-based raw materials.

### 6. Electrification of the chemical industry

Electrification of the chemical industry can significantly decrease CO<sub>2</sub> emissions due to the replacement of fossil fuels by renewable electricity. However, the sensitivity of petrochemical processes besides the high temperature and pressure requirements of this energy-intensive sector needs robust and reliable green electricity resources, which can impose enormous technical and economic hurdles (Centi et al., 2019).

#### 6.1. Renewable electricity technologies for industrial usage

The essential energy requirement of industries is under development to reach the industrial scale replacement of fossil-based heat by electricity or bio-based methanol. Hydrogen from the electrolyzers has been the other significant electrified technique that can play an important role in emission reduction of refineries and petrochemical plants. On the other hand, electrolysis can be an electricity-intensive process that requires low-cost green electricity (IRENA, 2014; Li et al., 2021b). In parallel, process integrations beside the new processes that are assisted by the novel catalysts can optimize the energy consumption of petrochemical plants. However, the renewable energy resources and technologies are not sufficient yet to fulfill the industrial energy demand. Therefore, a thorough energy demand investigation of high emission industrial subsectors, processes overview, data collection, and market modeling is vital for multi-pronged integration of various processes or replacement of the traditional ones with state-of-the-art technologies (IRENA, 2014).

#### 6.2. Cracking with electricity

Steam cracking, which is considered the most important chemical process worldwide, is a multi-product process in petrochemical sectors for the production of high-value chemicals. Long-chain hydrocarbons encounter high temperature and pressure steam to break down into chemical molecules with a short-chain (Boulamanti and Moya, 2017a). However, thermal steam cracking of light naphtha occurs at temperatures above 800 °C, and cracking furnaces were followed by quenching, compressing, and separation units including energy losses as well (Boulamanti and Moya, 2017b). Besides the heat delivery, steam is one of the chemical feedstocks at many petrochemical processes, where the products of steam crackers are mainly ethylene and propylene besides benzene, butadiene, and hydrogen (Boulamanti and Moya, 2017a). Ethylene is one of the commodity chemicals, which is being produced at the largest volume worldwide. It is one of the main building blocks for producing the polymer plastics and fibers organic chemical sectors to produce packaging materials as well as it is being utilized for transportation and construction industries (Boulamanti and Moya, 2017a).

In the steam crackers, steam participates in the reaction during the cracking of hydrocarbons, whose recycling is somewhat less feasible. Overall, the steam crackers are energy-intensive, which has taken high attention towards the possible electrification. Consequently, the production of these large amounts of heat has made the steam crackers one of the highest GHG emission sources. Electrification of steam crackers is

one of the ambitious goals that the Dutch industries are making efforts to reach out (Tsiropoulos et al., 2018). Heating with electricity requires new metallic materials with high thermal stability while encountering electric currents, but still, it is the most challenging issue ahead. The technologies under development are mainly to utilize coil surrounded tubes for heat generation and the new reaction system known as the Roto Dynamic Reactor (RDR). RDR is supplied by an electric motor to reduce both pressure drop and residence time, thereby achieving better selectivity leading to a lower specific energy consumption (Amghizar et al., 2020). Once, the required electricity is provided from renewable resources, significant emission reduction is viable. The mentioned electrification technologies are, thus in the research stage that is almost close to the pilot demonstration phase, which requires further study to be installed in industrial plants.

As per the primary results of different research findings, the pilot-scale of electrified crackers will be installed in the near future, while scaling up to industrial level requires more time. Once the electrified crackers become commercially available, all naphtha and ethane crackers will follow, and hence, this step is an important milestone in the development. The other issue ahead of the mentioned electrification is supplying electricity from renewable resources instead of natural gas (Layritz et al., 2021).

#### 6.3. Collaborative efforts of all stakeholders

In efforts to accelerate the electrification of industries collaborative efforts of all the stakeholders are required. Electrification provides new opportunities for chemical industries by establishing green replacements to the current burning of fossil fuels as well as introducing the new feedstocks and products, which are mainly in higher-value segments (van Kranenburg et al., 2016). Since the efforts of individual sectors should satisfy their confidentiality, keeping the essential data as black boxes is required. In this way, sharing of the data outside the battery limits of each plant or sector will facilitate the collaborative investigations, symbiosis, and electrification of the industrial sector during the energy transition period.

#### 6.4. Types of electrification

Parallel to the replacement of fossil fuel-based heat by the green electricity, management of demand-side, and installation of electrical and thermal storages, and electricity can well be converted into other resources at the industrial level. Hence, industries can participate actively in demand management through various routes of electrification, called Power-to-X, which are Power-to-Heat, Power-to-Hydrogen, Power-to-Specialties, and Power-to-Commodities (van Kranenburg et al., 2016). These terms refer to the conversion of renewable electricity into heat and chemical products when the grid electricity demand is less than the production capacity and these are further explained in the next sections.

##### 6.4.1. Power-to-heat

Power-to-heat is the conversion of electricity into heat for both enhancements of low-grade heat and steam generation. Electricity can be directly converted into heat to cover the process heat demand or can be utilized to upgrade the steam and waste heat to make them suitable for recirculation in chemical processes. Here, the availability of low-cost electricity in comparison to natural gas price is crucial and can be adjusted by getting integrated into a flexible energy network to utilize the electricity when its price is low. Implementation of heat pumps, which are driven with electricity belongs to this category as well and can provide low-cost heat. Moreover, the fast response of power-to-heat technologies provides good resilience for fluctuating green electricity, which is expected to be the first approach for chemical industries towards electrification on a large scale (van Kranenburg et al., 2016). Hence, the stakeholders of power-to-heat are petrochemical industries,

energy sectors, equipment suppliers, business customers, and consumers as the end markets. Governments also play an important role to satisfy the requirements of stakeholders for the implementation of this technology. Fig. 3 depicts the relations of stakeholders and their interests as a whole picture (van Kranenburg et al., 2016):

### 6.4.2. Power-to-Hydrogen

The current produced  $H_2$  is called grey  $H_2$  due to being fossil-based and having  $CO_2$  as a by-product (Chai et al., 2021). Power-to-hydrogen is about the utilization of electricity for water electrolysis to produce hydrogen for commercial applications at many industrial processes (Ayers, 2017; van Kranenburg et al., 2016). For example, hydrogen is a critical feedstock for the chemical processes to generate methanol, ethylene, and ammonia. However, hydrolysis-based hydrogen production is currently more expensive than its production from natural gas, which is an electricity-intensive process (van Kranenburg et al., 2016). Some of the biggest challenges for using the power-to-hydrogen are their lifetime, maintenance issues, and improvement of their efficiency. On the positive side, electrochemical synthesis is the emerging new production route for chemical molecules, which are expensive or require severe conditions in traditional pathways. Moreover, this route enhances the petrochemical sectors by providing higher selectivity and purity of the final products (van Kranenburg et al., 2016).

The novel electrolyzers that are equipped with new technologies such as anion exchange membrane or solid oxide electrolyzers are under development, but these are not matured yet on a commercial scale, but they can lead to significant cost reductions in parallel to the supply chain establishment (Lu and Jiao, 2016; van Kranenburg et al., 2016). Many laboratories and industries have utilized the controlled flow reactor containing parallel plane electrodes for industrial and commercial applications (Rivera et al., 2015). Fig. 4 depicts the enlarged typical electrochemical cell and its components that are now commercially available (van Kranenburg et al., 2016). The produced hydrogen can be utilized directly, stored for future utilization or it can go to methane production processes together with CO<sub>2</sub>. Both H<sub>2</sub> storage and E-molecules productions are the methodologies for storing low-cost seasonal renewable electricity for later consumption (van Kranenburg et al., 2016).

The hydrogen from electrolysis covers a short portion of current production that suffers from energy and cost insensitivities. Steam reforming of biomass is one of the new technologies, which can make the greener production of  $H_2$  (Chai et al., 2021; Li et al., 2022b; Spragg et al.,

2018). Numerous biological upgradation techniques were used to convert CO<sub>2</sub> and hydrogen into CH<sub>4</sub> (Chen et al., 2022; García et al., 2021). The main metabolic pathways for H<sub>2</sub> production from the bio-feedstocks are categorized as direct and indirect pathways. However, the direct methodology is through the hydrogenotrophic methanogens conversion of CO<sub>2</sub> into methane, while the indirect one utilizes homoacetogenic bacteria to convert carbon dioxide into acetate and then to CH<sub>4</sub>. The other indirect routes are bio-photolysis, photobiological fermentation, and the utilization of carbonic anhydrase enzyme for the enhancement and breakdown of CO<sub>2</sub> and CH<sub>4</sub> production with purities between 95 and 99% (Chai et al., 2021; Thiruselvi et al., 2020).

### 6.4.3. Power-to-specialties

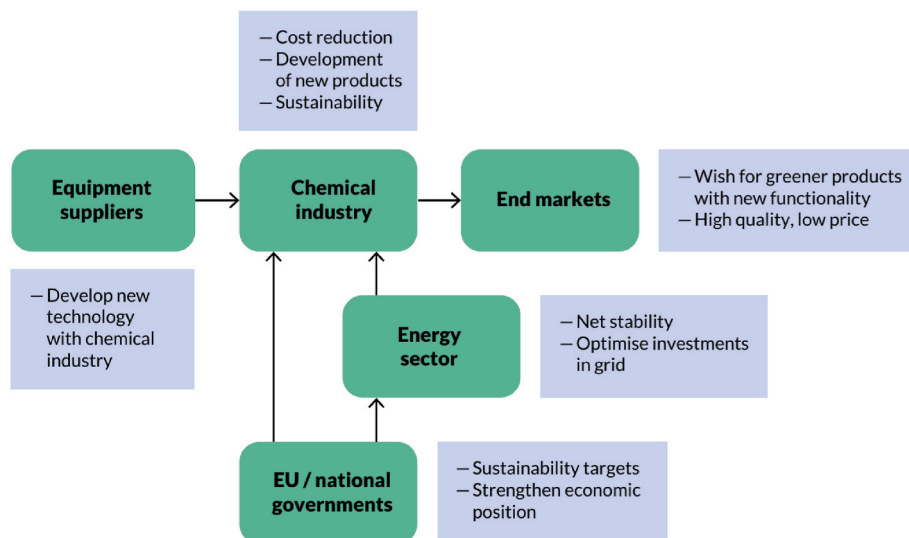
Power-to-specialties is another direct production of fine and specialty chemical intermediates and products by the direct electrochemical synthesis routes from both the conventional and biomass-derived feedstocks. This methodology is already employed by some companies to substitute highly inefficient traditional production routes and for the cost-savings, but the worldwide implementation of electrochemical technologies requires more time (van Kranenburg et al., 2016).

#### 6.4.4. Power-to-commodities

Power-to-commodities is the direct production of chemical commodities in large volumes by the direct electrochemical synthesis (both centralized and decentralized). This process can utilize both conventional and sustainable feedstocks such as CO<sub>2</sub>. For specific cases, decentralized electrochemical production is a proper strategy for mid-term chemical commodities production. For long-term energy transition to renewables, the centralized power-to-commodities will improve the replacement of oil and natural gas via clean electricity (van Kraenburg et al., 2016).

### 6.5. Attention-seeking technologies

The focus of power-to-x is the direct utilization of electricity for heat generation and chemical conversion. However, there are other technologies for the chemical conversion of molecules such as microwave, plasma, and photo-catalysis having considerable benefits in some processes over conventional electrochemistry. These technologies activate the molecules, which are different from the activation that occurs through electrochemistry or conventional thermochemical processes. The mechanism involves the generation of free radicals and specific vibrational excitation, which makes these technologies suitable for the



**Fig. 3.** Stakeholders and their interests in electrification (van Kranenburg et al., 2016).

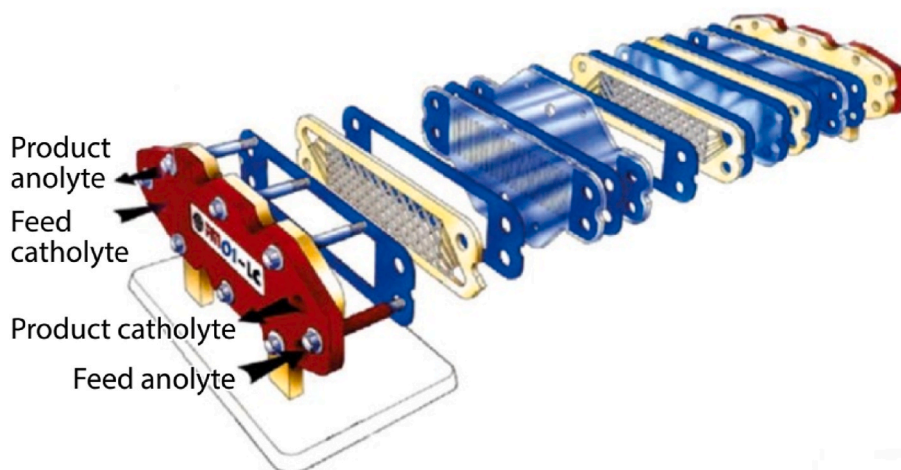


Fig. 4. Schematic view of FM01-LC electrochemical cell involving the fabrication components (van Kranenburg et al., 2016).

reduction of high stable molecules such as  $\text{CO}_2$ . Moreover, these technologies that are not yet mature at the commercial scale, lead to an increment of product yields and energy efficiencies. Hence, chemical industries will encounter an evolution that can act as the game-changers encountering electrification (van Kranenburg et al., 2016). As a case in point, microwave plasma and catalyst-assisted plasma (Ge et al., 2019b) technologies have been developed for  $\text{CO}_2$  reduction; its major concept is depicted in Fig. 5a, in which the enlarged plasma reactor is illustrated in Fig. 5b (Ashford and Tu, 2017; Javier et al., 2016; van Kranenburg et al., 2016).

#### 6.6. Need for flexibility in electricity system

One important aspect of sustainability targets is their influence on the energy sector. For example, emission-free electricity will drastically change the landscape of power generation and as a result in new standards, while fossil energy sources will phase out by 2050. Transition to renewable energy is thus the only possible way by expanding the low-capacity decentralized energy generation. Hence, the role of individuals and companies in electricity and heat production is increasing that will lead to considerable changes in supply and demand profiles (van Kranenburg et al., 2016; Zhang et al., 2016a).

The local and decentralized renewable electricity is not steady due to fluctuations in the resources. To overcome this instability and improve the reliability, boosting of flexibility at both production and demand sides as well as the development of dispatched models are required. Furthermore, advanced energy storage is becoming important in the integration of renewable energy sources with electricity systems (Alavi et al., 2020; Arbabzadeh et al., 2019; Mehrizi et al., 2020). Several studies have investigated various energy storage technologies to optimize the investment and operational costs taking into account the different  $\text{CO}_2$ -tax policies along with the varying renewable penetrations. Both thermal and electrical storage is required to improve the stability of the energy system (Arbabzadeh et al., 2019; Fragkos et al., 2017).

The electrification of the chemical industry can play an important role in conquering the fluctuating renewable availability and enhancement of the demand-side flexibility, which is a win-win approach for both the chemical industries and the energy sectors. While the energy sectors take advantage of a flexible grid for investment optimization, benefits for chemical sectors remain on the cost reduction to upgrade the output and products. The optimization parameters also are to include other parameters such as high efficiencies over the oscillating loads, the fast-respond start-up and shutdown times, low-cost maintaining, higher lifetime as well as flexible operation (van Kranenburg et al., 2016).

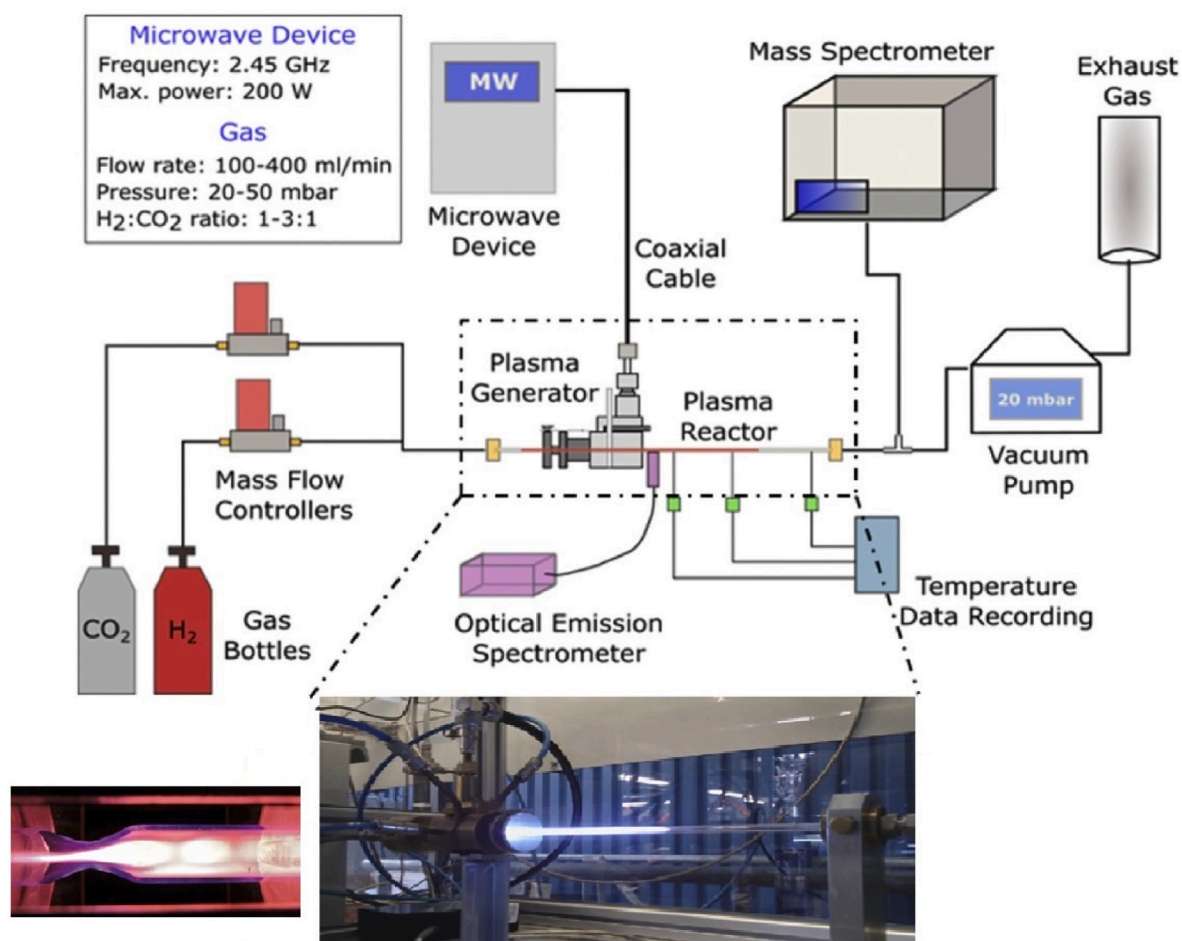
Overall, the potential benefits of electrification can be categorized as an increment of the controllable load in the electricity system to better align the demands with the fluctuating supply. Therefore, hybrid systems that can switch between fossil fuels, electricity, and multifunctional equipment driven by either natural gas or electricity are required. For the initiating steps, the potential of load balancing capacity at different industries and their sub-sectors can provide a horizon towards the application installation. Therefore, developing a merit-order graph for different electrification options, industrial sectors and their operational margins become necessary (van Kranenburg et al., 2016).

#### 7. A roadmap for innovation

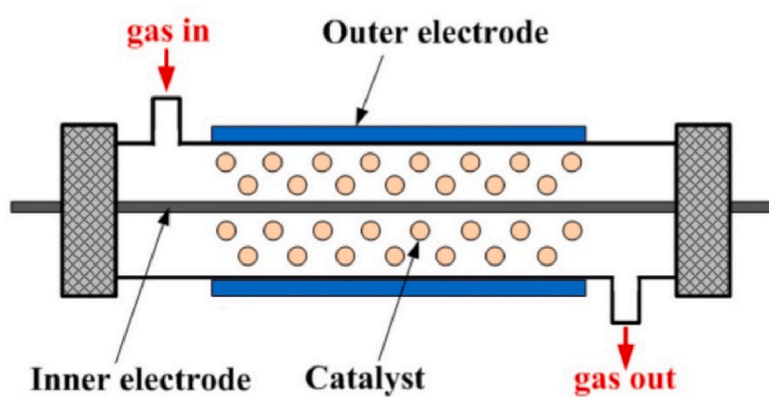
The necessity of co-operation and possible integration of different sectors towards the energy transition and industrial decarbonization can generate a multi-aspect symbiosis. However, putting along the various efforts to reach the aim of emission-free energy and material production will help to make regulations for the development of a circular economy and ecosystem. This multi-faceted regulations provides tasks for the stakeholders to be benefitted (van Kranenburg et al., 2016). These include: (i) identifying the 'low hanging fruit' for short term application and electrification of industrial sub-sectors; (ii) continual technology and business development; (iii) collaborative efforts on innovative technologies and research infrastructure use; (iv) building the innovative business models based on the demand- and load-response merit orders and (v) upgrading the costs scenarios for energy, raw materials, and finished products.

For a multi-faceted approach, three main approaches are identified and discussed towards the GHG emissions in chemical industries, but the potential of  $\text{CO}_2$  reduction is the lowest in the case of classic decarbonization solutions. The major efficiency improvement technologies and energy consumption optimizations are carried out within the majority of the companies, which consequently have led to emission reduction. Furthermore, newer technologies such as innovative waste-heat recovery and utilization of novel efficient process equipment can assist the GHG emission reduction further as a typical way and in short-term approaches. However, the classic solutions include low costs and risks; in contrast, the state-of-the-art technologies, which are emerging and not available commercially yet, bring the highest emission reduction potential, while imposing the highest costs and risks at these initiating steps. Green electricity is somewhere in between the aforementioned technologies since the basic developments and demonstrations already started (Ashrafi et al., 2021).





(a)



(b)

**Fig. 5.** (a). The microwave plasma (Javier et al., 2016; van Kranenburg et al., 2016) and (b) catalyst assisted plasma reactor for CO<sub>2</sub> reduction (Ashford and Tu, 2017).

## 8. Conclusions and outlook

Facing the energy transition and emission reduction at various sectors has been the inspirational driving force of extensive research efforts that are initiated to recognize the emission sources accurately. One of the most important sectors for emission reduction, which requires further attention, is the industrial segment that has a considerable share of global emissions. This review covers a wide selection of research articles that investigate the solutions for emission reduction in industrial sectors. Although the optimization and process enhancement in the industrial plants are developed smoothly during the last century, their focus was mainly on profit improvement and higher productivity by adopting simple methodologies. The present review covers a structured approach by focusing on the creative and state-of-the-art researches done on emission prevention. Based on the literature results, the complexity of the required actions for energy transition illustrates the importance of circular production, integration of processes, expansion of renewable resources both the green electricity and the bio-based feedstocks, ingenious reactions, inventive processes, and multi-pronged efforts. The new vision, therefore, requires combining the traditional goals on the outcomes of industrial plants with new trends of environmental benefits. In the other words, the new approach includes optimization of current processes and implementation of modern ones. Hence, this review covers briefly new technologies for heat integration and reduction of energy consumption, carbon capture technologies, electrification of industrial processes and heat generation, replacement of traditional fuel-based energy sources by renewable energies, while at the same time imposing on the new processes and reaction routes for the final products, and altering the feedstocks such as the utilization of biomass or CO<sub>2</sub> and renewable H<sub>2</sub> for hydrocarbon production.

Besides, the petrochemical and refinery sectors as the main focus of this study are further investigated providing the advanced technologies and processes, which are published in these fields. Although most of the discussed contemporary methodologies are not ready at the industrial scale yet, they require further investigations to ensure tackling of the environmental management issues ahead and provide the essential roadmaps to reach the modernized, green, sustainable, and profitable product lines. These initiative attempts are shaping the cleaner industries in the close future to seek alternatives for the new energy and feedstocks resources, novel technologies, and sustainable growth, which will create new careers, products, and lifestyles in the world.

## 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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