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PHD THESIS SUMMARY

Global warming and climate change concerns have triggered international efforts to reduce the amount and concentration of carbon dioxide (CO_2) emissions to ward-off massive economic and environmental damages. In recent years, the development of efficient and cost-effective technologies for reducing anthropogenic CO_2 emissions have been gaining momentum all over the world.

Currently carbon capture, utilization, and storage (CCUS) play a key role to the prompt and necessary mitigation of greenhouse gas (GHG) emissions generated from large point sources such as power plants. For some industrial process emissions which result from chemical reactions, CCUS is one of the most cost-effective solutions available for large-scale emissions reduction.

Although other sources of low-carbon power generation receive extensive policy support affiliated with today's capital markets, CCUS projects lack sufficient policy support to obtain conventional financing. This suggests that carbon management solutions such as CCUS still constitute the weakest link in new energy and climate policies; therefore, additional policies are needed to bring CCUS forward in commercial power market deployment.

Research Focus, Objective, and Scope

The main subject of this research revolves around the CO_2 molecule, a low-value, low-energy, stable waste gas, often available in large quantity in single locations. This work evaluates three carbon (CO_2) capture technologies, the reutilization of the CO_2 to produce carbon-base products, and potential storage application.

The three CCUS applications studied are; (1) use of CO_2-blended gas (biogas) generated at a WWTP through anaerobic digestion for the process of energy production using high temperature fuel cells such as SOFC, where the CO_2 has a role of reforming agent to increase the energy efficiency of the general process of energy generation, (2) the capture and transformation of CO_2 to produce sustainable, synthetic hydrocarbon or carbonaceous fuels (e.g., e-methane and e-methanol), mainly for the transportation industry, (3) CO_2 capture and mineralization through the process of direct carbonation in order to create "carbonated" fly ash (FA) for its use in the cement and construction industries.

The commonality of the above applications is that they all reuse captured CO_2 to yield a product in different forms (power and heat in case of SOFC, synthetic fuels in case of methane and methanol, construction material in case of carbonated fly ashes).

The objective of this work is to examine and evaluate viable processes and technologies that can be used to capture, utilize, and store CO_2 (CCUS)- with the main motivation of reducing GHGs emission and global warming, but also taking advantage in economic terms of these processes of carbon re-use. The study also examines various paths to accelerate the commercialization of carbon-based products and their technologies studied in this work. To accomplish this objective, the research includes the following:

1. A thorough investigation of three emerging CCUS pathways based on renewable energy sources (RES) (e.g., biogas & fuel cells, synthetic fuels, mineral carbonation of fly ashes) that fall into the CCUS paradigm and are either potentially marketable within the next decade, relatively new, or advanced forms of the mainstream energy sources. Each assessment is followed by the determination of market share, commercialization challenges, and policy framework.
2. Analysis of experimental work related to the direct use of CO_2-containing fuel of biological origins to supply an electrochemical process devoted to the production of power at high efficiency. The proof of concept was investigated at the first industrial size wastewater treatment plant (WWTP) in Europe in Torino, Italy; the name of the project is DEMOSOFC. The DEMOSOFC plant produces high efficiency energy with solid oxide fuel cells (SOFC) technology that can use the biogas generated at the WWTPs. From an energy and CCU point of view the system demonstrates how fuel cell systems are a key driver for future energy plants, based on renewable fuels, with very high electrical efficiencies and total recovery of the processed elements (carbon, hydrogen and oxygen), where the CO_2 has the role of enhancing the global efficiency of the process acting as a reforming agent.
3. Analysis of experimental and modeling work conducted at Politecnico di Torino linked to the use of the Carbon molecule to produce synthetic fuels (e-methane (CH_4) and e-methanol (CH_3OH)) by means of two processes: steam electrolysis + methanation, and steam electrolysis + methanol production. Furthermore, an energy analysis was performed with special consideration to the thermal integration via pinch analysis and a final estimation of power-to-fuel overall efficiency. The energy analysis (based on the process modeling developed for both systems) and the heat exchange network design enabled the development of capital expenditure estimation. Additionally, an economic analysis comparison for the production cost of both synthetic fuels was performed with the purpose of highlighting any potential risk related with the system.
4. Analysis of technical procedures concerning the capture of CO_2 from the flue gas of a coal fired power plant; the recovery of fly ash (in this case high-calcium fly ash (HCFA)) produced by the combustion of coal; and the mineralization of CO_2 through the process of direct MC; consequently, producing carbonated fly ash to use as supplementary cementitious materials for

construction applications. The study investigates and compares American (ASTM) vs. European (EN) standards and specifications related to the utilization of HCFA fly ash and evaluates the possibility of having a standardized classification system based on potential common grounds.

5. Literature review, analysis and comparison of United States[1] and Europe[2] mechanisms on national renewable energy policy. Evaluation of circular economy and cost carbon capture. Examination of economies of scale, barriers, and opportunities related to CCUS technologies; furthermore, breakdown of recommended approaches to accelerate the commercialization of CCUS technologies and carbon-based products.

Research Questions:

1. At a mitigation of climate change level, how does the stability of CO_2 compare when evaluating its reuse in the three carbon-based products studied in this work (i.e., biogas, synthetic fuels, carbonates)?
2. What are the technical and economic conditions for the direct use of CO_2-containing fuel of biological origins to produce power and heat at high efficiency using SOFC in a WWTP?
3. What are the technical and economic conditions for the reutilization of CO_2 to produce synthetic fuel?
4. What are the similarities and/or differences of the current HCFA specifications (ASTM vs. EN)? Is it possible to standardize the specifications for international use? What are the challenges to accelerate the commercialization of carbonated HCFA?
5. How to foster the commercialization of carbon-based products and their technologies? What are the barriers to accelerate the pace to commercialize and some potential remediations to overcome them?

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[1] When discussing the United States, it encompasses the nation's 50 states, D.C. and its Territories.

[2] When discussing Europe (EU), it encompasses the 27 Member countries of the European Commission.

Brief Answers to Research Questions:

1. One way that CO_2 can be utilized is by chemically processing and converting it into chemicals and synthetic fuels. This can be achieved through carboxylation reactions where the CO_2 molecule is used to produce chemicals such as methane, methanol, syngas, urea and formic acid. CO_2 can also be used as a feedstock to produce fuels (e.g., in the Fischer–Tropsch process). However, using CO_2 in this manner is energy intensive since it is thermodynamically highly stable: a large energy input is required to make the reactions happen. Furthermore, chemicals and fuels are stored for less than six months before they are used, and the CO_2 is released back into the atmosphere very quickly. As with mineral carbonates, this is CCU, and not CCS. Taking the CO_2 released from fossil fuel combustion and converting the gas into valuable chemicals and materials is a promising approach to protect the environment. But because CO_2 is a very inert and stable molecule, it is difficult to get it to react using conventional conversion processes. Captured CO_2 can theoretically be made into any kind of fuel or chemical that is currently based on petroleum. The trick is figuring out how to do it so the product is cost-competitive with fossil fuel-derived products and ends up benefitting the environment. Because CO_2 is a stable and non-reactive molecule, meaning that it won't react to form other chemicals unless a substantial amount of energy is added, processes to convert it to other products can be expensive. Ultimately the benefit of CO_2-based chemicals depends on the carbon intensity of the energy inputs, as well as the durability of the product. (CO_2-based chemicals and fuels may be burned or processed within days or weeks, releasing their CO_2 back into the atmosphere.). Overcoming this means finding products that are less energy-intensive to convert CO_2. The processes to convert CO_2 to a product require many reaction and separation steps and large energy inputs along the way.

2. Technical and economic states for the direct use of CO_2-containing fuel of biological origins to produce power at high efficiency using SOFC. It was determined that the CCUS biogas creation used in conjunction with SOFCs to produce power and heat, is not profitable from a venture point of view (assuming current market and economic conditions). For this reason, policies and subsidies should be considered to support the research, development, and roll-out of such technology, until competitive prospects can be reached. In other words, this new technology is

currently not commercially attractive to investors when compared to the status quo of using fossil fuels to produce power and heat.

Based on the technical and economic analysis generated for the case study addressed in this work, it was resolved that to have a successful market entry, the sales of fuel cells need to reach the break-even point; unfortunately, this alone will not guarantee the successful market penetration. A combination of making the fuel cell technology more affordable, the creation of policies that will assure the implementation of financial support schemes, and the need of initial investment capital to help accelerate the deployment of new projects, are imperative for the successful commercialization of SOFC.

3. Technical and economic states for the reutilization of CO_2 to produce synthetic fuels (methane and methanol). Two synthetic fuel (methane and methanol) production plants, using hydrogen and CO_2, were modeled, compared, and assessed. It was concluded that the economic viability to produce these fuels require significant investment capital reduction in order to be competitive with fossil fuels. This study considered some potential solutions that would help mitigate the issues; (1) reduction of electrolysis technology, (2) project cost optimization (e.g., mutualization of infrastructures and standardization of processes, procedures, and equipment manufacturing) and (3) low-cost of electricity is imperative; hence, the power required to support the processes should originate from renewable technologies such as solar or wind. However, albeit the high initial investment capital challenges, the production of methanol shows potential prospect for competitive commercialization if the utilization factor (UF) is between 65%-80%. Nonetheless, policies and subsidies should be considered to support the research, development, and roll-out of such technology, for synthetic fuels can comfortably compete in a competitive market.

4. Similarities and differences of existing standards and national specifications concerning the use of HCFA in construction in the regulatory framework of EU and US. Challenges presented for the utilization and potential commercialization of carbonated HCFA. The ASTM standard and national specifications for the use of fly ash involves some vague parameters and unclear language in the context of the specifications. Furthermore, the US EPA has delegated responsibility to the states to ensure that coal combustion byproducts are properly used. Each state, therefore, has its own specification and environmental regulations. Some states allow free use of fly ash while others allow limited application; consequently, this leaves the specifications vulnerable to partisan interpretation. Additionally, ASTM C618 differentiates the two classes of fly ash based only their coal source and chemistry. There are requirements on physical properties

of fly ash for use in concrete, but the requirements do not differentiate classes of fly ash. Fly ash classification based on coal source and the sum of three principal constituents was felt to be inadequate as the variations in the constituents for any fly ash have not been seen to correlate with the properties of fresh and hardened concrete. On the other hand, European standards (EN) and testing requirements are more restrictive than the ASTMs. For example, differentiates the two classes of fly ash based only their coal source and chemistry. There are requirements on physical properties of fly ash for use in concrete, but the requirements do not differentiate classes of fly ash. Fly ash classification based on coal source and the sum of three principal constituents was felt to be inadequate as the variations in the constituents for any fly ash have not been seen to correlate with the properties of fresh and hardened concrete. Major challenges for commercialization are:

(1) Lack of government incentives for producers and manufacturers to embrace the process,
(2) Changes in construction codes and standards could delay the use of CFA in the construction industry,
(3) Coal power plants are being decommissioned and there is almost no new construction currently in place. Consequently, the production of fly ash will be dwindling in the not so far future.
(4) New entrants may not have the deep pockets an established company possess.
(5) The underlying technology has the immediate need to be protected in terms of IP. Based on literature, this topic has not been addressed properly.

5. Fostering and accelerating the commercialization of CCUS the three subject carbon-based products and their technologies and processes. Challenges and opportunities in the CCUS market. CCUS faces some specific challenges in the initial deployment phase; for example, (i) scale and economics of CO_2 utilization (ii) techno-economic barriers to scaling, (iii) potential market barriers to new technologies, (iv) high capital investment requirements for CO_2 capture and related infrastructure.

   A major scale-up of deployment is needed to put in hastened motion technological progress, cost cutbacks and support investment in industrial applications of CCUS. Failing to accelerate these major challenges will hinder the large-scale commercialization of CCUS technologies over the next few years; hence, obstructing the long-term goal to combat climate change set by the Paris Agreement.

   Accelerating the deployment of CCUS in industry is complex and critically indispensable. It entails the collaboration of governments, industries, and financial and academic institutions to implement new business models where the burden of costs, risks, and liabilities can be shared. It should include partnerships amongst developing countries to substantiate CCUS capacity to build and execute this monumental global change.