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Utilitarian Technological Solutions to Reduce CO_2 Emission in the Aspect of Sustainable Development

Utylitarne rozwiązania technologiczne ograniczające emisję CO_2 w aspekcie zrównoważonego rozwoju

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Abstract

The state of the environment is an important element of sustainable development. Emissions of greenhouse gases, including carbon dioxide, are monitored. Observed rise in CO_2 emissions is forcing us to search for process solutions, which will significantly reduce its emissions, while meeting the economic criteria for the operation of the installation. EU legislation requires Member States to undertake research and implementation on industrial CO_2 capture and processing. Filed under development refers to the guidelines of the European Commission, expressed in the document *Towards an Integrated Strategic Energy Technology (SET) Plan: Accelerating the European Energy System Transformation*. There are many innovative solutions related technologies CCS (Carbon Capture and Storage) operating on a laboratory scale and pilot plant. The most common methods that have found use in the binding of CO_2 produced during the combustion process appropriate amine solvents, aqueous ammonia capture, absorption, ionic liquids, adsorption and membrane. Some of the above mentioned technology has been used application on the industrial scale after earlier financial calculations for their use and possible scenarios with process calculations based on value-to-cost criterion.

Key words: carbon capture and storage, sustainable development, green houses emission,

Streszczenie

Stan środowiska naturalnego to ważny element zrównoważonego rozwoju. Poziom emisji gazów cieplarnianych, w tym ditlenku węgla, jest monitorowany, a zaobserwowany wzrost emisji CO_2 zmusza do poszukiwań rozwiązań procesowych, znacząco zmniejszających jego emisję, przy jednoczesnym spełnieniu ekonomicznych kryteriów funkcjonowania instalacji. Ustawodawstwo UE wymusza na państwach członkowskich podejmowanie prac badawczych oraz wdrożeniowych dotyczących przemysłowego wychwytywania i przeróbki CO_2. Zakres tematyczny opracowania nawiązuje do wytycznych Komisji Europejskiej, wyrażonych w dokumencie *Towards an Integrated Strategic Energy Technology (SET) Plan: Accelerating the European Energy System Transformation*. Istnieje wiele innowacyjnych rozwiązań związanych z technologiami CCS (Carbon Capture and Storage) funkcjonujących w skali laboratoryjnej i półtechnicznej. Najbardziej popularne metody, które znalazły zastosowanie w wiązaniu CO_2 powstającego podczas procesu spalania to zastosowanie rozpuszczalników aminowych, przechwytywanie wodą amoniakalną, absorbcja, ciecze jonowe, adsorpcja oraz membrany. Część ww. technologii znalazła zastosowanie aplikacyjne w skali wielkoprzemysłowej po wcześniejszych finansowych kalkulacjach ich stosowania oraz możliwe scenariusze uwzględniające kalkulacje procesu w oparciu o value-to-cost kryterium.

Słowa kluczowe: wychwytywanie i składowanie węgla, zrównoważony rozwój, emisja gazów cieplarnianych

Introduction

Pollution of the atmosphere with greenhouse gases, especially carbon dioxide, is a threat to the climate and the whole biosphere and consequently, to the sustainable development of present and future generations.

Assessment of CO_2 capture and storage calls for a comprehensive delineation of CO_2 sources. The attractiveness of a particular CO_2 source for capture depends on its volume, concentration and partial pressure, as well as integrated system aspects, and its proximity to a suitable reservoir. Emissions of CO_2 arise from a number of sources, mainly fossil fuel combustion in the power generation, industrial, residential and transport sectors. In the power generation and industrial sectors, many sources have large emission volumes that make them amenable to the implementation of CO_2 capture technology (Azar et al., 2003). Large numbers of small point sources and, in the case of transport, mobile sources characterize the other sectors, making them less favourable for capture at present. Technological changes in the production and nature of transport fuels, however, may eventually allow the capture of CO_2 from energy use in this sector. Over 7,500 large CO_2 emission sources (over 0.1 $MtCO_2$ yr-1) have been identified (McCarthy, 2013). These sources are distributed geographically around the world, but four clusters of emissions can be observed: in North America (the Midwest and the eastern coast of the USA), Europe, South East Asia (eastern coast) and Southern Asia (the Indian sub-continent). Projections for the future (up to 2050) indicate that the number of emission sources from the power and industry sectors is likely to increase, predominantly in Southern and South-Eastern Asia, while the number of emission sources suitable for capture and storage in regions like Europe may decrease slightly (Dooley and Wise, 2003). Carbon capture and storage (CCS) is widely seen as a critical technology for limiting atmospheric emissions of carbon dioxide (CO_2) – the principal *greenhouse gas* linked to the global climate change – from power plants and other large industrial sources.

The goal of engineering activities is to provide a realistic assessment of prospects for improved, lower-cost technologies for each of the three approaches to CO_2 capture, namely, post-combustion capture from power plant flue gases using amine-based solvents such as monoethanolamine (MEA) and ammonia; precombustion capture (also via chemical solvents) from the synthesis gas produced in an integrated coal gasification combined cycle (IGCC) power plant; and oxy-combustion capture, in which high-purity oxygen rather than air is used for combustion in a pulverized coal (PC) power plant to produce a flue gas with a high concentration of CO_2 amenable to capture without a post-combustion chemical process (Munasinghe and Swart, 2005). Currently, post-combustion and pre-combustion capture technologies are commercially available and widely used for gas stream purification in a variety of industrial processes. Several small-scale installations also capture CO_2 from power plant flue gases to produce CO_2 for sale as an industrial commodity. Oxy-combustion capture, however, is still under development and is not currently commercially available.

Scale up processes

There are certain key areas that might be converted from the laboratory and bench scales at the early stage of process development into successfully constructed and operated in a controlled environment. The conceptual design stage of a CO_2 capture process is one for which the basic science has been developed, but no physical prototypes exist yet.

Post-Combustion Capture

The most advanced systems today employ amine-based solvents, while the processes at the earliest stages of development utilize a variety of novel solvents, solid sorbents, and membranes for CO_2 capture or separation (Edmonds et al., 2001). The amine systems can be installed at power plants (burning coal). The CO_2 captured at these power plants might be sold e.g. to food processing facilities, which use it for the production of dry ice or carbonated beverages. The oldest and largest commercial CO_2 capture system operating on such a way is the IMC Global soda ash plant in California. Here, the mineral trona is mined locally and combined with CO_2 to produce sodium carbonate (soda ash), a widely used industrial chemical. All these products soon release the CO_2 to the atmosphere (e.g., through carbonated beverages). Certain Polish cities possess power plants to produce heat or chemical plants treated with soda.

Amine-Based Capture Processes use solvents called amines (more properly, alkanolamines) are a family of organic compounds that are derivatives of alkanols (commonly called the alcohols group) that contain an *amino* (NH_2) group in their chemical structures. These processes are limited by the energy cost required for solvent regeneration, which has a major impact on process costs. In order to employ A-B CP in full industrial scale a certain financial mechanism can be applied to lower the overall cost of installation and maintenance (Beecy and Kuuskraa, 2005).

Ammonia-Based Capture Processes seem to be very promising due to the overall cost of an ammonia-based system would be substantially less than an amine-based system for CO_2 capture. Since ammonia could potentially capture multiple pollutants simultaneously (including CO_2, SO_2, NO_x), the overall plant cost could be reduced even further. Ammonia-based systems are attractive in part because ammonia is inexpensive, but also because an ammonia-based process could operate with a fraction of the en-

ergy penalty of amines. The use of CCS technology in laboratory scale has been summarized in Table 1 (Rubin et al., 2012).

Table 1. Post-Combustion Capture Approaches Being Developed at the Laboratory or Bench Scale

Liquid Solvents	Solid Adsorbents	Membranes
Advanced amines	Supported amines	Polymeric
Potassium carbonate	Carbon-based	Amine-doped
Advanced mixtures	Sodium carbonate	Integrated with absorption
Ionic liquids	Crystalline materials	Biomimetic-based

Table 2. Technical Advantages and Challenges for Post-Combustion Solvents

Description	Advantages	Challenges
Solvent reacts reversibly with CO_2, often forming a salt. The solvent is regenerated by heating (temperature swing), which reverses the absorption reaction (normally exothermic). Solvent is often alkaline.	Chemical solvents provide fast kinetics to allow capture from streams with low CO2 partial pressure. Wet scrubbing allows good heat integration and ease of heat management (useful for exothermic absorption reactions).	The large amount of steam required for solvent regeneration derates the power plant significantly. Energy required to heat, cool, and pump non-reactive carrier liquid (usually water) is often significant. Vacuum stripping can reduce regeneration steam requirements but is expensive; bad economy of scale. Multiple stages and recycle stream may be required.

Liquid Solvents (typically a mixture of a base and water) selectively absorb CO_2 through direct contact between the chemical solvent and the flue gas stream. In general, the aim of solvent research is to identify or create new solvents or solvent mixtures that have more desirable characteristics than the currently available ones. Such properties include increases in CO_2 capture capacity, reaction rates, thermal stability, and oxidative stability, along with decreases in regeneration energy, viscosity, volatility, and chemical reactivity. The main advantages and challenges associated with liquid solvent-based approaches to post-combustion CO_2 capture have been presented in table 2 (U.S. Department of Energy, 2010).

Examples of promising solvents include new amine formulations, carbonates, certain blends of amines and carbonates, and ionic liquids. For example, piperazine is a promising new amine which is now receiving increasing attention. This solvent, currently being studied at the University of Texas, has been shown to exhibit faster kinetics, lower thermal degradation and lower regeneration energy requirements than MEA in experiments thus far. Further characterization studies are in progress.

Potassium carbonate solvents, which have been used successfully in other gas purification applications, absorb CO_2 through a relatively low-energy reaction, but the process is slow. Researchers are attempting to speed up absorption by blending potassium carbonate with various amines, yielding promising results (Cullinane and Rochelle, 2004).

Solid Sorbent Absorbtion (SSA)

Solid sorbents can absorb CO_2 on their surfaces. Then, they release CO_2 through a subsequent temperature or pressure change, thus regenerating the original sorbent. Solid sorbents have the potential for significant energy savings over liquid solvents, in part because they do not require large quantities of water that must be repeatedly heated and cooled to regenerate the solvent solution. Sorbent materials are also characterized by lower heat capacity than solvents and thus require less regeneration energy to change their temperature.

Table 3. Technical Advantages and Challenges for SSA to Post-Combustion CO_2 Capture

Description	Advantages	Challenges
Sorbent pellets are contacted with flue gas, CO_2 is absorbed onto chemically reactive sites on the pellet. Pellets are then regenerated by a temperature swing, which reverses the absorption reaction.	Chemical sites provide large capacities and fast kinetics, enabling capture from streams with low CO_2 partial pressure. Higher capacities on a per mass or volume basis than in relation to similar wet scrubbing chemicals. Lower heating requirements than for wet-scrubbing in many cases (CO_2 and heat capacity dependent).	Heat required to reverse chemical reaction (although generally less than in the case of wet-scrubbing). Heat management in solid systems is difficult. This can limit the capacity and/or create operational issues for exothermic absorption reactions. Pressure drop can be large in flue gas applications. Sorbent attrition may be high.

The key aim of solid sorbent research is to reduce the cost of CO_2 capture by designing durable sorbents with efficient materials handling schemes, increased CO_2 carrying capacity, lower regeneration energy requirements, faster reaction rates and minimum pressure drops. The main areas in which optimistic results could be achieved by employing post-combustion CCS are presented in table 3 (U.S. Department of Energy, 2010).

Membrane-Based Approaches (MBA)

The main and key challenges to use MBA in commercial scale include the need for large surface areas to process power plant flue gases, limited temperature ranges for operation, low tolerance to flue gas impurities (or requirements for additional equipment to remove those impurities) and high parasitic energy requirements to create a pressure differential across the membrane. Advantages and topics to be solved in that matter are presented in table 4.

Table 4. Technical Advantages and Challenges for MBA to Post-Combustion CO_2 Capture

Description	Advantages	Challenges
Uses permeable or semi-permeable materials that allow for the selective transport and separation of CO_2 from flue gas.	No steam load. No chemicals needed.	Membranes tend to be more suitable for high-pressure processes such as IGCC. Tradeoff between the recovery rate and product purity (difficulty to meet both at same time). Requires high selectivity (due to CO_2 concentration and low pressure ratio). Good pre-treatment. Poor economies of scale. Multiple stages and recycle streams may be required.

The researchers are investigating the development of ultra-high surface area porous materials for CO_2 capture. These materials are known as metal organic frameworks (MOFs, discussed earlier), zeolytic imidizolate frameworks, and porous organic polymers. These materials have pore sizes, surface areas, and chemistries that are highly *tunable*, meaning that the molecules can, in principle, be designed and fabricated by chemists and materials scientists to maximize CO_2 capture performance. Because the CO_2 capture research in this area is relatively new, very little work has thus far been done to assess these materials under realistic capture conditions or to incorporate them into workable capture technologies.

Industrial and semi-industrial plant's examples

Post-combustion CO_2 capture systems have been in use commercially for many decades, mainly in industrial processes for purifying gas streams other than combustion products. The use of amines to capture CO_2 was first patented 80 years ago and since then has been used to meet CO_2 product specifications in industries ranging from natural gas production to the food and beverage industry. A number of vendors currently offer commercial amine-based processes, including the Fluor Daniel Econamine FG Plus process, the Mitsubishi Heavy Industries KM-CDR process, the LummusKerr-McGee process, the Aker Clean Carbon Just Catch process, the Cansolv CO2 capture system, and the HTC Purenergy Process (McCarthy, 2013). Although several CO_2 capture systems have operated commercially for nearly two decades on a portion of power plant flue gases, no capture units have yet been applied to the full flue gas stream of a modern coal-fired or gas-fired power plant. Thus, one or more demonstrations of post-combustion CO_2 capture at full scale are widely regarded as crucial for gaining the acceptance of this technology by electric utility companies, as well as by the institutions that finance and regulate the power plant construction and operation. Several years ago, for example, the European Union called for 12 such demonstrations in Europe, while in the United States there have been calls for at least 6 to 10 full-scale projects (Tarr et al., 2013). One of the plants operating in full scale installation, that has 9,000 hours of operational experiences, is the carbon capture pilot plant at E.ON's Staudinger power plant near Hanau/Germany. The pilot plant started operation in 2009. During the first three years of operation, the process was tested and its technical features were proven and further optimized, e.g. with respect to operability and energy demand, by using a slip stream from the flue gas of a coal-fired power plant. In 2012 a gas burner was installed as an alternative source for CO_2, and the pilot plant was operated for approx. 3.500 h on a flue gas composition equal to a gas turbine power plant. In this period of time a Technology Qualification Program (TQP) for the Carbon Capture Mongstad project in Norway was completed together with Statoil/Gassnova to prove the maturity for a full scale implementation (Horn et al, 2015).

One of the key reasons why the full-scale operating installations to CCS processes do not operate yet, is the overall cost of installation. The cost of each project in developing phase, is estimated at roughly $1

billion for CO_2 capture at a 400 MW unit operating for five years (EIA, 2014).

For most large sources of CO_2 (e.g., power plants), the cost of capturing CO_2 is the largest component of overall CCS costs. Capture costs include the cost of compressing CO_2 to a pressure suitable for pipeline transport (typically about 14 MPa). However, the cost of any additional booster compressors that may be needed is included in the cost of transport and/or storage. The total cost of CO_2 capture includes the additional capital requirements, plus added operating and maintenance costs incurred for any particular application. For current technologies, a substantial portion of the overall cost is due to the energy requirements for capture and compression. A large number of technical and economic factors related to the design and operation of both the CO_2 capture system, and the power plant or industrial process to which it is applied, influence the overall cost of capture. For this reason, the reported costs of CO_2 capture vary greatly, even for similar applications.

The most widely studied systems are new power plants based on coal combustion or gasification. For a modern (high-efficiency) coal-burning power plant, CO_2 capture using an amine-based scrubber increases the cost of electricity generation (COE) by approximately 40 to 70% while reducing CO_2 emissions per kilowatt-hour (kWh) by about 85%. The same CO_2 capture technology applied to a new natural gas combined cycle (NGCC) plant increases the COE by approximately 40 to 70%. For a new coal-based plant employing an integrated gasification combined cycle (IGCC) system, a similar reduction in CO_2 using current technology (in this case, a water gas shift reactor followed by a physical absorption system) increases the COE by 20 to 55%. The lower incremental cost for IGCC systems is, in large part, due to the lower gas volumes and lower energy requirements for CO_2 capture relative to combustion-based systems. It should be noted that the absence of industrial experience with large scale capture of CO_2 in the electricity sector means that these numbers are subject to uncertainties.

Studies indicate that, in most cases, IGCC plants are slightly higher in cost without capture and slightly lower in cost with capture than similarly sized PC plants fitted with a CCS system. On average, NGCC systems have a lower COE than both types of new coal-based plants with or without capture for base-load operation. However, the COE for each of these systems can vary markedly due to regional variations in fuel cost, plant utilization, and a host of other parameters. NGCC costs are especially sensitive to the price of natural gas. Therefore, comparisons of alternative power system costs require a particular context to be meaningful. For the existing, combustion-based power plants, CO_2 capture can be accomplished by retrofitting an amine scrubber. However, a limited number of studies indicate that the post-combustion retrofit option is more cost-effective when accompanied by a major rebuild of the boiler and turbine to increase the efficiency and output of the existing plant by converting it to a supercritical unit. For some plants, similar benefits can be achieved by repowering with an IGCC system that includes CO_2 capture technology. The feasibility and cost of any of these options is highly dependent on site-specific circumstances, including the size, age and type of unit, and the availability of space for accommodating a CO_2 capture system. There has not yet been any systematic comparison of the feasibility and cost of alternative retrofit and repowering options for existing plants, as well as the potential for more cost effective options employing advanced technology such as oxyfuel combustion. The high cost of CO_2 capture is mainly due to the cost of CO_2 compression, since separation of CO_2 is already carried out as part of the H_2 production process. Recent studies indicate that the cost of CO_2 capture for current processes adds approximately 5 to 30% to the cost of the H_2 product. In addition to fossil-based energy conversion processes, CO_2 could also be captured in power plants fuelled with biomass. At present, biomass plants are small in scale (<100 MWe). Hence, the resulting costs of capturing CO_2 are relatively high compared to fossil alternatives. For example, the capturing of 0.19 MtCO2 yr^{-1} in a 24 MWe biomass IGCC plant is estimated to be about 82 USD/tCO2 (300 USD/tC), corresponding to an increase of the electricity costs due to the capture of about 80 USD MWh^{-1} (Audus and Freund, 2004). Similarly, CO_2 could be captured in biomass-fuelled H_2 plants. The cost is reported to be between 22 and 25 USD/tCO_2 avoided (80-92 US$/tC) in a plant producing 1 million Nm^3 d^{-1} of H_2 (Makihira et al., 2003). This corresponds to an increase in the H_2 product costs of about 2.7 US$ GJ^{-1} (i.e., 20% of the H_2 costs without CCS). The competitiveness of biomass CCS systems is very sensitive to the value of CO_2 emission reductions, and the associated credits obtained with systems resulting in negative emissions. Moreover, significantly larger biomass plants could benefit from economies of scale, bringing down the costs of CCS systems to broadly similar levels as those in coal plants. However, there is too little experience with large-scale biomass plants as of yet; hence, their feasibility has still not been proven and their costs are difficult to estimate. CCS technologies can also be applied to other industrial processes. Since these other industrial processes produce off-gases that are very diverse in terms of pressure and CO_2 concentration, the costs range vary widely. In some of these non-power applications where a relatively pure CO_2 stream is produced as a by-product of the process (e.g., natural gas processing, ammonia production), the cost of capture is significantly lower than in the case capture from fossil-fuel-fired power plants. In other processes like cement or steel production, the capture costs are similar to, or even higher than the capture from fossil-

fuel-fired power plants. New or improved technologies for CO_2 capture, combined with advanced power systems and industrial process designs, can significantly reduce the cost of CO_2 capture in the future. While there is considerable uncertainty about the magnitude and timing of future cost reductions, studies suggest that improvements to current commercial technologies could lower the CO_2 capture costs by at least 20-30%, while new technologies currently under development may allow for more substantial cost reductions in the future. Previous experience indicates that the realization of cost reductions in the future requires sustained R&D in conjunction with the deployment and adoption of commercial technologies.

Sustainable development of CCS technologies

Key drivers for the deployment of CCS Energy and economic models are increasingly being employed to examine how CCS technologies would deploy in environments where CO_2 emissions are constrained (i.e., in control cases). A number of factors that drive the rate of CCS deployment and the scale of its ultimate deployment in modeled control cases have been identified:

1. The policy regime; the interaction between CCS deployment and the policy regime in which energy is produced and consumed cannot be overemphasized; the magnitude and timing of early deployment depends very much on the policy environment; in particular, the cumulative extent of deployment over the long term strongly depends on the stringency of the emissions mitigation regime being modeled; comparatively low stabilization targets (e.g., 450 ppmv) foster the relatively faster penetration of CCS and the more intensive use of CCS (where *intensity of use* is measured both in terms of the percentage of the emissions reduction burden shouldered by CCS, as well as in terms of how many cumulative gigatonnes of CO_2 are to be stored) (Gielen and Podanski, 2004);
2. The reference case (baseline); storage requirements for stabilizing CO_2 concentrations at a given level are very sensitive to the choice of the baseline scenario. In other words, the assumed socio-economic and demographic trends, and particularly the assumed rate of technological change, have a significant impact on the application of CCS (Riahi et al., 2003).
3. The nature, abundance and carbon intensity of the energy resources/fuels assumed to exist in the future (e.g., a future world where coal is abundant and easily recoverable would use CCS technologies more intensively than a world in which natural gas or other less carbon intensive technologies are inexpensive and widely available).
4. The introduction of flexible mechanisms such as emissions trading can significantly influence the extent of CCS deployment. For example, an emissions regime with few, or significantly constrained, emissions trading between nations entails the use of CCS technologies sooner and more extensively than a world in which there is an efficient global emissions trading and, therefore, lower carbon permit prices (Scott et al., 2004). Certain regulatory regimes that explicitly emphasize CCS usage can also accelerate its deployment.
5. The rate of technological change (induced through learning or other mechanisms) assumed to take place with CCS and other salient mitigation technologies (Edmonds et al., 2004). For example, Riahi et al. (2003) indicate that the long-term economic potential of CCS systems would increase by a factor of 1.5 if it assumed that the technological learning for CCS systems would take place at rates similar to those observed historically for sulphur removal technologies when compared to the situation where no technological change is specified.

   Methodologies for incorporating CCS into national inventories, and accounting schemes are under development. CCS can be incorporated in different ways and data requirements may differ depending on the choices made.

The following gaps in knowledge and need for decisions by the political process have been identified:

- Methodologies to estimate physical leakage from storage, and emission factors (fugitive emissions) for estimating emissions from capture systems and from transportation and injection processes are not available.
- Geological and ocean storage open new challenges regarding uncertainty on the permanence of the stored emissions and the need for protocols on transboundary transport and storage, as well as accounting rules for CCS, and insight on issues such as emission measurement, long term monitoring, timely detection and liability/responsibility.
- Methodologies for reporting and verification of reduced emission under the Kyoto Mechanisms have not been agreed upon.
- Methodologies for estimating and dealing with potential emissions resulting from system failures, such as sudden geological faults and seismic activities or pipeline disruptions have not been developed.

To summarize, the sustainable development of the described processes concerning the Combustion Capture Technologies using different approaches should answer the following questions:

1. What are the prospects for any of these projects to result in a viable new process for CO_2 capture?

2. How much improvement in the performance or reduction in cost can be expected relative to current or near-term options?
3. How long will it take to see these improvements?

These answers allow to choose the best technology based on the value-to-money criteria as well as the environmental impact.

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