Assessment of different approaches in reducing co2 emissions

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Abstract: Fossil fuels will remain a key element in the development of global economy in coming decades. Therefore the accumulation of CO2 in the air caused by fossil fuel consumption must be prevented because of the environmental concerns. Therefore the global issue of CO2 production has been under concentration in recent years through declarations such as the Kyoto protocol and also by industry leaders. To solve this problem and stabilize CO2 levels, the leaders must look towards adopting CO2 management strategies across their various enterprises. The purpose of this paper is to review three different and currently used methods of reducing CO2 emissions
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Introduction

With the rapid development of modern civilization, carbon dioxide (CO2) is produced in large quantities in industry, for instance, by the combustion of coal, coke, and natural gas, in the fermentation of carbohydrate materials and sugars, in the manufacture of cement and lime, and etc. Indeed, more than 30 billion tons of CO2 are added to the atmosphere each year. However, the emission of CO2, one of the major greenhouse gases, has raised great concerns about the relationship between anthropogenic CO2 and global warming; the emission of CO2 may have contributed to urban smog, acid rain, and health problems [1,2]

Policies on sustainable development have resulted in the wide concern about clean and environmental-friendly energy production. Resolutions of Kyoto Protocol [1], for example, aim to reduce the emission of greenhouse gases (GHG) in order to mitigate the climate change. However, according to recent IEA reports [2,3], world energy demand is growing at a rate of about 1.6% per year, and is expected to reach about $700 * 10^{18}$ J/y by 2030, with more than 80% of worldwide primary energy production still coming from combustion of fossil fuels. Meanwhile, global carbon dioxide (CO2) emissions are expected to exceed $30 * 10^{9}$ t/y in the near future. This particular situation leads to inevitable conflict between satisfying increasing demand and reducing GHG emissions. In recent years, a lot of scientific effort has been put to compromise the needs and constraints. Since combustion process involves production and emission of CO2 as a GHG component, its reduction has become an important agenda for many research areas

The improvement of energy efficiency is seen as one of the most promising measures for reducing global CO2 emissions. The European Union has set an indicative objective to reduce its primary energy consumption by 20% by 2020 compared to projected 2020 energy consumption in order to reduce emissions and dependence on imported fossil fuels [3]. However, the emission reduction potential may seem different from the industrial plant and policy-makers perspectives. Therefore Co-operation with the government and industrial sector is essential for understanding the contribution of energy conservation measures towards meeting the energy efficiency target and CO2 emission reduction commitment at the national level. [4]

Some of the important technologies for carbon emissions abatement are liquid biofuels in transportation, and carbon dioxide capture and storage in power generation.
Despite the positive impact on environment, widespread use of these technologies has certain

disadvantages. In case of biofuels, their production may strain agricultural resources that are needed also for satisfying food demands and processing capacity for downstream conversion of biomass into biofuel. At the same time, CCS (carbon capture and storage) is rather expensive technology and its practical implementation in power facilities must be carefully considered and planned. One challenge with CCS is that the understanding of the techno- economics of capture and storage is rapidly evolving, so that the most economic system-wide specifications in (say) 2030 may be different from those envisaged today by individual participants.

In addition, there is the important question about whether CO2 should be treated (and regulated) as a commodity product (for example in EOR) or as a pollutant/waste [5].

Generally low carbon technologies include:

- Energy efficiency enhancements through process or product design, modification and retrofit.
- Alternative, non-combustion energy sources such as hydroelectric, wind, solar and nuclear power.
- Combustion of carbon neutral biomass-based fuels for both transportation and industrial applications.
- CO2 capture and storage (CCS) techniques in conventional fossil fired power plants and large industrial facilities. CCS is sometimes alternatively referred to as carbon dioxide sequestration.

Biofuels

Although world oil reserves have been estimated to suffice for about 40 years, its distribution is highly concentrated in small number of sites, making the oil scarce in many parts of the world. Furthermore, the transportation sector contributes up to 30% of CO2 emission. For these reasons, there has been significant interest in biofuels in both developed and developing countries [6–9]. In order to reduce both dependence on foreign oil and emission level, biofuels have entered development widely supported by governments' legislations. For instance, latest EU directive 2009/28/EC [10] requires all Member States to displace 10% of diesel and petrol used in transportation with biofuels by 2020. According to this directive, each Member's government is supposed to develop its own schedule for biofuels introduction. Biofuels are considered to be carbon–neutral in principle because of closed carbon cycle. Carbon dioxide produced in combustion process is subsequently fixed during the growth of the feedstock. Additional emissions may occur through other means, such as use of fossil fuels for farm inputs; emission of GHGs from land use change; and the production of biofuels with both biomass and fossil components (e.g. biodiesel based on methyl esters). On the other hand, there are many concerns about large-scale biofuel production. For instance, some regions suffer from limited land and water resources that may lead to the competition between biofuel and food crops. Large-scale biofuel production would result in either higher food prices or scarcity of resources (water in particular) [11–14]. Furthermore, expansion of farmland contributes to environmental degradation (e.g. deforestation, biodiversity loss). Finally, biofuels may not be completely carbon– neutral. Different life-cycle analyses (LCA) show that carbon footprint for biofuels is wide-ranged and may even exceed that of conventional fuels under unfavorable conditions [15]. Furthermore, supply of biofuels in growing markets may exhibit instability or oscillation, thus undermining the role of biofuels in enhancing energy security [16]. Summarizing the above, biofuel production is highly constrained with occurrence of multiple footprints [17]. Although fuel displacement has become mandatory in many countries due to governmental policies, it is of importance to introduce biofuels into the market without detriment to environment and economy.

Some recent works that addressed the problem of resource constrained biofuel production have been reported, with the objective being to satisfy demand with most effective utilization of available resources and minimum biofuel import [18,19]. Such an approach leads to maximizing self-sufficiency of the local market.

It has been reported also that in case of biofuel planning, combining all constraints in a single approach is essential [19]. However, instead of developing unified quality criterion for pinch analysis, as has been suggested [19], approach presented below takes full advantage of mathematical programming using the source–sink framework.

Carbon capture and storage

The application of Carbon Capture and Storage (CCS) technology to energy-intensive processes is starting to attract attention, presenting an opportunity for developing multi-user CO2 transportation networks. Recognizing that most industrial facilities have not been designed with CCS in mind,[5] The subject of Carbon Capture and Storage (CCS) for power stations running on coal or natural gas is both important and prominent. The application of CCS to other industries which have large carbon dioxide (CO_2) emissions is equally important but much less prominent. Industry accounts for 40% of global energy-related CO_2 emissions. In 2007 the global figure for direct CO_2 emissions from industry was 7.6 Gte of direct CO_2 emissions to which could be added 3.9 Gte of indirect CO_2 emissions from power stations supplying electricity to industry [20]. The much-quoted IEA ‘‘blue map’’ scenario for halving global CO_2 emissions between 2005 and 2050 shows a 19% contribution from CCS which is split roughly equally between the power generation sector and the rest of industry [20].

Pre-combustion carbon capture technology is often proposed for new power plant facilities such as Integrated Gasification Combined Cycle (IGCC), and oxyfuel combustion technology is being developed as a promising energy-efficient process, but for retrofit applications the main interest tends to be in post-combustion capture technology [21,22]. In its conventional form it carries an energy penalty because additional energy is expended in regenerating the solvent used to dissolve CO_2.

Several processes are available for retrofitting to power stations and process plants, capturing CO_2 from flue gases. Licensors of ammonia based chemical solvent processes claim lower operating costs than for the more familiar amine-based process (described below) because less energy is required for regenerating the solvent.

Amine scrubbing is a more common and more mature process for removing CO_2 from a flue gas stream although it is known to suffer from a significant energy penalty. The problems to be solved depend on the composition of the flue gas. For example, on a gasfired power station with 3–4% CO_2 in the flue gas compared with a coal-fired power station with 13–14% CO_2 in the flue gas, larger absorbers are required in order to capture the same quantity of CO_2, leading to high levels of solvent consumption and a large energy penalty for solvent regeneration [23]. Once the range of target plants is expanded to include other industries, the range of flue gas compositions also expands.

Alternative processes based on physical solvent adsorption have also been developed. They offer lower regeneration costs but tend to require a high operating pressure and are therefore less attractive in flue gas applications. A range of more advanced CO_2 separation technologies is under development, but they are not presently marketed for retrofits [22].

Turning to industrial facilities, the challenges of retrofitting CCS can in some cases be particularly demanding since CO_2 emissions are often an inherent part of the basic process itself. For example, the basic process of calcining limestone (calcium carbonate) to make cement must inevitably generate CO_2 as a by-product because of the fundamental chemical reaction involved.

UNIDO have analyzed five broad industrial sectors: high-purity CO_2 producers, refineries, cement, iron/steel and biofuels [24]. The processing of natural gas (which in its raw form contains between 2% and 70% CO_2) is an example of a high-purity CO_2 process where some people are already deploying CCS. Another large part of the high-purity sector is ammonia production for fertilisers. UNIDO estimate that the cost of capturing a tonne of CO_2 spans a wide range from $4 to $47 depending on the plant configuration.

For the other processes, the range is smaller (between $9 and $31), including production of ethylene oxide (a petrochemicals building block) where the CO_2 stream purity can be anywhere between 30% and 100%. In the cement sector CCS has not been deployed commercially yet. A post-combustion capture facility based on established amines technology could be retrofitted with minimal change but with an energy and cost penalty. Changing to a new process based on oxygen rather than air would be attractive in energy and operating cost terms but is not really a retrofit option. In the iron/steel industry there is interest in processing the blast furnace gas stream which is rich in CO_2 and carbon monoxide, and which can be reformed into a 60% pure CO_2 stream.

Refineries have the option of capturing CO_2 from their various hydrogen production processes such as steam methane reforming and gasification of heavy oils/residues. On complex refineries which include fluidized catalytic crackers, about 50% of the CO_2 emissions derive from catalyst regeneration and can in principle be captured in a post-combustion process. With CO_2 capture costs ranging from €19/te to €85/te across the various options, practical deployment has tended to be at the low-cost end (viz. steam methane reforming) where there is a nearby outlet for CO_2. The easiest retrofit option for biofuels plants is on fermentation processes since they produce large volumes of high-purity CO_2. For example, the Arkalan bioethanol plant in Kansas, USA, captures CO_2 from a 60% pure stream for use in EOR [24].

Carbon dioxide (CO_2) emissions are believed to be a major contributor to global warming. As a consequence, large anthropogenic CO_2 sources worldwide will eventually be required to implement CO2 capture and storage technologies to control CO2 emissions [25]

Unfortunately, no current technologies for removing CO2 from large sources like coal-based power plants exist which satisfy the needs of safety, efficiency, and economy; further enhancement and innovation are much needed.[25]

As a result, a variety of methods have been studied and patented for the removal and separation of CO2 from industrial waste and mine gases, from the air, and from gases produced by animal metabolism, such as human respiration.

Many technical challenges, however, are facing potential large scale implementation of CO2 capture in power plants [26]

CO2 capture is the key step economically and has two technology routes: (1) pre-combustion: capture from the reformed synthesis gas of an upstream gasification unit; and (2) post combustion: capture CO2 from the flue gas stream after combustion

Upon capture, CO2 can be stored underground, used for enhancing oil recovery, and as carbon resources to be converted into other useful compounds [27,28]

The current technologies for CO2 capture and separation mainly include solvent, sorbent, and membrane, and the mechanisms for CO2 capture depend on the chemistry of the capturing approaches or materials

In the case of industrial applications where large quantities of sorbents, solvents, and membranes are used, or in the case of extracting CO2 from an anesthesia gas system, the impact of carbon capture materials on the environment and health is more of a concern. Attempts have been made to reduce dust or vapor formation, for instance, by providing solid sorbents with a protective coating (e.g., US3259464 [29]); this process, however, may also impair the CO2 capture capacity of the sorbent. Use of filters has also been studied in applications like self-contained diving gear but the filters may increase back pressure and cause a serious reduction of air flow.

In many cases, an organic solvent is used for CO2 removal or is involved in the preparation of sorbents or membranes for CO2 removal. In sorbents or membranes, the organic solvent must be stripped before they can be used for CO2 removal. Obviously, solvent recovery systems are quite expensive and there is always a possibility that the solvent will not be completely stripped. In such cases, the sorbents or membranes may be odorous. If the solvent is toxic then the prepared sorbents or membranes may not be used in applications like an anesthesia flow system or a life-supporting gas system.[25]

It has been noted previously that the fossil fuels remain a primary resource in the worldwide energy production. This particular trend is likely to be sustained for many years since no alternative source is known at present to be applicable on such a scale. For reasons discussed above, nuclear energy contributes only about 10% to world supply (even if it is used widely in some countries e.g. France, Japan), leaving the bulk of electricity being produced in natural gas and coal-fired plants. However, coal and other fossil fuels are most carbon-intense sources of energy. Furthermore, it is difficult to financially justify the shutdown of fully functional power plants before they have served the full extent of their economic lives. Options to retrofit such plants to allow them to continue operating are thus considered attractive. Thus, CCS technologies are required to meet the requirements of CO2 emission reduction. Several techniques of CCS are considered to enter commercial application in the near future [30–33]:

- Post-combustion capture (PCC) that consists in absorption of CO2 from the flue gas using chemical agents.
- Integrated gasification combined cycle (IGCC), which uses self generated hydrogen in combustion process. This approach involves pre-combustion capture of CO2 from the fuel.
- Oxyfuel combustion (Oxyf), or combustion in pure oxygen instead of air, which eliminates the need to separate of CO2 from combustion gases.

All these capture methods offer the potential for at least 80% CO2 removal. Also, in all cases, compression of captured CO2 is required prior to storage in various sinks (e.g. impervious geological formations, unmineable coal deposits, depleted oil wells or saline aquifers, among others). Although retrofitting power plants with CCS is considered an attractive way to lower the carbon intensity of fossil fuels, its application entails additional expenses for installation and maintenance of CCS equipment (e.g. compressors, absorption units, etc.). According to estimates [34], capital and operating costs of retrofitted plants are 20–70% higher as compared with baseline plant. Furthermore, plants with CCS suffer from efficiency losses. Due to energy consumption of additional equipment for CO2 capture and compression, power output of retrofitted plant is 15–20% lower than baseline level [32]. This may result in a drop in plant thermal efficiency of 5–10% points. If CCS is deployed on a large scale, it is also necessary to compensate for the missing power by using additional carbon-free sources or introducing efficiency enhancements [35]. Otherwise the result would be raised CO2 emissions or power shortages. All these factors must be taken into account when planning CCS placement, as they combine to raise the final cost of electricity from the retrofitted plants

However, extensive retrofit would likely result in major expenses and power output drops [35], leading to increasing fuel consumption for a given power output and higher prices. Therefore, minimization of total cost is essential.

Pre-combustion technology advantages and challenges [25,36]

CO2 capture technology	Advantages	Challenges
Physical solvent	- CO2 recovery does not require heat to reverse a chemical reaction - Common for same solvent to have high H2S solubility, allowing for combined CO2/H2S removal - System concepts in which CO2 is recovered with some steam stripping rather than flashed, and delivered at a higher pressure may optimize processes for power systems	- CO2 pressure is lost during flash recovery - Must cool down synthesis gas for CO2 capture, then heat it back up again and re-humidify for firing to turbine - Low solubilities can require circulating large volumes of solvent, resulting in large pump loads - Some H2 may be lost with the CO2
Solid Sorbent	- CO2 recovery does not require heat to reverse a reaction - Common for H2S to also have high solubility in the same sorbent, meaning CO2 and H2S capture can be combined - System concepts in which CO2 is recovered with some steam stripping rather than flashed, and delivered at a higher pressure may optimize processes for power systems	- CO2 pressure is lost during flash recovery - Must cool synthesis gas for CO2 capture, then heat it back up again and re-humidify for firing to turbine - Some H2 may be lost with the CO2
H2/CO2 membrane	H2 or CO2 permeable membrane: - No steam load or chemical attrition H2 permeable membrane only: - Can deliver CO2 at high-pressure, greatly reducing compression costs - H2 permeation can drive the CO shift reaction toward completion – potentially achieving the shift at lower cost/higher temperatures	- Membrane separation of H2 and CO2 is more challenging than the difference in molecular weights implies - Due to decreasing partial pressure differentials, some H2 will be lost with the CO2 - In H2 selective membranes, H2 compression is required and offsets the gains of delivering CO2 at pressure. In CO2 selective membranes, CO2 is generated at low pressure requiring compression
Water gas shift membrane	- Promote higher conversion of CO and H2O to CO2 and H2 than is achieved in a conventional WGS reactor - Reduce CO2 capture costs - Reduce H2 production costs - Increase net plant efficiency	- Single stage WGS with membrane integration - Improved selectivity of H2 or CO2 - Optimize membranes for WGS reactor conditions

Post-combustion technology advantages and challenges [25,36]

CO_2 capture technology	Advantages	Challenges
Solvent	- Chemical solvents provide a high chemical potential (or driving force) necessary for selective capture from streams with low CO_2 partial pressure - Wet-scrubbing allows good heat integration and ease of heat management (useful for exothermic absorption reactions)	- Trade off between heat of reaction and kinetics. Current solvents require a significant amount of steam to reverse chemical reactions and regenerate the solvent, which de-rates power plant - Energy required to heat, cool, and pump nonreactive carrier liquid (usually water) is often significant - Vacuum stripping can reduce regeneration steam requirements, but is expensive
Solid sorbent	- 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 similar wet-scrubbing chemicals - Lower heating requirements than wet-scrubbing in many cases (CO_2 and heat capacity dependent) - Dry process—less sensible heating requirement than wet scrubbing process	- Heat required to reverse chemical reaction (although generally less than in wet-scrubbing cases) - Heat management in solid systems is difficult, which can limit capacity and/or create operational issues when absorption reaction is exothermic - Pressure drop can be large in flue gas applications - Sorbent attrition
Membrane	- No steam load - No chemicals - Simple and modular designs - 'Unit operation' vs. complex 'process'	- Membranes tend to be more suitable for high-pressure processes such as IGCC - Trade off between recovery rate and product purity (difficult to meet both high recovery rate and high purity) - Requires high selectivity (due to CO_2 concentration and low pressure ratio) - Poor economy of scale - Multiple stages and recycle streams may be required

Energy management and planning techniques

To identify the optimum use of low-carbon technologies, detailed reliable planning methods are required. Examples of energy planning techniques that have been used previously are life cycle assessment [37, 38] and system perturbation analysis [39], which place emphasis on descriptive modeling of the linkages that exist within complex energy supply chains. Pinch analysis and process integration methods have also been extended for energy planning applications. Among many applications of carbon-constrained planning some address optimization within single facility [40], while other focus on more general, regional-level targeting [41–47]. In terms of techniques, both graphical targeting and mathematical programming have been used so far. Recently presented pinch analysis approach [41], had proven again to be an effective technique, portable between various fields of application due to well-established principles. Pinch analysis was initiated for the synthesis of heat exchanger networks (HENs) and other energy recovery system [48–50], which was then extended to a range of other problems such as industrial resource conservation [51–53], supply chain planning [54–56] and batch plant scheduling [57]. Most pinch analysis methods rely on graphical displays that provide decision- makers with an intuitive understanding of the problem structure. Such insights, in turn, facilitate proper planning. However, pinch approaches suffer from inherent simplifications and lower expandability than mathematical programming. Hence, mathematical programming should be used when detailed planning scenarios are encountered.

Tan and Foo [41] emphasized that energy planning cannot be limited only to the stationary applications such as industrial and residential. About 30% of global final consumption is contributed by transportation sector, which is mainly powered by petroleum products and is thus considered particularly vulnerable to price and supply fluctuations [58].

Several measures associated with thermal energy management are considered as [3]:

1- Usage of low quality exhaust heat in refrigeration cycles by absorption.
2- Use of thermal residues for preheating feedstock (for example recovery systems can recover the heat produced in coking processes).
3- Design of energy and/or mass (water and hydrogen) integration basically employing the Pinch Techniques; the use of Pinch Techniques provides energy savings in refineries of 20%.
4- Improving burners through better burning control.
5- Direct feeding of intermediate products to the processes without cooling and storage, aiming at recovering part of the residual heat in these products. For example, the thermal energy of the products of the distillation column can be directly recovered in the downstream units, thereby avoiding storage and cooling.
6- Using heat pumps.
7- Increasing turbulence in the heat exchange surfaces.
8- Adoption of a steam management system. For example, the quality of steam used in stripping and vacuum generation is normally lost in the cooling water or wasted to the atmosphere. Normally steam used for stripping ensures the flashpoint temperature and improves the fractioning of products, increasing the yield of the refining units.

Besides reducing the area of heat exchangers fouling causes maintenance problems and risk of accidents. Heat exchange networks with incrustations have approach temperatures higher than 40 C [59] when typical values in refineries hover between 10 and 20 degrees centigrade. Estimates done in the early 1980s for a typical refinery of its period with a primary processing capacity of 100 thousand barrels per day suggest that fuel consumption could be 30% less in the atmospheric distillation column by controlling fouling in the heat exchangers [60]. A more recent study, however, pointed to a lower potential. Although still significant, the reduction was only 10% [61] Yet incrustation in heat exchange networks is a bottleneck impeding the application of heat recovery systems. The gains achieved from reducing fuel consumption by controlling incrustation were estimated at 2% for refineries in the United States [62]. Meanwhile, Panchal and Huangfu [63] analyzed the effects of incrustation in a 100 kbpd atmospheric distillation column and found an additional energy consumption of 13.0 MJ per barrel processed (or around 3.4% of specific energy consumption in Brazilian refineries).

Depending on the design of the power plant, heat conservation can lead to either reduced or increased electricity output from an industrial CHP (combined heat and power) plant. In the case of a back-pressure plant, reduced heat output leads to reduced electricity output, which enables fuel conservation at the site but at the same time increases the demand for grid-based electricity. On the other hand, if there is a condensing unit in the steam turbine, heat conservation enables increased electricity output from the industrial CHP plant, and therefore less grid-based electricity is needed [4]

Khrushch et al. [64] defined the CO2 emission reduction potential in the US chemicals and pulp and paper industries by applying CHP technologies. In this study, the emission reduction was evaluated based on the assumption that CHP electricity production replaces electricity purchased from the grid. So, significant emission reduction potential at negative cost was found.

Axelsson [65] found that the opportunities for energy and cost savings and emission reductions in industry are heavily dependent on the existing design of the process and the energy system, the electricity-to-fuel price ratio, and the emissions of purchased electricity production.

Laukkanen [66] studied process integration in the pulp and paper industry, including the influences of steam saving on CHP production. He found that steam saving is not always profitable if the conserved heat cannot be somehow utilized, e.g. for the production of district heat or additional electricity from a condensing unit in the steam turbine. Therefore, the energy utility system and the production plant should be optimized together. According to Axelsson and

Berntsson [67] heat conservation can, depending on energy prices, be realized as fuel savings or increased electricity production by investing in a new steam turbine

Since cost-effective production and profit maximization are usually the main goals of industrial operation, the attractiveness of CHP production has to be ensured by proper energy policy and supporting mechanisms. Therefore, many EU countries have supported CHP within their national allocation plans due to its favorability from the wider perspective. For example, double benchmarking and CHP bonuses have been applied in order to promote CHP [68].

A wider perspective can be considered by widening the system boundary. The importance of clearly defining the system boundary has been noted in some industry related energy efficiency studies, such as Larsson et al. [69] and Tanaka [70]. In addition, wider system boundaries have been used when the integration of industrial energy production into the district heating system of outside society has been studied in Sweden [71,72]. These studies have focused on evaluating the increase in energy efficiency and the reduction in CO_2 emissions in integrated systems.

Conclusion

Generally, low-carbon technologies are either well-developed (as in the case of first generation biofuels) or emerging (like CCS technology for power plants or second-generation biofuels for motor vehicles). However, their potential for widespread use in the immediate future remains uncertain due to various limitations. For instance, CCS is subject to uncertainties inherent in unproven technologies, particularly with regard to the reliability of long-term carbon dioxide storage in various sinks. It is also expected to significantly increase the cost of electric power. Also first generation biofuels that are derived from agricultural crops consume valuable land and water resources and their ability to displace large proportions of global petroleum demand is now in doubt. On the other hand, associated technologies for second-generation biofuels are still not yet commercially viable due to high costs. Thus, it is of some interest to policy-makers to determine the minimal level of deployment of low-carbon technologies needed to meet desired GHG emission levels.

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