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Potential of Chemical Looping Combustion for Cleaner Energy Generation from Fossil Fuels

Sandra Sajen^{1,4}, Sunit Kumar Singh¹, Govindachetty Saravanan¹, Anis Hamza Fakeeha², Ahmed Sadeq Al-Fateh^{2*}, Ahmed Aidid Ibrahim², Mokhtar Ali Amrani³, Amit B. Mahindrakar⁴ and Nitin Labhsetwar¹

¹Energy and Resource Management Division, CSIR-National Environmental Engineering Research Institute (CSIR-NEERI), Nehru Marg, Nagpur 440020, India.

²College of Engineering, King Saud University, P.O Box 800, Riyadh 11421, Saudi Arabia

³School of Engineering Sciences and Technology, University of Hyderabad, Hyderabad 500046, India

⁴School of Civil and Chemical Engineering, VIT University, Vellore 632014, Tamil Nadu, India

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ABSTRACT

Increased carbon dioxide (CO₂) emissions from combustion of fossil fuels are the major contributor towards overall greenhouse gas emissions. Considering the significant reserves of fossil fuels in India and elsewhere, producing cleaner energy using fossil fuels with CO₂ capture and sequestration is one of the practical options to meet future energy demand and greenhouse gas commitments. Chemical Looping Combustion (CLC) is one of the efficient techniques with inherent potential for Carbon Capture. CLC is a greener way for combustion of fuel, using a metal oxide as oxygen carrier for providing the necessary oxygen for the fuel combustion. The reduced metal or metal oxide can again be oxygenated through air oxidation to form its original chemical state. This review sheds light on current energy scenario in India as one of the major energy users in future, the relevance and technical advancements in chemical looping combustion, with special reference to oxygen carriers

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1. Introduction

Climate change is prominent among the greatest threats that our planet faces today, which induces increase in global mean temperature, increase in sea level, variation in precipitation, a series of weather related disasters etc. The secondary impacts related to food, water, health, etc. are the major consequences of climate change. There are several natural as well as anthropogenic reasons for the climate change that involve burning of fossil fuels (e.g., coal, oil, natural gas, etc.), land clearing, intensive farming and other human activities. All these activities, however, produce large amount of greenhouse gases (e.g., water vapour (H₂O), carbon monoxide (CO), carbon dioxide (CO₂), nitrous oxide (NO), methane (CH₄), ozone (O₃), etc.) that lead to the *Global Warming phenomenon*. A “warmer world” has been believed to be a disease vector. Warmer oceans and surface waters would mean an outbreak of cholera and other diseases caused by bacteria. The increasing global mean temperature aids in the rapid growth of plants and help them to mature faster than usual that creates more potent allergens. Climate change influences the patterns of precipitation and temperature that results in natural disasters, which affects the safety of human life. Climate change is also a threat to global food production. It results in reducing productivity or yield of crops, creates changes in planting and harvesting, aggravates pest infestation, causes shifts in abundance of aquatic animals and decreases arability. It has profound effects on water accessibility, availability and the quality due to the loss of mountain snow packs, shrinkage of mountain glaciers, and rise in sea level. Therefore, it has become imperative to slow down or reverse global

warming, which otherwise poses the catastrophic impacts on the environment.

Global warming occurs because of trapping of various greenhouse gases in the atmosphere. It can't be controlled by a single solution due to the different greenhouse gases and significant difference in their global warming potential. For instance, the global warming potential for CO₂, CH₄, N₂O, and CCl₂F₂ (Freon-12) is 1, 21, 310, and 10,900, respectively (Edenhofer et al., 2014). Human activities emit mostly CO₂ to the atmosphere, the primary greenhouse gas among other greenhouse gases. It has been evidenced that the economic and population growth are the important driver for the increased generation of CO₂ and its release in the environment. According to Intergovernmental Panel for Climate Change (IPCC)'s technical summary report, the total anthropogenic greenhouse gas emissions increased substantially between 2000 and 2010 compared to the previous decades and reached to 49 (± 4.5) gigatonnes of CO₂-equivalents (Gt CO₂ eq) per year. 78% of CO₂ was emitted solely from the fossil fuel combustion and industrial processes among the anthropogenic greenhouse gas emissions. Therefore, CO₂ becomes the confocal attention as far as global warming is concerned. According to World Resource Institute's the data for cumulative CO₂ emissions between 1850 and 2011, India contributed only 3% to the total world emissions. In India, most of the power plants are based on coal and therefore the releasing of CO₂ was inevitable to the environment. 1.3 Gt CO₂ equivalent was released by India in 2007 and it increased up to 1.7 Gt CO₂ equivalent in 2010. The consumption of coal in India per capita (0.3 MT) is relatively lesser than that of the US (1.5 MT), China (1.4 MT), EU (0.5 MT), Japan (1 MT) etc. (Penney and Cronshaw, 2015).

* Corresponding Author: aalfatesh@ksu.edu.sa

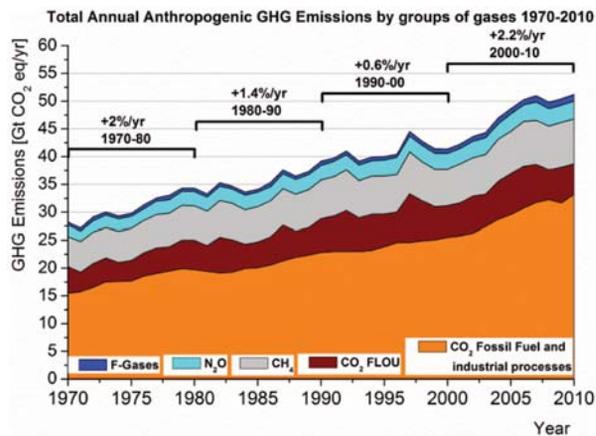


Figure 1. Year-wise total anthropogenic GHG emissions (Edenhofer et al. 2014, IPCC: Technical Summary)

IPCC report shows that the increased usage of energy derived from the coal-based power plants has reversed the long standing pattern of decarbonization of the world (Figure 1). Therefore, various strategies need to be developed to control the global warming effectively. Several technologies were explored and deployed to enhance the energy efficiency, use of renewable energy, reducing the use of fossil fuels, promoting of agriculture as well as forests, employing nuclear and other alternate energy options etc. that ensures a sustainable development with zero or low carbon emission technologies.

This overrun poses the stress on the availability and deployment of cleaner energy technologies like CO₂ capture and storage (CCS), bioenergy with CO₂ capture and storage (BECCS), CO₂ removal (CDR), usage of nuclear energy and other renewable energy like solar and wind. IPCC report states that the technological options available for mitigation of GHG greatly influence the costs and the atmospheric CO₂ concentration levels that may be expected to reach from 450 to about 550 ppm CO₂ eq. by 2100. The technologies of CCS and bio-energy have considerable influence on the mitigation of costs and environmental effects.

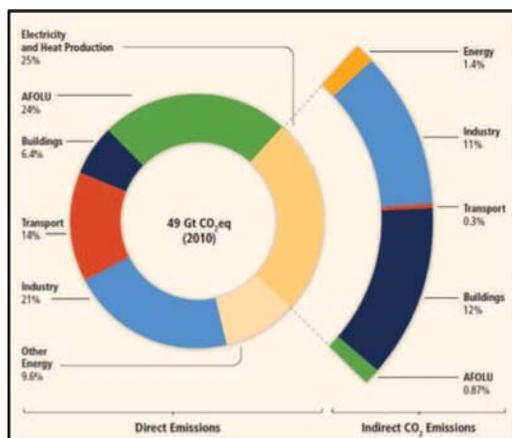


Figure 2. GHG gas emissions by Economic Sector (Edenhofer et al. 2014, IPCC: Technical Summary)

2. Carbon Capture and Sequestration (CCS)

A set of technologies are used to pre-concentrate the CO₂ in a CCS approach. It is either utilized to value added chemicals from the large volume of CO₂ emissions generated from the existing coal and gas fired power plants or stored away from the atmosphere for long periods of time.

CCS includes three step processes:

- i. Capturing and compressing of CO₂ from the sources through adsorption or any other available methods
- ii. Transfer of captured and compressed CO₂ through pipelines
- iii. Geological sequestration and/or storage.

CO₂ capture involves pre-combustion, post-combustion, and oxy-fuel combustion approaches.

(i) Pre-combustion: Fuels in any forms (solid, liquid, gas) can be primarily converted to a mixture of CO, H₂, CO₂, etc., through combustion reaction in air. The mixture of CO and H₂, also called *syngas*, further undergoes water-gas shift reaction in which CO can be converted into CO₂ by taking of oxygen from water molecules. Thus CO₂ generated through pre-combustion can be easily captured and transported (Fan et al., 2012). In pre combustion technique, fossil fuels are gasified at high pressures of 30-40 atm with low stoichiometric amount of oxygen into syngas. This process is identified as gasification, partial oxidation or reforming. This is followed by steam addition in to the syngas stream over fixed bed catalytic system. In presence of steam, CO reacts with steam (H₂O) via water-gas shift reaction to produce CO₂ and H₂. From this stream, CO₂ is separated and compressed to liquid state for transportation and H₂ is utilized via direct combustion for electricity production (Gibbins et al. 2008). Another option, being developed, is to utilize this pure H₂ in fuel cells or utilize it as transportation fuel (Blomen et al. 2009). The separation of CO₂ from the stream is done using a physical solvent such selexol and rectisol. At high pressure, CO₂ dissolves in this solvent and is releases back as the pressure is lowered. Considering the energy aspects of this process, due utilization of physical solvent, the energy and cost inputs are lower than post combustion techniques (Figueroa et al. 2008).

(ii) Post-combustion: CO₂ can be separated from the flue gases using different processes for instance absorption, adsorption, high pressure membrane filtration, cryogenic separation (Fan et al., 2012; Fang et al., 2009). Post-combustion CO₂ capture is a downstream process. This process is mostly associated with CO₂ capture from thermal power plants. The major challenge in this process is low concentration of CO₂ in flue gases; typically 13-17% in coal fired thermal power plants and 7-8% in gas fired thermal power plants (Mondal et al. 2012). Absorptive removal of CO₂ from flue gases at such a low concentration compels handling of large volume of gases which in turn requires larger size of equipments and high capital investments. Alkanolamines, monoethanolamine, diethanolamine, etc. as solvents were used for the chemical absorption process and the solvents (e.g., methanol, sulfolane and dimethylether) were used for physical absorption process. The presence of additional contaminants like NO_x and SO_x in the flue gases, have further negative impacts on the solvent performance (Hossain and de Lasa, 2008). The corrosion of equipment in the presence of oxygen and the energy intensive process related to the regeneration of solvent are the major problems of this approach and so far limited this to pilot scale projects.

Other technologies such as adsorption, membrane separation and cryogenic separation are also less suitable for post combustion capture due to low CO₂ concentration and impurities in flue gases. Several adsorbents for instance zeolites, activated carbon, Al₂O₃, molecular sieves, etc. were used to capture CO₂ selectively from the flue gases (Hossain and de Lasa, 2008). The regeneration of the adsorbents, however, is again the energy intensive process. Various types of porous membranes include polymers, metal-rubber composites, etc. are available that can separate CO₂ but the major disadvantage of this method is low gas throughputs (Hossain and de Lasa, 2008).

(iii) Oxy-fuel combustion: This process is similar to post-combustion process with some advantageous upgradations. Here, pure oxygen is generated using cryogenic air separator. This pure oxygen is mixed with recirculated flue gas (RFG) to maintain conditions similar to air fired configuration and fuel is combusted in this oxygen (Fan et al., 2012). The advantage of combustion in pure oxygen is complete oxidation of fuel to CO₂ and H₂O. The mixing of oxygen with RFG is necessary as combustion of coal in pure oxygen leads to very temperatures and currently available material of construction cannot withstand these high temperatures. The CO₂ capture from the flue gas stream of this system is comparative easy with existing separation technologies as CO₂ concentrations is high in the range of 70-95% depending on type of fuel, O₂ purity, and O₂ excess. The major disadvantage in this process is high capital cost and energy penalties involved in pure oxygen generation (Olajire, 2010). However, improvement in membrane technologies operating at high temperature can resolve this limitation to considerable extent (Luo, et al., 2018).

In 2012, the Department of Energy of United States of America, implemented the concept of CO₂ capture, utilization, and storage (CCUS), which has the potential for making not only the fossil fuel gasification greener but also helping in the extraction of the fuels with a little energy. CCUS technology offers several emerging applications in particular for Enhanced Oil Recovery (EOR) (i.e. injection of CO₂ into depleted oil wells for extraction of untapped oil (Goel et al., 2008; TERI, 2013). CO₂-EOR is a well-established technology that provides 6% of oil production in U.S. It has been anticipated that CCUS has the great potential

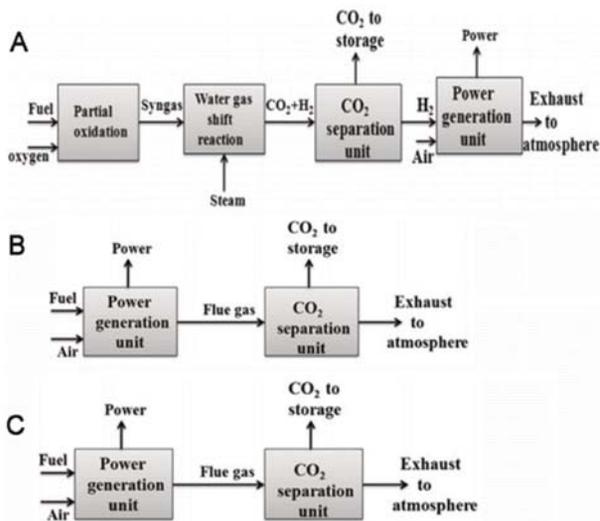


Figure 3. Principle of A) Pre-combustion capture, B) Post-combustion capture and C) Oxy-fuel combustion CO₂ capture.

to add further 60 billion barrels of crude oil. Supercritical CO₂ has been used as a green solvent due to its less-toxic, chemically stable, readily available, easily recyclable nature and exploited for the synthesis as well as modification of polymer, polymer bending, microcellular foaming and particle production (Nalawade et al., 2006). Therefore, there is potential scope for utilization of CO₂ to value added products, once captured in concentrated form.

Even though CO₂ in several forms have been used for various applications including fisheries, food production, chemical, rubber or leather production etc., the estimates show that the overall usage of CO₂ is very less compared to that of the total CO₂ emissions (Hossain and de Lasa, 2008). Therefore, adequate methods need to be identified to store CO₂ in the suitable locations like empty oil or gas fields, saline aquifers and terrestrial sequestration like plantation or forestry in degraded areas. Non-minable coal deposits can be considered as another potential alternative for the CO₂ storage, due to their greater affinity towards CO₂ than methane. It also helps extraction of methane at ease from these fields (i.e., enhanced methane recovery). CO₂ can also be stored by dissolving it in saline aquifers at higher pressure. This process has already been employed by the Statoil Company and approximately 1 million tonnes of CO₂ was sequestered per year in the North Sea (Halmann and Steinberg, 2001). Even though deep sea provides the largest area for the sequestration compared to other methods, it may pose the threats to the marine life and the environment.

Like any other physico-chemical process, sequestration of CO₂ can also be associated with environmental and health impacts. Accidents for instance leakage of CO₂ from the pipe lines can be hazardous. Potable water can become acidic by the dissolution of CO₂. Disasters for instance earthquakes, landslides and volcanic eruptions can cause large and sudden leaks of CO₂ from underground storage. Therefore, in depth and extensive research is still required to explore different technological options for capture and sequestration of CO₂.

2.1. Need for CCS in India

India is a home for more than 1.2 billion people which makes it the second highest populous country in the world. India has witnessed a rapid economic growth during the last two decades, which obviously improved the quality of life of citizen with increased demand of energy and resources. The electricity is produced from a number of sources like coal, lignite, natural gas, hydroelectric, nuclear and other renewable resources, (e.g., solar, wind, etc.) in India.

Recent statistical data show that 9.46% growth rate for thermal alone followed by nuclear, hydro and other utilities (Figure 3). The specific emissions from the coal based industries in India are about 1.07 KG/kWh. Coal supplies 62% of India's energy and it accounts for 30% of the world's energy supply. Considering the coal reserves available and increasing energy demand, coal would remain a dominant source of energy supply for the years to come, thus further aggravating the climate change issue. Therefore, India is thrusting a great deal of importance on the CCS technology, ensuring a vital solution for Global warming and increased energy efficiency.

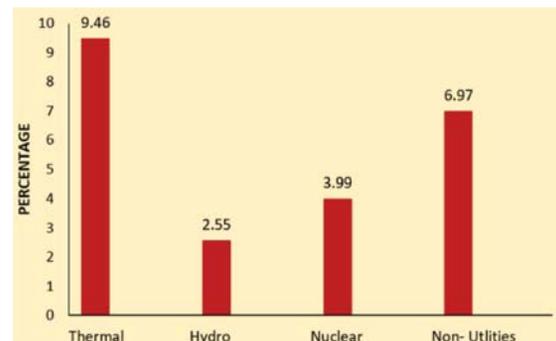


Figure 4. Compound Annual Growth rate of Installed Generating Capacity of Electricity in Utilities and Non-Utilities in India from 2005 to 2014 (Government of India Ministry of Statistics and Programme Implementation 2015)

The Energy and Resource Institute (TERI) India conducted a study to identify the potential of CCS in India with the cooperation of Global CCS institute in 2013 (TERI, 2013). As per the report, the CO₂ emissions including those from Land Use, Land Use Change and Forestry (LULUCF) were 1727.71 million tonnes of CO₂ eq. and the gross CO₂ emissions were 1497.03 million tonnes. The per capita emission was 1.3 tonnes capita⁻¹ without including LULUCF. In 2007, about 66% of CO₂ emissions came from the energy sector out of which 48% was contributed by the generation of electricity alone. Considering India's economic growth, and energy demand, the annual CO₂ emissions would be expected to increase up to 5.5 billion tonnes by 2030 (Planning Commission 2005). India does recognize the seriousness of the problem but it faces the challenges of meeting the requirements of their citizens for their socio-economic growth (TERI, 2013).

India has many reserves for fossil fuels; however, due to higher demand it imports significant quantity of oil as well as natural gas. Importantly India is the world's third largest coal producer, and therefore, clean coal technology will be an important target to meet future energy demand.

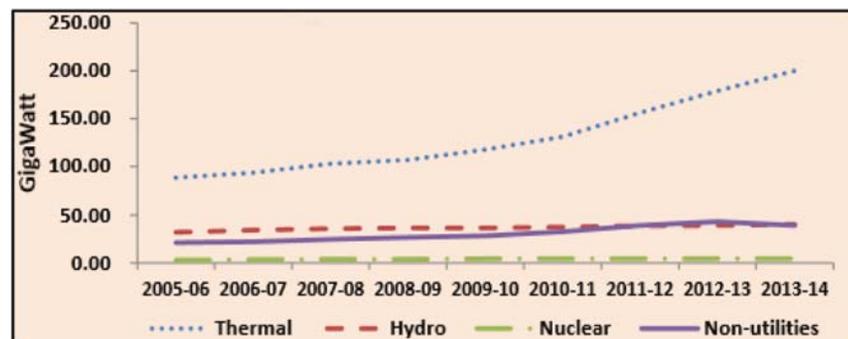


Figure 5. Electricity Generation Capacity Trends from 2005 to 2014 (Government of India, Ministry of Statistics and Programme Implementation 2015)

The compound annual growth rate for total installed electricity generation was 7.72% i.e., from 145.7 GW in 2006 to 284.6 GW in 2014 (Figure 4). From the statistics on coal reserves, it is clear that coal would be significantly used to ensure energy security in India.

India has at the same time started witnessing the impacts of global warming caused due to the usage of fossil fuels and therefore planning to aggressively address the GHG emissions issue. The unprecedented flooding and change in precipitation pattern are being considered as possible impacts of global warming, as it can severely affect agriculture dominant economy of the country. India's National Action Plan on Climate Change (NAPCC) in 2008, explains how much importance that India gives on limiting the GHG emissions, which would not emit further than the already developed nations, as it pursues development. Many national missions have already been set up to curb the effects of climate change. A great part of NAPCC efforts are on dealing with GHG mitigations in the power sector. It provides the various measures for reducing the emissions from the power plants, increasing the efficiency of systems, employing clean coal technologies and switching to other fuel alternatives. Import of higher grade coal or metallurgical coal is also needed for the production of steel.

The crude oil reserves in India come up to 757.44 million tonnes, which is inadequate to meet its growing demands. The gap between the oil production and consumption is getting wider with every passing year. In 2010, it was estimated that the natural gas reserves are 1241 billion cubic meters. The fertilizer and power sectors account for nearly three-quarters of natural gas consumption in India. The public sector units (PSUs) in the oil and gas sector of India become the important stakeholders since they are the major producers of CO₂ emissions.

There are many R&D activities going on CCS in India. It is mainly taken up by the National Program on Carbon Sequestration (NPCS) under the Department of Science and Technology (DST). It concentrates largely on the development of carbon capturing process. Some of the projects include modeling and simulation of Carbon Recycling Technology through conversion of CO₂ into the useful multi-purpose fuel by Rajiv Gandhi Technological University, Bhopal. National Geophysical Research Institute (NGRI) is focusing on the sequestration of CO₂ into geological environment. The end-pipe treatment for CO₂ capture is carried out based on chemical absorption, membrane separation, physical adsorption and cryogenic separation methods. All these processes were employed for a long time in chemical and petrochemical industries. Various projects were also done on carbon sequestration through micro algae bio-fixation and other sequestration modeling. Council of Scientific and Industrial Research (CSIR)-National Environmental Engineering Research Institute (NEERI) developed a bio-reactor at a pilot scale using biological as well as chemical methods for CO₂ sequestration. The National Aluminium Company (NALCO) plans to set up a carbon capture unit in the coal power plant at Angul, Odisha (TERI, 2013). The National Thermal Power Corporation (NTPC), India's largest power company (and world's one of the largest CO₂ producers) has also been conducting some research on CCS, especially on Deccan basalt formation as a possible carbon storage option as well as that on CO₂ capture options. Bharat Heavy Electrical Ltd., and Andhra Pradesh Power Generation Corporation Ltd., (APGENCO) explores cheaper techniques for carbon capture and it adopts Integrated Gasification Combined Cycle (IGCC), a cheaper carbon capture technique.

Many new adsorbents are developed and tested for the post-combustion carbon capture by the Indian Institute of Petroleum (IIP) in Dehradun as well as at NEERI, Nagpur. Institute of Reservoir Studies is carrying out carbon capture and EOR studies at large scale in Gujarat (TERI, 2013). NGRI is also testing the feasibility of storing the CO₂ in basalt formations. Government of India is currently focusing on CCS related activities and it is a participant of FutureGen programme. The wide exploitation of currently available CO₂ capture and sequestration (CCS) is hindered in India due to the requirement of high capital cost as well as energy as a result of the energy intensive separation of CO₂ from the large volume of flue gases.

3. Potential Fuels in India

3.1. Coal

Coal is one of the low-cost fossil fuels available at large scale in India. India would predominantly use coal as a domestic source of energy in the coming years. Approximately 27 coal reserves are found mainly in southern and eastern parts of India. Coal India Limited (CIL) accounted for about 462 million tonnes in 2013-14 and showed 2.3% growth rate compared to the previous year. The total estimated reserves of coal came around 301.05 billion tonnes with 0.7% increase in 2014 (Government of India, Ministry of Statistics and Programme Implementation 2015)

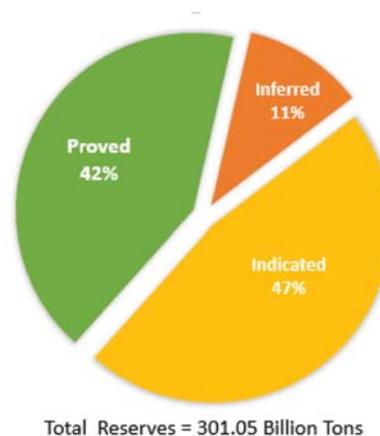


Figure 6. Estimated Reserves of Coal (Government of India, Ministry of Statistics and Programme Implementation 2015)

It has been identified that coal would remain India's primary energy source till 2032. 50% of the total coal production would account for commercial energy consumptions in India. It has been estimated that 78% of the total domestic coal production would be consumed for power generation. India's growth therefore greatly depends on power sector that would be depended largely on coal. Central authorities like NTPC (National Thermal Power Corporation) contributes a major share in thermal power production (TERI, 2013). Bharat Heavy Electricals Limited (BHEL) has a share of 62 % of India's total installed power capacity and has been the backbone for providing pulverized coal (Chikkatur and Sagar, 2007; TERI, 2013). Singherani Collieries Company Limited (SCCL) continues to be a main provider of coal for the southern region. Small quantities of coal are also being produced by Indian Iron and Steel Company (IISCO), Tata Iron and Steel Company Limited (TISCO) and Damodar Valley Corporation (DVC).

Considering the limited reserves for natural gas and crude oil and the restrictions of alternatives, coal would play the main role in the country's energy scenario. As it is inevitable that coal would continue as energy resources, however, considering the need to reduce the stress on the environment, Clean Coal Technologies on efficient energy extraction processes and CCS are being explored as a possible practical option to address energy and climate change in a short and even medium term. Seven CSIR laboratories are currently involved in the issues of coal and its emissions through Cross Cluster Projects (CCP) titled TapCoal that includes the CO₂ capture and sequestration, including the biological routes and coal combustion and gasification. This review is prepared under the objectives which partly covers pilot scale investigations on oxy-fuel combustion, chemical looping combustion, circulating fluidized bed gasification, co-combustion and co-gasification of coal with biomass.

3.2. Natural gas and gas hydrates

Though India largely depends on coal, its poor quality hinders wider exploitation for power generation. Efforts were made to identify low-cost alternatives to Indian coal, for instance natural gas. Natural gas is one of the fuels with relatively lesser CO₂ emissions when compared to coal or other hydrocarbon fuels. There was an increase of about 5.34% during the year 2013-14 for the estimated gas reserves, majorly contributed by Eastern offshore followed by Western offshore. Domestic natural gas, piped natural gas and imported liquefied natural gas are the three major options in India for getting natural gas. The natural gas exploration was initially carried out by the National Oil Companies, Oil and Natural Gas Corporation (ONGC) and Oil India Limited (OIL). It may be anticipated that diesel generator sets may be replaced with natural gas turbines in the future due to the significant reduction in transmission losses.

The estimated natural gas reserves stood at 1427.15 billion tonnes as of 2014. National Thermal Power Corporation (NTPC), the largest Indian power generating company, has 7 gas stations and it targets to generate 1,28,000 MW with a mixed energy sources comprising of 56% coal, 16% natural gas, 11% nuclear power and renewable energy sources including hydropower, solar energy, etc. by 2032.

Lignite experienced a compound annual growth rate of 3.85% when compared to all the other conventional resources (Figure 7). Coal and natural gas will continue to play a vital role in electricity generation not

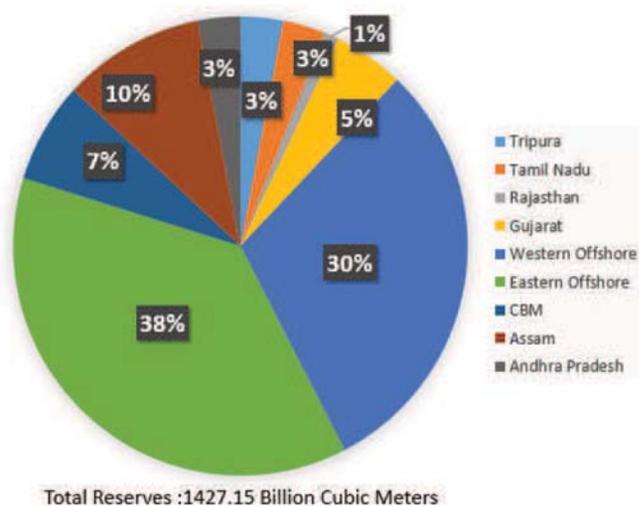


Figure 7. Estimated Reserves of Natural Gas (Government of India, Ministry of Statistics and Programme Implementation 2015)

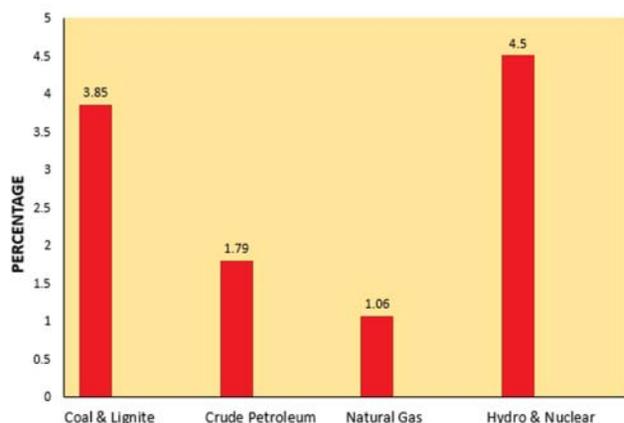


Figure 8. Estimated Reserves of Natural Gas (Government of India, Ministry of Statistics and Programme Implementation 2015)

only in India but also in many parts of world including China, Indonesia. The Central Electrical Authority (CEA) of India has predicted that the energy demand would increase more than a two-fold from 132 GW in 2007 to 280 GW in 2017 of which at least 80 GW will be solely based on coal (Chikkatur and Sagar, 2007). The demand for natural gas in India has increased substantially up to 10% of India's total energy consumption over the last two decades and this should be expected further to increase by 25% in 2030.

As it can be seen, it can be guaranteed that there wouldn't be any sudden decline in demand of coal and natural gas for thermal power generation. India has already taken major efforts in CCS and it became a member to Carbon Sequestration Leadership Forum (CSLF). India is the first country that signed an agreement with the US government on FutureGen, aiming at building and operating world's first coal power plant which sequesters CO₂. India is an institutional partner in BIG SKY Carbon Sequestration Partnership and Asia Pacific Partnership on Clean Development. The development of CCS is important because of the challenges associated with other alternative energy sources and therefore usage of coal and natural gas as the major sources of energy would continue in the near future despite very ambitious plans on solar energy utilization in India.

4. Chemical Looping Combustion: A Potential Option for CO₂ Capture

A mixture of flue gases is produced upon coal and natural gas combustion due to the use of air as oxidant that makes difficult in separation of CO₂ from the flue gases for the carbon capturing process. CO₂ should be separated from the flue gases from the power station's chimney and

pre-concentrated prior to CCS processes. Separation of CO₂ is an energy intensive process, as it needs to be separated from the mixture of N₂, O₂, H₂O etc. Minimization of energy penalty, CO₂ selectivity, degradation of absorbent/ adsorbent are the major limitations with CO₂ capture technologies, which are driving forces for alternate technologies like oxy-fuel and chemical looping combustion.

Various forms of chemical looping have been employed for many years, however, the efficiency, recyclability, and reactivity needs to be improved further to exploit its complete potential (Fan et al., 2012). There are a number of chemical looping reactions, of which the important ones are discussed below in detail:

4.1. Chemical Looping Hydrogen (CLH)

Chemical Looping Hydrogen (CLH) also known as Chemical Looping Gasification (CLG) produces hydrogen through *water splitting* reactions. Metal oxides can be reduced into metal upon injection of fuel in the fuel reactor and fuel can be oxidized into CO₂ and water. Metal or oxygen depleted metal oxides can be re-oxidized by the injection of steam in the second reactor, also known as the oxidizer or hydrogen generator, which produce virtually pure hydrogen. Carbonaceous fuels can be used efficiently in CLH as similar to CLC (Fan et al., 2012). Iron-based oxides are mainly employed as oxygen carrier for CLH (Fang et al., 2009). CLH system sometimes comprises three reactors namely air reactor, fuel reactor and steam reactor.

4.2. Chemical Looping Reforming (CLR)

Another strategy employed in chemical looping is to produce hydrogen fuel or partially oxidized fuel in the fuel reactor (syngas-a mixture of carbon monoxide and hydrogen), so called Chemical Looping Reforming (CLR) (Dawoud et al., 2007; Fan et al., 2012). The partial oxidation can be achieved by reducing of air-fuel ratio. The addition of water and CO₂ to the fuel in the fuel reactor can alter the concentration of H₂ and CO. Steam reforming is used for lighter fuels or gaseous fuels (e.g., natural gas). Partial oxidation is carried out for heavier fuels (e.g., coal or oils) followed by chemical looping reforming reaction that produces a higher percentage of carbon monoxide in the syngas (Fang et al., 2009). The selected oxygen carrier should have higher selectivity towards the formation of carbon monoxide and hydrogen rather than CO₂ and water or decomposition of the fuel to hydrogen and carbon. Majority of the CLR experiments were conducted using nickel oxides as oxygen carrier (Fan et al., 2012; Fang et al., 2009).

4.3. Chemical Looping Oxygen Uncoupling (CLOU)

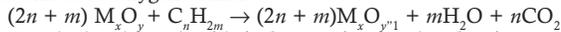
The major technological breakthrough in chemical looping is that the development of materials, which have chemical looping with oxygen uncoupling (CLOU) properties. Metal oxides having reversible redox properties release gaseous oxygen upon heating through CLOU mechanism in the fuel reactor that aids combustion of the solid fuels (Moghtaderi, 2012). CLOU contains three step process in the two interconnected reactors. In the first step, the metal reacts with air and oxygen coupling takes place in the air reactor. In the second step, the metal oxide decouples the oxygen in the fuel reactor and in the third step, the uncoupled oxygen reacts with the coal or any solid fuel. Solid fuels were gasified through both ex-situ and in-situ methods and used for earlier CLC processes. In the ex-situ method, the solid fuels are gasified in a separate chamber and the gases generated are fed into a gas-phase CLC system. Whereas, the solid fuels were gasified in the fuel reactor and the off-gases are fed into the oxygen carrier particles in the in-situ method. Fast gasification of the solid fuels were observed when they react with the gaseous oxygen. The oxides of Fe, Mn, Cu, etc. have the tendency of releasing gaseous oxygen. The mixed oxides of Fe, Mn, and Cu (FeMnO₃, CuMn₂O₄, etc.) also exhibit CLOU property (Mungse et al., 2014, 2015). Therefore, CLOU-based technology seems to have a potential for the combustion of coal in India.

4.4. Chemical Looping Combustion (CLC)

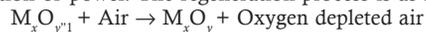
Chemical looping combustion (CLC) is another innovative approach that helps carbon capture in the combustion process. Pure CO₂ can be produced virtually and readily stored without any further processing steps through CLC. The release of oxygen in the combustion chamber can be achieved through a metal and metal oxide reaction. The oxides of Cu, Ni, Fe, etc. are the examples of oxygen carrier for CLC. According to IPCC, CLC has a potential in reduction of the cost for the carbon capturing process. Types of oxygen carriers, development of low-cost oxygen carriers and operational problems in CLC process are discussed below in detail.

Chemical looping combustion was initially developed by Richter and Knoche in 1983. Ishida et al. (1998) and other groups initially developed several oxygen carriers in 2002. After that, almost 300 different oxygen carriers were tested and the new concepts like CLC and CLR were studied in detail by 2006. These methods avoid direct contact between the air and the fuel. CLC is also known as 'flameless combustion' process and can be varied depending upon the nature of the fuels. Chemical looping combustion has been tested with a variety of feed materials. The efficiency of the system would solely depend on the strength of the oxygen carrier. Methane, syngas, biofuels, coal, etc. were used mainly as fuels (de Diego et al., 2004). Methane was used extensively as a fuel for CLC.

CLC process (Figure 8) generally uses a metal oxide as the oxygen carrier and is configured with interconnected, two fluidized bed reactors namely air and the fuel reactor. In the fuel reactor, the fuel is oxidized by the oxygen released from the metal oxides. The oxidation of the fuel with the metal oxide is mostly an endothermic process. In the case of copper based oxygen carriers, the reactions taking place both in the air reactor and the fuel reactor are both exothermic in nature (Mungse et al., 2014). CO₂ and water vapour are formed as the products after the complete combustion of fuels. CO₂ can be easily then separated by condensing of water vapour that eliminates the need of an additional energy and cost. The following equation describes the oxidation of fuel in the fuel reactor using metal oxides as oxygen carrier:



The oxygen depleted metal oxide is then re-circulated to the air reactor for their regeneration, where it reacts with the oxygen from air and regenerates again to the original form. The regeneration process is an exothermic and the heat generated is used for the fuel combustion as well as production of power. The regeneration process is as follows:



The oxygen carrier is separated from the other gases in a cyclone separator and the outlet gas stream from the air reactor would contain unreacted oxygen and nitrogen that have virtually no or minimal environmental impact

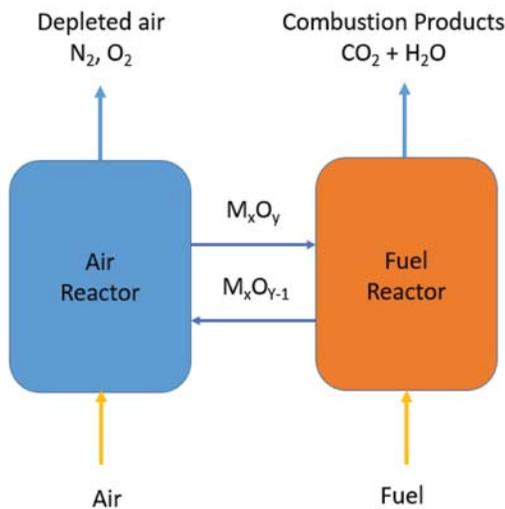


Figure 9. Schematic illustration of chemical looping combustion

The oxidation reaction is exothermic whereas the reduction reaction is endothermic in nature. The heat of reaction would depend on the type of oxygen carrier and the fuel that are being used. The net heat evolved during the combined process remains equal to the amount of heat produced during a normal combustion process. Even though CLC does not provide any enthalpy gains, the heat of generation is equal to the heat of combustion. However, it helps in the separation of CO₂ from the flue gases. The endothermic process is always accompanied with a temperature drop that should be compensated from the air reactor along with the recirculation of the oxygen carrier (Chiu and Ku, 2012). Also, the formation of NO_x can be avoided due to the oxidation of fuel in the absence of air as well as the regeneration of oxygen carrier in the absence of fuel. Usually the formation of NO_x occurs at a temperature above 1200 °C, which is the maximum temperature for any CLC process (Hossain and de Lasa, 2008).

5. Reactor design

Three types of reactors namely (1) interconnected fluidized bed reactor (2) alternating fixed-bed reactor and (3) rotating reactor were used mainly in CLC (Tang et al., 2015). Higher CLC performance can be obtained by achieving of proper contact between the fuel and the oxygen carrier. The intimate contact between the gaseous fuel and the metal oxide is strongly depended upon the reactor configurations. Wolf et al. (2004) reported the essential features that follow for an efficient CLC system (Halmann and Steinberg, 2001): (i) Transportation of particles between the air and the fuel reactor for proper fuel conversion (ii) No exchange of gases between the reactors (iii) Provide proper retention time for both oxidation and reduction reactions (iv) Withstand high pressure and high durability for overall efficiency (v) Withstand high temperature to ensure turbine efficiency.

Interconnected fluidized bed reactors are used commonly in CLC. The oxygen carriers are transferred between the fuel and the air reactor through a circulating fluidized bed setup, which has one riser and one bubbling component. Both the reactors are connected using loop seal devices to avoid any mixing of the feed gases. The oxygen carriers are kept stationary and they are exposed to both oxidation and reduction conditions by switching the feed gases periodically in the case of fixed bed setup (Tang et al., 2015). The oxygen carriers were rotated between the different gas feeds, which flows radially outward through the oxygen carrier bed in the case of rotating reactor. Inert gas is introduced in between the reactions to avoid the mixing of the feed gases (Tang et al., 2015).

6. Types of carriers – Oxygen carriers and Carbon dioxide carriers

Oxygen carriers and CO₂ carriers have been used in the chemical looping processes. The oxygen carrier that release oxygen for the fuel combustion is called CLC. CO₂ carriers were also used to adsorb CO₂ that was formed after fuel combustion (Fan et al. 2012). While using CO₂ carriers, the activity takes place in two reactors namely the carbonator and the calciner. This process is used for the in situ removal of CO₂ using metal oxides through adsorption process. The metal oxide is converted to its metal carbonate form during the carbonation reaction. Metal oxides can be regenerated back to its original form during calcination step of metal carbonates which produces CO₂ and it can be readily captured and stored. The success of this system lies in the availability of low-cost metal oxide and their efficiency in adsorption. One of the applications of this system is the enhancement of water-gas shift reaction favoring hydrogen production. Calcium oxide (CaO) and calcium hydroxide (Ca(OH)₂) have been extensively studied as metal oxide sorbents that can be used in calcination-carbonation process (Fan et al. 2012). Air was used mainly to regenerate the oxygen carriers after oxidation of fuels. However, steam and CO₂ was also used to regenerate the oxygen carriers in some cases.

Adanez et al. (2012) reported that the possible usage of steam to regenerate the oxygen carrier as well as the production of gaseous H₂ in the air reactor. The major shortcoming of this method is the reactivity of the oxygen carrier with steam that affects the regeneration as well as H₂ production (Figure 9). Various metal oxides were studied in detail and found that Fe-based oxides are efficient for the water-gas shift reaction or for the production of H₂.

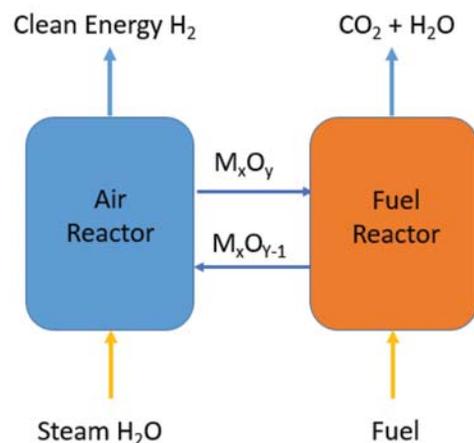


Figure 10. Schematic illustration of chemical looping combustion for H₂ production

Experiments were also carried out using CO_2 for the oxidation of the oxygen carrier. A part of the CO_2 captured from the fuel reactor can be directed to the air reactor that can re-oxidize the oxygen carrier (Figure 10). This method has been considered as one of the potential methods for the utilization of CO_2 . The major drawbacks of using CO_2 is 1) the production of carcinogenic carbon monoxide after the oxidation of the oxygen carrier and therefore careful handling is essential 2) low oxidation kinetics 3) highly endothermic in nature.

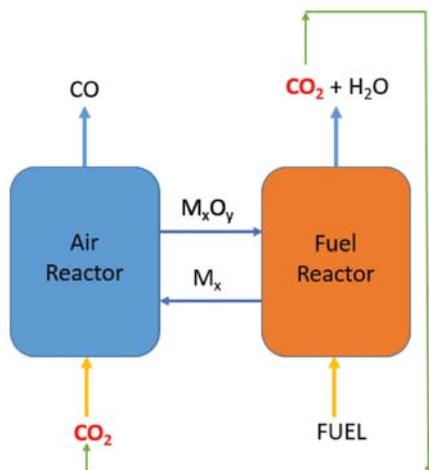


Figure 11. Schematic illustration of chemical looping combustion using CO_2 as the oxidizing agent

6.1. Oxygen carriers

Selection of oxygen carrier is one of the important issues among other issues for CLC. The oxygen carrier can be selected based on oxygen carrying capacity (OCC), reactivity, favorable thermodynamic properties, resistance towards attrition, agglomeration, carbon deposition etc. The important characteristics of oxygen carrier and its environmental as well as economic impacts are discussed here in detail (Tang et al., 2015).

6.1.1. Oxygen carrying capacity:

Oxygen carrying capacity (OCC) is one of the important properties as it affects directly the process design and rate of recirculation of oxygen carrier. The circulation rate of oxygen carrier increases with the decrease of OCC (Adanez et al., 2012). The ratio between the amounts of oxygen, depleted from the oxygen carrier and the stoichiometric amount of oxygen needed for the complete combustion of the fuel is important to obtain a better CLC performance. Both supported and unsupported oxides of Ni, Cu, Co, Fe, Mn, etc. were found to be a good oxygen carrier. Dispersion of metal oxides on various available supports changes the OCC due to the reaction between the supports and oxides under CLC condition. Some of the supported metal oxides (e.g. Ni-oxides on Al_2O_3) showed a better CLC performance. It should be noted that not all the supported oxides, however, show the better CLC performance due to the formation of more stable and less reactive compounds.

The method of preparation of the oxygen carriers also has an impact on its OCC. The oxygen carriers are prepared usually by mechanical mixing and extrusion, spin flash, spray drying, freeze granulation, co-precipitation, sol-gel, impregnation, etc. The extent of distribution of the carrier on the support determines its OCC as well as the mechanical stability.

6.1.2. Thermodynamic properties:

Thermodynamic property of the oxygen carrier is very important that would decide ultimately the conditions for CLC. In any CLC system, the rate of oxygen transfer should be high enough to maintain proper heat balance of a CLC reactor. The heat released from air- and fuel- reactors is equal to that of net heat released from a normal combustion processes. The energy involved in a CLC reaction depends on the type of a fuel used. The energy required for the oxidation of methane will be different from the energy that required for syngas oxidation. Oxidation of methane is usually endothermic in nature but oxidation of syngas is exothermic. Moreover, when the reduction reactions are endothermic in nature, the heat of reaction for the oxidation step will be higher than the usual amount of heat produced during combustion of fuel with air (Adanez et

al. 2012). The oxygen carriers were classified into three categories based on their equilibrium constants of the reaction between oxygen carrier and syngas. The oxygen carriers (e.g., CuO/Cu , $\text{Mn}_2\text{O}_3/\text{MnO}$ and $\text{Fe}_2\text{O}_3/\text{Fe}_3\text{O}_4$) having the equilibrium constant above 1000, can yield 100% conversion of syngas. The oxygen carriers (e.g., NiO/Ni , CoO/Co and $\text{Fe}_2\text{O}_3/\text{FeO}$) can yield 95-99% of syngas conversion that has the equilibrium constant of the order of 100. The oxygen carriers having the equilibrium constant of the order of 10 are not generally recommended as oxygen carrier for CLC applications (Adanez et al., 2012).

6.1.3. Attrition:

Attrition is another important property of oxygen carrier in the case of fluidized bed reactor. The attrition is caused by the chemical stresses under harsh CLC conditions due to the several redox cycles at high temperatures. The attrition resistance of the oxygen carrier can be measured by measuring of its crushing strength. Attrition can also act as an indicator that whether the oxygen carrier is capable to undergo the reaction without any loss of fines (the size of particle is usually smaller than $45\ \mu\text{m}$).

6.1.4. Agglomeration:

The CLC performance of oxygen carrier decreased as a result of their defluidization due to the agglomeration of oxygen carrier under harsh CLC conditions. Agglomeration of the oxygen carrier is undesirable behavior and it can be controlled by dispersing it on the support. Ni-based oxygen carrier showed the resistance towards agglomeration under CLC conditions. Mattisson et al. (2013, 2014) observed that the rate of agglomeration increased due to the fuel combustion in the fuel reactor.

6.1.5. Carbon deposition:

Carbon deposition on the oxygen carriers due to the decomposition of hydrocarbons in the fuel reactor is another major problem that also reduces the CLC performance. Carbon deposition is strongly dependent on the availability of oxygen and it accelerates on the oxygen-depleted oxygen carrier (i.e., end of the oxidation reaction of fuels). The deposited carbon reacts with air and forms CO_2 in the air reactor (Adanez et al., 2012). Carbon deposition can be avoided using a fully mixed fluidized bed reactor.

6.1.6. Economic Aspects

Cost of the oxygen carrier that includes raw materials, precursors, the method of preparation, etc. plays a major role on the overall CLC performance. Iron-, manganese-based oxides as oxygen carriers are cheaper among other metal oxides and these minerals are abundantly available in the earth. The oxides of cobalt, nickel, copper are relatively expensive. If we consider the overall expenditure of the oxygen carrier for CLC, it would mainly depend on the life of the metal oxide, i.e. number of oxidation and reduction cycles. The higher initial costs of the oxygen carriers may be cancelled out by increasing their lifetime of CLC performance. The oxygen carrier with long-term performance with lower cost would decrease the overall cost for CLC significantly.

6.1.7. Environmental and Health Considerations

The indirect impacts of oxygen carrier to the environment as well as health need to be considered seriously when selecting the oxygen carriers for CLC process. The health effects of nickel-based oxygen carrier have been discussed in several reports and its emissions are reported to show carcinogenic properties. Cobalt-based oxygen carriers also need to be handled with care due to their harmful effects. Iron- and manganese-based oxygen carriers are less toxic as compared to other oxygen carriers (Adanez et al., 2012; Chiu et al., 2012).

Several individual metal oxides have been tested for the CLC applications that are discussed here in detail (Fang et al., 2009).

6.1.8 Ni-based oxygen carriers

Ni-based oxygen carriers are some of the most tested oxygen carriers because of their higher reactivity even though they are relatively expensive. The unsupported NiO proved to be inefficient as the cyclic performance is poor due to its agglomeration behaviour (Hossain and de Lasa, 2008). NiO coated yttria stabilised zirconia (YSZ) was studied using natural gas as the fuel, and it was observed that the oxidation rate is faster than that of pure NiO. The advantage of using Al_2O_3 as an inert support is its low cost compared to other supports. When using Al_2O_3 support, a part of NiO is converted into a spinel NiAl_2O_4 , through a solid state reaction with Al_2O_3 during the sintering process, which reacts slowly with the fuel (Fang et al., 2009). Therefore, extra amount of NiO needs to be used to compensate the loss of NiO. NiO supported Mg- or Ca- Al_2O_3 was found to be more

reactive and showed higher selectivity towards methane combustion (Mattisson et al., 2006). NiAl_2O_4 was also used as support instead of Al_2O_3 . Studies have also been conducted using silicon-, titanium-, and zirconium- oxides as the support.

6.1.9. Cu-based oxygen carriers

Cu-oxides have been recognized as potential oxygen carriers as they have higher OCC and reaction rates. Cu-oxides showed 100% conversion of the fuel that was converted into CO_2 and H_2O . It is also relatively cheaper compared to cobalt- and nickel- oxides. Both the oxidation and reduction reactions are exothermic in nature in the case of Cu-oxides, which is a big advantage. Cu-oxides were dispersed on the support to increase the mechanical stability, and higher oxidation/reduction rates for multi-cycle performance. de Diego et al. (2012) showed that the activity of the pure Cu oxides ceased after three cycles. Cu based oxygen carriers prepared by co-precipitation showed a better performance and had a longer lifetime (de Diego et al., 2004).

6.1.10. Fe-based oxygen carriers

Fe-oxides are some of the most attractive oxygen carriers for CLC due to their lower cost, availability and their environmentally benign nature. Fe_2O_3 can be reduced into a number of oxidation states for instance Fe, FeO, and Fe_3O_4 . The conversion of Fe_2O_3 to Fe_3O_4 is thermodynamically favourable. Fe-oxide shows the higher reactivity especially for syngas than that for methane. Fe-oxides are supported on various supports for instance Al_2O_3 , TiO_2 , MgAl_2O_4 , SiO_2 and ZrO_2 . Al_2O_3 was used commonly as support among other supports, mainly due to its lower cost and easy availability. Fe-oxides react with Al_2O_3 through solid-state reaction, however, that have the higher reactivity as well as OCC due to the formation of FeAl_2O_4 . Fe-based oxides are studied in detail for their use with solid fuels (e.g., char, coal, biomass, etc.) as well. The combustion efficiency of Fe-oxides for syngas was found to be 99% (Azimi et al., 2014).

6.1.11. Mn-based oxygen carriers

Mn-oxides have been considered as oxygen carriers due to their low-cost, relatively non-toxic nature, and their availability of minerals. Mn-oxides also have a number of oxidation states like Fe-oxides. Mn_2O_3 is thermodynamically stable at a temperature lower than 900 °C (de Diego et al., 2012). However, Mn_3O_4 is stable at higher temperatures. Therefore, the conversion of Mn_3O_4 into MnO was considered for CLC. The pure phase of Mn-oxides show, however, less reactivity, therefore, Mn-oxides were dispersed on the various support. The disadvantage of Mn-oxides is the formation of irreversible and unreactive phases with some supports (de Diego et al., 2012). Moreover, some other supports decreased its mechanical strength. One of the promising supports for Mn-oxides was found to be bentonite and ZrO_2 , which showed the activity for the reaction with syngas.

6.1.12. Co-based oxygen carriers

Co-oxides have been considered as a possible candidate for the oxygen carrier because of its high OCC regardless of its higher cost. Co_3O_4 is not stable and converted into CoO at higher temperatures. The transformation of CoO to Co is considered for CLC (Fan et al., 2012; Tang et al., 2015). The efficiency of conversion of syngas to CO_2 and H_2O is, however, less compared to other oxygen carriers. Co-oxides were supported on YSZ to increase its reactivity and to avoid carbon deposition (Adanez et al., 2012). Al_2O_3 supported CoO showed higher reactivity towards methane conversion.

6.2. Mixed Metal Oxides

Despite the advantages of individual metal oxides, their CLC performance decreased with the increase of cycles due to the harsh CLC conditions. Therefore, the pure phase of mixed metal oxides and its supported form were prepared from the precursors and the selected support to overcome the limitations of individual metal oxides. The characteristics of individual metal oxides can be retained or even enhanced by mixing of appropriate individual oxides for CLC application in terms of multi-cycle CLC performance (cost, activity, stability, mechanical strength, reduction in carbon deposition, etc.).

The mixed oxide of Fe and Mn has been developed in our lab as a possible candidate for CLC. Fe-Mn mixed oxide possesses the promise as oxygen carrier for the CLC applications due to availability of low-cost minerals precursors, relatively high OCC, stability and environmentally benign nature. We have reported the pure phase of iron-manganese oxides (FeMnO_3 and $\text{Fe}_3\text{Mn}_3\text{O}_8$) that exhibits CLOU property. It was found that

$\text{Fe}_3\text{Mn}_3\text{O}_8$ was reduced into FeMnO_3 at higher temperatures. Fe_3O_4 and MnO were observed as reduced products after methane combustion reaction of FeMnO_3 (Munse et al., 2015). Nickel manganese oxides were also prepared for methane combustion (Adanez et al., 2012).

CoO-NiO oxides were prepared as mixed oxide based oxygen carrier, however, the reaction rate was lower than that of its individual oxides due to the formation of a solid solution of NiCoO_2 . However, carbon deposition was not observed in the case of mixed oxide form (Jin et al., 1998). Co-Ni oxides were also synthesized on YSZ- and Al_2O_3 -support as oxygen carrier. Both Co-Ni oxides and its supported form showed complete conversion of methane under the CLC reaction (Chiu et al., 2012; Jin et al., 1998).

Fe-Ni oxygen carriers were prepared by mixing of NiO and FeO, which showed the increased reactivity, however, its mechanical strength and stability of the mixed oxides were decreased. Cu-Mn oxides (e.g., CuMn_2O_7) were also prepared through co-precipitation method, which showed higher reactivity towards methane combustion (Munse et al., 2014).

6.3. Ternary metal oxides

Recently, the oxygen carriers were prepared using ternary metal oxides. Tri-metallic ferrites with different ratios of Fe, Cu and Mn were synthesized by Fan et al. (2015) and tested for chemical looping combustion using methane, syngas and carbon as fuels. $\text{CuFeMn}_3\text{O}_{11}$ and $\text{CuFe}_{0.5}\text{Mn}_{1.5}\text{O}_4$ showed a stable performance for hundred cycles tested using thermogravimetric analysis. These oxygen carriers perform efficiently even without supports. CuFeMnO_4 was also found to be suitable for solid fuels. Other ternary oxides were developed using iron, manganese and silica ($\text{Fe}_{0.66}\text{Mn}_{1.33}\text{SiO}_3$ and FeMnSiO_3), which showed higher OCC and methane conversion. Both the carriers release the oxygen at a temperature range between 800°C and 950°C (Källén et al., 2014)

6.4. Oxygen carrier supports

Both metal oxides and mixed metal oxides were mostly supported on an inert material. The supporting materials provide a higher surface area for the reaction as well as the stability to the oxygen carriers by acting as a binder. The supports provide the resistance against attrition and increase the reactivity as well as durability. It has been found that most of the supports showed the enhanced CLC performance. The oxides of aluminum, titanium, zirconium and silicon and the mixed oxides of NiAl_2O_4 and MgAl_2O_4 were used as supports (Fang et al., 2009).

6.5. Development of ores, industrial wastes based materials as low cost oxygen carriers

Cost of oxygen carrier is one among other major criteria when selecting the oxygen carriers for CLC. The oxygen carriers were used for the combustion of fuels both in the form of gaseous (e.g., methane) as well as solid (e.g., coal). Both fuel and oxygen carrier are thoroughly mixed in the case of solid fuel combustion. There may be expected to lose some amount of oxygen carrier along with the exhaust gases during CLC conditions. Therefore, it would be more economical if we use low-cost ores, industrial wastes, etc. as oxygen carriers for CLC application. Low-cost oxygen carriers are also tested for gaseous fuels.

Adanez et al. (2012) demonstrated the use of ore (e.g., ilmenite) as an oxygen carrier for CLC applications. Recently, a number of studies were performed using ilmenite as oxygen carrier and showed the acceptable CLC performance. The quality and performance of ores can be varied depending on the location. Norwegian ilmenite showed a higher CLC performance for both solid and gaseous fuels compared to the oxygen carrier synthesized from the iron ores.

A number of natural ores are also being explored for manufacturing metal oxides based oxygen carrier. Iron- and manganese- ores are in confocal attention to prepare a low-cost oxygen carrier. Iron ores like hematite are also experimented in detail. Natural iron ores were also found to be suitable for both coal- and natural gas- combustion. However, they showed agglomeration, attrition and loss of fines under CLC condition. It has been found that manganese ores can be a promising oxygen carrier for a CLC process. They were capable of undergoing a significant number of cycles, however, poor mechanical stability and fluidization properties are the major constraints to use them as oxygen carrier.

Other industrial by-products including red-mud from Al_2O_3 manufacturing and the oxide scales obtained from the rolling of steel sheets in steel plants have been considered as oxygen carrier for CLC (Adanez et al., 2012). Some of the oxides scales showed much more reactivity than the iron oxides and ilmenite. Red-mud was tested mainly

with methane and syngas and showed a higher reactivity without attrition as well as agglomeration. CaSO_4 is also used as an alternative oxygen carrier to other metal oxides. It is a very economical product and has high OCC. But it showed the small amounts of unreacted syngas as well as the evolution of SO_2 which reduces the OCC. CaS is the preferred reduced product of CaSO_4 .

7. Challenges in CLC

The formation of coke during the fuel combustion and the presence of sulphur content in fuels are the major problems in CLC operations that are discussed here in detail.

7.1. Coke formation

The formation of coke due to the pyrolysis reaction ($n\text{CH}_4 + m\text{O}_2 \rightarrow x\text{C} + y\text{CO}_2 + z\text{H}_2\text{O}$) during the CLC process is one of the major problems that affects the CLC performance significantly. The coke formation is favoured at high temperatures and it is endothermic in nature (Hossain and de Lasa, 2008). Coke is also formed through Boudouard reaction ($2\text{CO} + \text{O}_2 \rightarrow \text{C} + \text{CO}_2$) and this reaction is exothermic in nature at low temperatures (Nguyen, 2011). These reactions take place usually in the absence of a catalyst. The deposition of coke on the surface of the oxygen carriers decreases their activity. Temperature is another important criteria for coke deposition. Care should be taken while selecting the operating temperatures of CLC as it would also contribute towards the sintering of oxygen carriers. Higher amount of coke was formed at higher temperatures. Fuel ratio to the oxygen carrier need to be optimized to avoid coke formation as higher ratio of fuel results coke formation. It was found that coke formation was more on nickel-based oxygen carriers compared to that of iron-based oxygen carriers. The lower oxygen content in the oxygen carriers facilitates the coke formation. Coke formation can be controlled by using steam with the fuel and dispersion of noble metals with the oxygen carrier.

7.2. Sulphur in fuels

Both coal and natural gas contains sulphur content that varies in the range between 20 and 8000 ppm. The presence of sulfur moieties in fuels can affect not only the oxygen carrier but also the reactor (Hossain and de Lasa, 2008). The sulphur moieties can react with the metals (i.e., reduced form) and form metal sulphides, thus adversely affecting the performance of oxygen carrier. Also, metal sulphides have a lower melting point that results agglomeration under CLC condition (Hossain and de Lasa, 2008). It was also found that the rate of the redox cycles decreases in the presence of hydrogen sulphide. The formation of the SO_2 gas due to the reaction between oxygen and sulphur moieties in air reactor increased both at higher temperatures and/or lower pressure. Such toxic emissions need to be controlled separately and it is also essential to get the permissions from the authorities.

7.3 Mechanical stability of oxygen carrier in fluidized bed operation

During the CLC process difficulties arise due to the inferior mechanical properties of the oxygen carriers. Many experiments show that copper based oxides show problems due to the agglomeration. Most of the materials undergo agglomeration once they are subjected to high temperatures. Cu-oxides undergoes this deformity at fully reduced state –elemental state, as it has very low melting point (de Diego et al., 2005, 2007). Agglomeration of particles causes de-fluidization of the bed which results in forming separate channels for the gas to flow. This channeling would affect the contact between the oxygen carrier and the gas (Adanez et al., 2012). Combination of metal oxides helps reduce agglomeration and increases the efficiency in oxidation of the fuel (Quddus, 2013). Another major challenge encountered is attrition or fragmentation of the particles. In fluidized bed reactors, the weak oxygen carrier particles get fragmented due to the high velocity of the gas coming through the nozzles (Pour et al., 2013). Fragmentation was also found to be result of the excessive number of oxidation-reduction cycles required for a typical CLC operation (de Diego et al., 2007). The fines that are generated due to the less resistance towards attrition is often removed using cyclone precipitators (Tang et al., 2015). Fines of these particles if not removed affects the downstream gas turbine especially in the case of interconnected fluidized bed reactors. Oxides of Ni exhibit excellent attrition resistance compared to other metal oxides. The attrition resistance of these materials can be increased with using oxygen carriers with higher crushing strength (Pour et al., 2013). Supporting oxygen carrier on a stable material is therefore an essential need for majority of metal oxides, however with significant compromise on oxygen carrying capacity, which would lead to more frequent circulation of OC between air and fuel reactors. As mentioned before this also sometimes results in formation of undesired compounds

through solid state reactions of OC with support. We have recently explored self-supported mixed metal oxides of Cu-Mn and Fe-Mn which shows high OCC with good mechanical strength (Mungse et al., 2014, 2015).

8. Research on CLC in India

Council of Scientific and Industrial Research (CSIR)-National Chemical Laboratory (CSIR-NCL), India has done some research in this field. Bhoje et al. (2013) studied the engineering aspects of CLC in terms of net enthalpy, maximum product as well as net energy output from the reactions using different oxygen carriers in the reactors. The observed carbon deposition formed in the fuel reactor was oxidized in the air reactor, which resulted in increased net energy from the CLC process. CaSO_4 was found to be a suitable oxygen carrier for methane combustion as it produced the maximum energy per gram of the oxygen carrier (Bhoje et al., 2013). CaS was obtained as the reduced product after combustion of fuels with CaSO_4 and it can be regenerated readily in air. CaO was also obtained as by-product, which was converted into CaSO_4 through the reaction between CaO and aqueous H_2SO_4 solution. Kale et al. conducted a thermodynamic study of CLC and combined reforming (CR) reactions of LPG (Kale et al., 2010). The CLC reaction of propane was carried out in a temperature range of 400 and 783° C to obtain syngas as a product, which is useful in petrochemical industries. CaSO_4 was used as oxygen carrier in this study. The large amount of thermal energy was produced and it can be utilized for different purposes. Borkhade et al. (2013) conducted a thermodynamic study on the gasification of coal coupled with CLC. The study was concentrated on understanding the effects of pressure, temperature and combined gasification using CO_2 . These results provides an outlook on practical utility of CLC using syngas as fuel (Borkhade et al., 2013).

Experiments were conducted using waste materials like rice husk as fuel for CLC (Monga et al., 2015). Steam and CO_2 were used for the gasification of rice husk in the temperature range of 500-1200 °C using NiO as oxygen carrier. The oxygen carrier was reduced into Ni by oxidation of carbon and hydrogen present in the rice husk.

Studies on CLC have also been carried out by Indian School of Mines, Dhanbad and CSIR-Central Institute for Mining and Fuel Research (CSIR-CIMFR) Dhanbad. Experiments have been conducted using Indian coal as fuel for CLC and copper oxide as oxygen carrier. Two interconnected reactors were used for the process. Low ash Indian coal and CuO was taken and tested in different ratios for CLC. N_2 was passed in between the oxidation and reduction reaction in order to avoid the mixing of the air and fuels. Both experimental and the theoretical studies showed that the direct combustion of Indian coal is feasible in the case of CuO as oxygen carrier.

Various studies on CLC have been conducted at IIT Delhi. Sharma et al. (2014) suggested that recirculating of fluidized bed reactor instead of the interconnected reactor system may help to solve the problems like cluster formation, low residence time, high attrition of the oxygen carrier etc. The generated results can be used to optimize the reactor that can be employed in a CLC power plant (Sharma et al., 2014). It was also found that the bed mass, bed height, residence time of the oxygen carrier influenced the CLC performance and the pressure drop of the CLC reactor decreased with the increase of conversion rates.

Majority of research on development of oxygen carrier has been conducted at CSIR-National Environmental Engineering Research Institute (CSIR-NEERI). Studies are being carried out to develop an efficient, reusable and economically feasible oxygen carriers for CLC. As mentioned earlier, Mungse et al. (2014, 2015) developed mixed oxide systems based on abundantly available metal precursors (Cu, Fe, and Mn). Methane was used as fuel and its complete combustion and high selectivity towards the formation of CO_2 was observed. The pure phase of the mixed oxide of Cu and Mn (CuMn_2O_4) and Fe and Mn (FeMnO_3 and $\text{Fe}_3\text{Mn}_3\text{O}_8$) was prepared using co-precipitation method followed by calcination at high temperatures. The prepared mixed oxides showed CLOU property under inert atmosphere. 100% methane combustion was possible till the complete exhaustion of oxygen from the oxygen carrier. Cu and MnO as well as Fe_3O_4 and MnO were the by-products after CLC reaction. The complete regeneration of the mixed oxides of Cu and Mn as well as Fe and Mn was observed upon re-oxidation in the presence of air. The performance of Cu and Mn as well as Fe and Mn mixed oxides was not altered for continuous four cycles. Though the morphology of oxygen carrier was changed, the OCC was not altered (Mungse et al., 2014). The lattice of CuMn_2O_4 was altered upon heating under inert atmosphere (CLOU property), however, virtually reinstated upon cooling down to room temperature in air. Cu and MnO are the final reduced

products after CH_4 combustion reaction and the mixed oxide phase of CuMn_2O_4 was readily regenerated in air. The average OCC of the oxygen carrier was found out to be 114 mg g^{-1} . The methane combustion efficiency as well as the OCC was not changed in all the tested cycles, thus suggesting very high OCC for this carrier. CO_2 but no toxic CO was formed solely after CH_4 combustion reaction. The mixed oxides of Cu and Mn as well as Fe and Mn show the potential as a CLC material (Mungse et al., 2014). Mn-based mixed oxides may eliminate the possibility of using support for the oxygen carrier in future as MnO can provide structural stability to the reduced mixed oxide (self-supported oxygen carriers) (Mungse et al., 2014).

Cost-effective oxygen carriers based on the ores and minerals are also of interest at CSIR-NEERI. Direct usage of metal oxides instead of metallic salts would reduce the cost significantly to prepare the mixed oxides. Efforts will be made to obtain manganese-, iron- and copper-based ores and minerals to prepare the mixed oxides at large scale with low-cost. Other institutes including CIMFR Dhanbad and CMERI Durgapur are also associated with this work, as well as those institutes will also explore the oxygen carriers using cold cycle in a fluidized bed system under the CSIR funded TapCoal project.

Since coal is most abundant fossil fuel available in India, experiments are also being conducted using coal as the fuel for CLC. Both solid and gasified coal (syngas) will be used to examine the efficiency of the mixed oxides developed at CSIR-NEERI. Sulfur poisoning tests are being performed to examine the stability of the mixed oxides under CLC conditions. There is however a clear need to explore engineering aspects of Chemical Looping Combustion in India, which also includes, testing of these potential oxygen carriers at bench scale, optimization of process and identification of critical parameters for enhanced performance. There is a lot of work being done at international labs on reactor design optimization and heat transfer aspects of CLC reactions, and these would add to the tech-economic feasibility of CLC in future. Such studies will also be essential to understand feasibility of newly developed oxygen carriers as well as CLC technology for future applications.

Conclusion

The consumption of fossil fuels is inevitable in the coming years for even in the modernized globe due to the vast requirement of energy which release, however, CO_2 to the environment. Therefore, the production of cleaner energy using these available fossil fuels and applying possible methods of CO_2 capture and sequestration (CCS) can be expected to form a short and medium term strategies in India and many other developing and developed countries. Coal, natural gas and gas hydrates are the major fossil fuels available in India. Very low prices of crude oil in the recent past, is also encouraging use of fossil fuels in many countries. CLC offers the possibility of production of cleaner energy due to its intrinsic advantage of separation of CO_2 compared to the currently available CCS techniques as they are energy intensive processes. CLC is therefore one of the promising options to control CO_2 through CCS in India and elsewhere, as it produces the electricity largely from fossil fuels. The gaseous hydrogen can also be generated in addition to the cleaner energy generation from fossil fuels using CLC technique. Several individual metal oxides as well as their supported forms were developed for CLC applications at the initial stage, however, mixed oxides and ternary oxides as oxygen carriers were developed later to overcome some of the limitations of individual metal oxides. Ores, industrial wastes, etc. have also been studied as possible low-cost oxygen carrier for CLC applications, as this is one of the important criteria for CLC application. The mixed oxides of Cu and Mn and Fe and Mn were developed and it showed the promise as oxygen carrier in terms of cost of raw materials, availability, multi-cycle stability and its environmentally benign nature. These mixed oxides showed stable multi-cycle performance towards methane combustion as well as CO_2 -selectivity. These can be used as self-supported oxygen carriers, as one of the reduced products (MnO) of these mixed oxides provides the structural stability. These oxygen carriers can be regenerated readily in the presence of air under CLC conditions. India with its significant coal and natural gas reserves should be expected to invest more in finding techniques to extract maximum energy through greener way using CLC in near future.

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References:

- Abad, A., J. Adánez, F. García-Labiano, L. de Diego, P. Gayán, J. Celaya. 2007. Mapping of the range of operational conditions for Cu-, Fe-, and Ni-based oxygen carriers in chemical-looping combustion. *Chemical Engineering Science*. 62:533–549
- Adanez, J., A. Abad, F. García-Labiano, P. Gayan, L. de Diego. 2012. Progress in chemical-looping combustion and reforming technologies. *Progress in Energy and Combustion Science*. 2: 215–282
- Aghabararnejad, M., G. Patience, J. Chaouki. 2014. TGA and kinetic modelling of Co, Mn and Cu oxides for chemical looping gasification (CLG). *The Canadian Journal of Chemical Engineering*. 92: 1903–1910
- Azimi, G., H. Leion, T. Mattisson, A. Lyngfelt. 2011. Chemical-looping with oxygen uncoupling using combined Mn-Fe oxides, testing in batch fluidized bed. *Energy Procedia*. 4:370–377
- Azimi, G., H. Leion, T. Mattisson, M. Ryde, F. Snijders, A. Lyngfelt. 2014. Mn²⁺Fe Oxides with Support of MgAl₂O₄, CeO₂, ZrO₂ and Y₂O₃/ZrO₂ for Chemical-Looping Combustion and Chemical-Looping with Oxygen Uncoupling. *Industrial and Engineering Chemical Resources*. 53:10358-10365
- Azimi, G., H. Leion, M. Rydén, T. Mattisson, A. Lyngfelt. 2013. Investigation of different Mn-Fe oxides as oxygen carrier for chemical-looping with oxygen uncoupling (CLOU). *Energy and Fuels* 27:367–377
- Azimi, G., T. Mattisson, H. Leion, M. Rydén, A. Lyngfelt. 2015. Comprehensive study of Mn-Fe-Al oxygen-carriers for chemical-looping with oxygen uncoupling (CLOU). *International Journal of Greenhouse Gas Control*. 34:12–24
- Bhoje, R., G. Kale, N. Labhsetwar, S. Bhorkade. 2013. Chemical Looping Combustion of Methane: A Technology Development View. *Journal of Energy*. 2013:1-15
- Blomen E, Hendriksa C, Neele F. 2009. Capture technologies: improvements and promising developments. *Energy Procedia*. 1:1505-12
- Borkhade, S., P. Shriwas, G. Kale. 2013. Gasification Coupled Chemical Looping Combustion of Coal: A Thermodynamic Process Design Study. *ISRN Chemical Engineering*. 2013:1-11
- Cai, L., Y. Guo, A. Lu, P. Branton, W. Li. 2012. The Choice Of Precipitant And Precursor In The Co-Precipitation Synthesis Of Copper Manganese Oxide For Maximizing Carbon Monoxide Oxidation. *Journal of Molecular Catalysis. A Chemical*. 360:35–41
- Chikkatur, A., A. Sagar. 2007. Cleaner Power in India: Towards a Clean-Coal-Technology Roadmap. *Energy Technology Innovation Policy-Discussion Paper. Harvard University*
- Chiu, P., Y. Ku. 2012. Chemical looping process - A Novel Technology for Inherent CO₂ Capture. *Aerosol Air Quality Research*. 12:1421–1432
- Cho, P., T. Mattisson, A. Lyngfelt. 2004. Comparison of iron-, nickel-, copper- and manganese-based oxygen carriers for chemical-looping combustion. *Fuel*. 83: 215–1225
- Dahl, I., E. Bakken, Y. Larring, A. Spjelkavik, S. Håkonsen, R. Blom. 2009. On the development of novel reactor concepts for chemical looping combustion. *Energy Procedia*. 1:1513–1519
- Damen, K., M. Troost, A. Faaij, W. Turkenburg. 2007. A comparison of electricity and hydrogen production systems with CO₂ capture and storage-Part B: Chain analysis of promising CCS options. *Progress in Energy and Combustion Science*. 33: 576–605
- Dansie, J., A. Sahir, M. Hamilton, J. Lighty. 2015. An investigation of steam production in chemical-looping combustion (CLC) and chemical-looping with oxygen uncoupling (CLOU) for solid fuels. *Chemical Engineering Research and Design*. 94:12–17
- Davison, J. 2007. Performance and costs of power plants with capture and storage of CO₂. *Energy*. 32:1163–1176
- Dawoud, B., A. Amer, D. Gross. 2007. Experimental investigation of an adsorptive thermal energy storage. *International Journal of Energy Resources*.31:135–147
- de Diego, L., F. García-Labiano, P. Gayán, J. Celaya, J. Palacios, J. Adánez. 2007. Operation of a 10 kWth chemical-looping combustor during 200 h with a CuO-Al₂O₃ oxygen carrier. *Fuel*. 86:1036–1045
- de Diego, L., P. Gayán, F. García-Labiano, J. Celaya, A. Abad, J. Adánez. 2005. Impregnated CuO/Al₂O₃ oxygen carriers for chemical-looping combustion: Avoiding fluidized bed agglomeration. *Energy and Fuels*. 19: 1850–1856
- de Diego, L., F. García-Labiano, J. Adánez, P. Gayán, A. Abad, B. Corbella, J. Palacios. 2004. Development of Cu-based oxygen carriers for chemical-looping combustion. *Fuel*. 83:1749–1757
- Dubey, A., V. Saxena, P. Sarkar, A. Samanta. 2014. Chemical Looping Combustion Of Indian Coal With Copper Oxide As Oxygen Carrier. *CHEMCON*.
- Edenhofer, O., R. Pichs-Madruga, Y. Sokana. 2014. IPCC: Technical Summary.
- Fan, L., F. Li. 2010. Chemical looping technology and its fossil energy conversion applications. *Industrial and Engineering Chemistry Research*. 49:10200–10211
- Fan, L., L. Zeng, W. Wang, S. Luo. 2012. Chemical looping processes for CO₂ capture and carbonaceous fuel conversion – prospect and opportunity. *Energy and Environmental Science*. 5:7254- 7280
- Fan, Y., R. Siriwardane, H. Tian. 2015. Trimetallic Oxygen Carriers CuFeMnO₄, CuFeMn₂O₄, and CuFe_{0.5}Mn_{1.5}O₄ for Chemical Looping Combustion. *Energy & Fuels*. 29: 6616–6624
- Fang, H., L. Haibin, Z. Zengli. 2009. Advancements in development of chemical-looping combustion: A review. *International Journal of Chemical Engineering*. doi:10.1155/2009/710515.

- Figuerola JD, Fout T, Plasynski S, McIlvried H, Srivastava RD. 2008. Review - Advances in CO₂ capture technology e the U.S. department of energy's carbon sequestration program. *International Journal of Greenhouse Gas Control*; 2:9-20
- Gibbins J, Chalmers H. 2008. Carbon capture and storage. *Energy Policy* 36: 4317-22.
- Goel, M., B. Kumar, N. Charan. 2008. Carbon Capture and Storage- R&D Technologies for Sustainable Energy Future. Narosa Publishing House
- Government of India: Ministry of Statistics and Programme Implementation. 2015. Energy Statistics
- Halmann, M., M. Steinberg. 2001. Greenhouse Gas Carbon Dioxide Mitigation: Science and Technology. *Journal of American Chemical Society*. 123: 7197-7197
- Hossain, M., H. de Lasa. 2008. Chemical-looping combustion (CLC) for inherent CO₂ separations-a review. *Chemical Engineering Science*. 63:4433-4451
- Jin, H., T. Okamoto, M. Ishida. 1998. Development of a Novel Chemical-Looping Combustion/ : Synthesis of a Looping Material with a Double Metal Oxide of CoO - NiO. *Energy & Fuels*. 12:1272-1277
- Jing, D., E. Hermans, H. Leion, M. Rydén, J. Noyen, A. Lyngfelt. 2012. Manganese-silica combined oxides as oxygen carrier for chemical-looping combustion. *2nd International Conference on Chemical Looping, Darmstadt, Germany*.
- Kale, G, B. Kulkarni, A. Joshi. 2010. Thermodynamic study of combining chemical looping combustion and combined reforming of propane. *Fuels*. 89:3141-3146
- Källén, M., P. Hallberg, M. Rydén, T. Mattisson, A. Lyngfelt. 2014. Combined oxides of iron, manganese and silica as oxygen carriers for chemical-looping combustion, *Fuel Processing Technology*. 124: 87-96
- Källén, M., M. Rydén, T. Mattisson, A. Lyngfelt. 2014. Operation with Combined Oxides of Manganese and Silica as Oxygen Carriers in a 300 Wth Chemical-looping Combustion Unit. *Energy Procedia*. 63: 131-139
- Kierzkowska, A., C. Bohn, S. Scott, J. Cleeton, J. Dennis, C. Muller. 2010. Development of Iron Oxide Carriers for Chemical Looping Combustion Using Sol^oGel. *Industrial and Engineering Chemical Research*. 49:5383-5391
- Lambert, A., C. Delquié, I. Clémeneçon, E. Comte, V. Lefebvre, J. Rousseau, B. Durand. 2009. Synthesis and characterization of bimetallic Fe/Mn oxides for chemical looping combustion. *Energy Procedia*. 1: 375-381
- Leion, H., E. Jerndal, B. Steenari, S. Hermansson, M. Israelsson, E. Jansson, M. Johnsson, R. Thunberg, A. Vadenbo, T. Mattisson, A. Lyngfelt. 2009. Solid fuels in chemical-looping combustion using oxide scale and unprocessed iron ore as oxygen carriers. *Fuel*. 88:1945-1954
- Leion, H., T. Mattisson, A. Lyngfelt. 2008. Solid fuels in chemical-looping combustion. *International Journal of Greenhouse Gas Control*. 2:180-193
- Luo, C., Liu, J., 2018. Chapter 13 - Oxygen Production for Oxy-fuel Combustion. *Oxy-Fuel Combustion Fundamentals, Theory and Practice*. Academic Press, Published by Elsevier Ltd., 263-287.
- Lyngfelt, A. 2014. Chemical-looping combustion of solid fuels - Status of development. *Applied Energy* 113:1869-1873
- Lyngfelt, A., M. Johansson, T. Mattisson. 2008. Chemical-Looping Combustion Status of Development. *9th International Conference on Circulating Fluidized Beds (CFB-9)*. Hamburg Germany
- Mondal, M.K., H. K. Balsora, P. Varshney. 2012. Progress and trends in CO₂ capture/separation technologies: A review. *Energy*. 46: 431-441
- Mattisson, T., A. Lyngfelt, P. Cho. 2001. The use of iron oxide as an oxygen carrier in chemical-looping combustion of methane with inherent separation of CO₂. *Fuel*. 80:1953-1962
- Mattisson, T., M. Johansson, A. Lyngfelt. 2004. Multicycle Reduction and Oxidation of Different Types Chemical-Looping Combustion. *Energy & Fuels*. 18:628-637
- Mattisson, T., M. Johansson, A. Lyngfelt. 2006. CO₂ capture from coal combustion using chemical-looping combustion - Reactivity investigation of Fe, Ni and Mn based oxygen carriers using syngas. *Proc. International Technical Conference on Coal Utilization and Fuel Systems*. 2: 879-890
- Mattisson, T., M. Johansson, A. Lyngfelt. 2006. The use of NiO as an oxygen carrier in chemical-looping combustion. *Fuel*. 85:736-747
- Mattisson, T., F. García-Labiano, B. Kronberger, A. Lyngfelt, J. Adánez, H. Hofbauer. 2007. Chemical-looping combustion using syngas as fuel. *International Journal Greenhouse Gas Control*. 1:158-169
- Moghtaderi, B. 2012. Review of the recent chemical looping process developments for novel energy and fuel applications. *Energy and Fuels*. 26:15-40
- Mattisson, T. 2013. Materials for Chemical-Looping with Oxygen Uncoupling. *ISRN Chemical Engineering*. 2013:1-19
- Mattisson, T., J. Adánez, K. Mayer, F. Snijkers, G. Williams, E. Wesker, O. Bertsch, A. Lyngfelt. 2014. Innovative Oxygen Carriers Uplifting Chemical-looping Combustion. *Energy Procedia*. 63:113-130
- Monga, R., G. Kale, S. Guhe. 2015. Chemical Looping Combustion of Rice Husk. *International Journal of Engineering Resources and Applications*. 5:132-138
- Mungse, P., G. Saravanan, T. Uchiyama, M. Nishibori, Y. Teraoka, S. Rayalu, N. Labhsetwar. 2014. Copper-manganese mixed oxides: CO₂-selectivity, stable, and cyclic performance for chemical looping combustion of methane. *Physical Chemistry and Chemical Physics*. 16:13-15
- Mungse, P., G. Saravanan, S. Rayalu, N. Labhsetwar. 2015. Mixed Oxides of Fe and Mn as Low-cost, Potential Oxygen Carrier for Chemical Looping Combustion. *Energy Technology*. 3:856-865
- Nalawade, S., F. Picchioni, L. Janssen. 2006. Supercritical carbon dioxide as a green solvent for processing polymer melts: Processing aspects and applications. *Progress in Polymer Science*. 31(1):19-43
- Nguyen, T. 2011. System analysis of chemical and carbonate looping processes in IGCC power plants for CO₂ separation. *Master Thesis Dissertation, Chalmers University, Sweden*.
- Olajire, A. A., 2010. CO₂ capture and separation technologies for end-of-pipe applications - A review. *Energy*. 35: 2610-2628
- Planning Commission, Government of India. 2005. Draft Report of the Expert Committee on Integrated Energy Policy.
- Pour, N., H. Leion, M. Ryde, T. Mattisson. 2013. Combined Cu / Mn Oxides as an Oxygen Carrier in Chemical Looping with Oxygen Uncoupling (CLOU). *Energy Fuels*. 27: 6031"6039
- Quddus, M. 2013. A Novel Mixed Metallic Oxygen Carrier for Chemical Looping Combustion/ : Preparation, Characterization & Kinetic Modeling. *Ph. D Dissertation, The University of Western Ontario London, Canada*.
- Rubin, E., C. Chen, A. Rao. 2007. Cost and performance of fossil fuel power plants with CO₂ capture and storage. *Energy Policy*. 35: 4444-4454
- Rydén, M., A. Lyngfelt, T. Mattisson. 2011. Combined manganese/iron oxides as oxygen carrier for chemical looping combustion with oxygen uncoupling (CLOU) in a circulating fluidized bed reactor system. *Energy Procedia*.4:341-348
- Ryu, H., D. Bae, K. Han, S. Lee, G. Jin, J. Choi. 2001. Oxidation and reduction characteristics of oxygen carrier particles and reaction kinetics by unreacted core model. *Korean Journal of Chemical Engineering* 18:831-837
- Sahir, A., J. Dansie, A. Cadore, J. Lighty. 2014. A comparative process study of chemical-looping combustion (CLC) and chemical-looping with oxygen uncoupling (CLOU) for solid fuels. *International Journal of Greenhouse Gas Control*. 22:237-243
- Sharma, R., A. Delebarre, B. Alappat. 2014. Chemical-Looping Combustion- an overview and application of recirculating fluidized bed reactor for improvement. *International Journal of Energy Resources*. 38:1331-1350
- Shulman, A., E. Cleverstam, T. Mattisson, A. Lyngfelt. 2009. Manganese/iron, manganese/nickel, and manganese/silicon oxides used in chemical-looping with oxygen uncoupling (CLOU) for combustion of methane. *Energy and Fuels*. 23: 5269-5275
- Siriwardane, R., H. Tian, T. Simonyi, J. Poston. 2013) Synergetic effects of mixed copper-iron oxides oxygen carriers in chemical looping combustion. *Fuel*. 108: 319-333
- Siriwardane, R., H. Tian, D. Miller, G. Richards. 2015. Fluidized bed testing of commercially prepared MgO-promoted hematite and CuO-Fe₂O₃ mixed metal oxide oxygen carriers for methane and coal chemical looping combustion. *Applied Energy*. 157:348-357
- Song, K., Y. Seo, H. Yoon, S. Cho. 2003. Characteristics of the NiO/hexaaluminate for chemical looping combustion. *Korean Journal of Chemical Engineering*. 20: 471-475
- Tang, M., L. Xu, M. Fan. 2015. Progress in oxygen carrier development of methane-based chemical-looping reforming: A review. *Applied Energy*. 151:143-156
- TERI. 2013. India CCS Scoping Study/ : Final Report. *The Global CCS Institute*
- Wolf, J. 2004. CO₂ Mitigation in Advanced Power Cycles - Chemical Looping Combustion and Steam-Based Gasification. *Ph. D Dissertation, Royal Institute of Technology, Stockholm, Sweden*
- Zhao, H., D. Zhang, F. Wang, T. Wu, J. Gao. 2008. Modification of ferrite-manganese oxide sorbent by doping with cerium oxide. *Process Safety and Environmental Protection*. 86:448-454.