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CHEMICAL LOOPING COMBUSTION: A PIONEER PROCESS TOWARDS CLEAN ENERGY

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Abstract— *Since the industrial revolution, the concentration of carbon dioxide (CO_2) in the atmosphere has increased by 43%. As a major greenhouse gas, CO_2 emissions have been directly correlated with global warming and the climate change which has been noticed in the recent decades. Experts predict that the negative effects range from an increase in natural disasters, to the displacement of millions due to an increase in global average sea level. Until sources of renewable energy such as solar and wind power become economically viable and electrically efficient, new, cleaner methods of energy production need to be implemented.*

One such method, called chemical looping, is pioneering a way to achieve cleaner energy production. Chemical looping is a process that combusts fuels such as coal and natural gas and once initiated is a self-propagating reaction that sequesters CO_2 as it moves through the reaction. This method of combustion has the potential to change the way humans create energy and how it affects the planet in the process. Chemical looping's main selling point is being able to capture over 90% of resulting carbon dioxide without a loss in efficiency. However, the main roadblock to widespread implementation of this emerging technology is the rate at which metal oxides, which facilitate an essential redox reaction, deteriorate.

In order to move towards commercial application, new types of metal oxides are being researched and developed. If we are able to create an oxide which can last, chemical looping could be industrialized and give us a clean technology to keep our planet afloat until renewable energy sources can be effectively harnessed. With the right research, it will become a sustainable method of energy production which is cost effective, clean, and beneficial to everyone involved.

Key Words—Agglomeration, Attrition, Carbon sequestration Chemical Looping, Energy, Environmental technology, Metal oxides, Synthesis gas (syngas), Stopgap technology.

CLIMATE CHANGE AND ITS ADVERSE EFFECTS

Global warming, better known as climate change, is the rising of the Earth's temperature that is slated to bring severe environmental and financial consequences for humans. Climate change is directly correlated with the increasing levels of CO_2 and other greenhouse gases (GHGs) in the atmosphere [1]. As each year passes, surface temperature records are set. According to independent analyses by NASA and the National Oceanic and Atmospheric Administration, the globally-averaged temperatures in 2016 were the highest observed since recordkeeping of such began in 1880. The mean in this year was 1.78°F warmer than the recorded mid-20th century mean, 2016 marked the third year in a row where a new high temperature was recorded. Not only was 2016 the warmest year overall, but record highs were set for 8 out of the 12 months within the year. Moreover, since 2001, 16 of the 17 warmest years *ever* recorded have occurred [1].

In addition to the increase in temperature, other measurable and observable changes are happening around the globe. Almost all these other changes prove to be either dangerous or destructive. One of the major changes developing, as a result of global warming, is a rise in sea level. This is due to both the melting of glaciers and the expansion of sea water as it warms [2]. With a rate of increase of about 3mm/year during the last 20 years, areas located within lower elevations are in danger. For example, in Bangladesh, if sea level rises approximately 1 meter, the country is predicted to lose around 17.5% of its land, which would displace millions in an already fairly impoverished nation [3]. Figure 1 below provides a visual of the current state of Bangladesh, as well as how much land would be lost if sea level rose 1 meter to 1.5 meters.

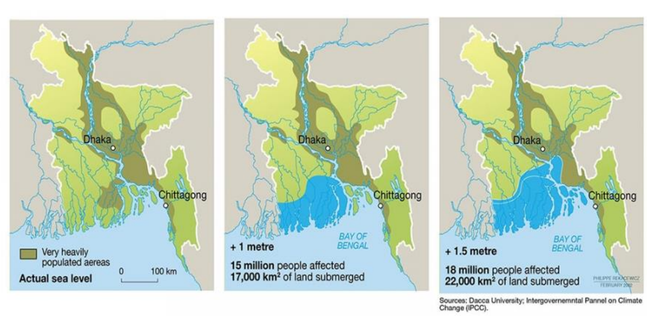

FIGURE 1 [4]

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Visualization of sea level rise in Bangladesh

Coastal areas similar to Bangladesh would, in addition to losing land, suffer from more severe ocean storms such as monsoons and hurricanes, which come hand in hand with the rising sea level and temperature [5]. If we can physically measure the amount our earth has changed and predict exactly how much land a populated area will be losing in the near future, something must be changed to remedy this problem.

Greenhouse Gases: The Culprit of Climate Change

Over the last 150 years, a majority of the increase in greenhouse gasses can be attributed to human activity. Since the industrial revolution, the concentration of CO_2, the most prevalent GHG, has increased by 43% in the atmosphere [3]. The growing need for electricity has risen at a rate of 3.6% annually from 1971 to 2009 and with it the burning of fossil fuels [3]. As of 2013, global electricity production was 23,127,000 Giga-watt hours. As the world continues to develop, this number will only grow [2]. Fossil fuels contribute to 67% of total energy production and spew enormous amounts of GHG into the earth's atmosphere [2]. As the concentration of gases grow, the effects of climate change will get worse. GHGs work exactly how their name suggests. Like a greenhouse, the gasses allow for shortwave radiation from the sun to enter freely into our atmosphere but block the long-wave infrared radiation which radiates back from the earth, trapping it in our atmosphere [6]. Therefore, instead of being released back into space, the heat remains and warms our planet. As more and more greenhouse gasses are released, we start to observe the effects mentioned earlier in the paper such as rising sea level, and global warming. These are the issues our paper's described technology looks to fix, as CO_2 would be captured and not released into the atmosphere.

The production of power and electricity for homes, business, and industry contributes 50% of the GHG emissions in the US [7]. This energy comes mainly from power plants where natural gas or pulverized coal is combusted in hot air to heat water in a boiler and in the process create steam. This steam then powers an engine called a turbine which converts the heat energy from the steam into mechanical energy which spins the turbine [7]. The spinning turbine then powers a generator, a machine that converts this mechanical energy into electrical energy using powerful electromagnets around a spinning copper wire [8]. While this process produces electricity, used by virtually every human on the planet, it spews an enormous amount of CO_2.

Current Means of Carbon Sequestration and Sustainability

The environmental impact of fossil fuel energy has been seen and felt, but it is predicted that only 13.3% of the global energy consumption will be provided by renewable sources by 2030 [9]. Recognizing this, ways to reduce cumulative carbon emission have been developed. The various methods include the following: reducing energy consumption while increasing energy efficiency; using low-carbon fuels; increasing the use of renewable sources; promoting planting of forests, and CO_2 sequestration [9]. Implementing these steps at the earliest possible time would be the only way to avoid reaching a catastrophic concentration of CO_2 in the atmosphere [10]. This thought, while not entirely impossible, is economically and culturally improbable. Therefore, the most practical step towards sustainability is through Carbon Capture and Storage (CCS), a current technology that can provide clean energy from fossil fuels while capturing CO_2 [10]. This technology has the potential to capture around 90% of CO_2 produced by traditional combustion [9].

From a 2012 United Nations conference on sustainable development, sustainability is defined as, "a holistic, equitable, and far-sighted approach to decision-making at all levels. It emphasizes not just strong economic performance, but intragenerational and intergenerational equity. It rests on integration and a balanced consideration of social, economic, and environmental goals and objective in both public and private decision-making" [11]. Sustainable technologies consider and try to achieve the three main goals as mentioned in the quote: social, economic, and environmental.

The social factors related to sustainable technology address how current issues will affect a small-scale and global society and what can be done to make these issues as negligible as possible [12]. For instance, CCS technologies look to solve the problem of rising sea levels which will eventually displace millions of people. Stopping this will inevitably save the health and well-being of these peoples.

Economic factors that influence sustainable technologies have to do with how cost can be minimalized now rather than in the future. Investing in the solutions to these problems now can drastically reduce the economic cost in the future. In relation to CSS technology, the cost of keeping carbon out of the atmosphere now is considerably cheaper than fixing the problems it will cause in the future [12].

Lastly, sustainable technology looks to solve environmental problems that are currently seen as threats to the future health of the global environment. The most prolific effect that CCS technology would have is directly related to solving environmental problems. Many environmental issues are the result of the increasing concentration of greenhouse gasses in the environment, such as the loss of thousands of acres of coral in the Great Barrier Reef and the disappearance of polar environments. These two effects reside under the umbrella of climate change: the main issue CCS attempts to fix [12].

CCS technology consists of three main methods: pre-combustion capture, post-combustion capture, and oxy-fuel combustion [9]. In pre-combustion, the fuel is de-carbonized prior to combustion, while in post-combustion, CO_2 is captured from gases leaving the plant by means of a flue [13]. Oxy-fuel combustion uses pure oxygen which lessens the CO_2 released by the fuel [13]. By using these technologies, 9-16 billion tons of CO_2 could be saved from going into the atmosphere per year [9].

While CCS seems like an obvious decision to make for the health of the global environment, CCS also has limitations. CCS in traditional coal plants increases the required fuel by 25-40% [9]. Moreover, applying this technology would be expensive and, in most cases, would not make economic sense. Therefore, CCS technology, while benefitting the environment, comes at the cost of energy efficiency and the literal cost of money. Thus, a need to develop a process of energy production that takes the cost of fuel and efficiency into mind was needed. From this need came one of the most promising advances in clean fossil fuel production: chemical looping combustion.

CHEMICAL LOOPING: AN OVERVIEW

Due to the alarming rate at which CO_2 has increased as a result of human actions, clean coal burning technologies have been sought out to curb these effects; Chemical Looping Combustion (CLC) technology is so far one of the most promising sources for coal and natural gas combustion to date [9]. Beginning in 1954, CLC has made enormous progress, especially in the last 10-15 years. During these years, extensive developments in the process including the type of fuel, the reactor systems, and the kind of oxygen carrier, also called metal oxides, have thrust chemical looping combustion into the mainstream for alternative energy production.

Chemical Looping combustion utilizes a metal oxide, also called an oxygen carrier (OC), to facilitate the transfer of oxygen in the combustion reaction [9]. This process avoids direct contact between fuel and air and as a result carbon is inherently sequestered without expending any extra energy [9]. The process consists primarily of two reactors: an Air Reactor (AR) and a Fuel Reactor (FR) where the oxidation-reduction reaction occurs that produces the heat of combustion [9]. This reactor configuration allows for efficient means of energy production while maintaining a sustainable and reproducible reaction. Below is a diagram which details the reactors and how they proliferate the chemical reaction.

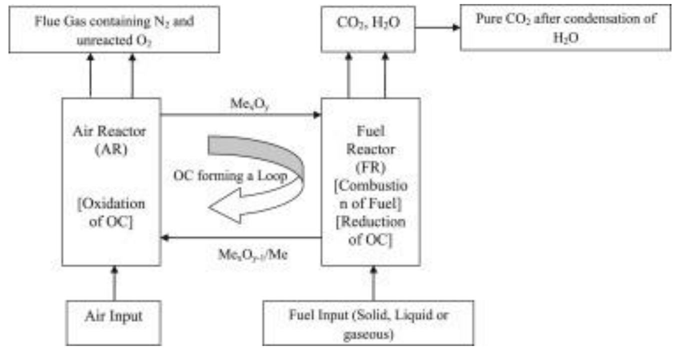


FIGURE 2 [9]
Diagram of the AR and FR used with CLC, as well as an overview of the reactants and products.

In the AR, air is brought in and the OC particles are oxidized by oxygen from air as shown by this reaction:

$$\underset{\text{Reduced form of OC}}{2\mathrm{Me}_x\mathrm{O}_{y-1}} + \mathrm{O}_2 \rightarrow \underset{\text{Oxidise form of OC}}{2\mathrm{Me}_x\mathrm{O}_y}$$

FIGURE 3 [9]
Chemical equation of the reaction which occurs within the air reactor.

The oxidized form of the oxygen carrier is then transported to the fuel reactor [10]. Depending on the type of fuel present in the reactor char (the remaining material left after light gases have been driven from a carbon containing substance) is gasified by steam (or CO_2); however, if the fuel is already present in gaseous form, steam nor CO_2 is needed [10]. The OC then enters the fuel reactor where gaseous fuel reacts with available oxygen in the oxygen carrier. The general chemical reaction that describes this is as follows:

$$\underset{\text{Fuel (gas/solid/liquid)}}{\mathrm{C}_n\mathrm{H}_{2m}} + \underset{\text{Oxidised form of OC}}{(2n+m)\mathrm{Me}_x\mathrm{O}_y} \rightarrow \underset{\text{Reduced form of OC}}{(2n+m)\mathrm{Me}_x\mathrm{O}_{y-1}} + n\mathrm{CO}_2 + m\mathrm{H}_2\mathrm{O}$$

FIGURE 4 [9]
Chemical equation of the reaction which occurs within the fuel reactor.

In the fuel reactor, the oxygen carrier gets reduced; the reduced metal oxides are then returned into to air reactor where they are re-oxidized by air. Airtight seals inhibit any gases from mixing between the two reactors. As a result, the CLC process transports oxygen and inherently removes CO_2 from the reaction altogether.

Not only does CLC capture carbon from the reaction, but it also manages to do this without any loss of efficiency. As a result of Hess's law—which states that regardless of the number of steps in any chemical reaction, the total change in enthalpy (or heat) is the sum of the changes in the steps—CLC produces an equivalent amount of heat as in conventional combustion [9]. What this means is that CLC can extract the same amount of energy as traditional means of energy production, such as coal burning [10]. Since CO_2 and H_2O are inherently separated from other flue gases, the energy used to capture CO_2 is minimized [9]. Chemical looping combustion processes come in a myriad of classifications and understanding the different kinds of chemical looping is necessary to understanding chemical looping combustion as a whole.

Types of Chemical Looping

Three main mechanisms define CLC: fuel type, the reactors, and the oxygen carriers. The fuel which CLC reactors can be boiled down into two main categories: gaseous and solid fuels. The CLC process needs to achieve certain criteria to be able to sustain an ongoing reaction [9]. These criteria, which will be discussed below, relate to the kind of reactor employed in the system [14]. There are currently three different kinds of reactors which include: moving bed or interconnected fluidized-bed reactors, alternately packed or fluidized bed reactors, and rotating reactors. Finally, the type of oxygen carriers, which are vital to the reaction process include nickel, copper, iron, manganese, cobalt, and mixed oxide and perovskite carriers [14].

The fuel used in the CLC process dictates what specific reactions take place inside the reactors, and what supplemental chemistry must take place in order for the reaction to be carried out [9]. CLC of gaseous fuels means that the combustion is done with fuels which come in gaseous states, such as natural gas, refinery gas, or synthesis gas. The oxygen carrier reacts directly with the fuel and follows the redox reaction discussed above (see figures 1,2).

Fuel Variants

The CLC of solid fuels utilizes materials such as coal, petroleum-coke, solid wastes, or biomass. These solid fuels can be further classified regarding whether they react directly with the oxygen carrier [10]. If indirect, the injected fuel is gaseous, although the main fuel is solid. Therefore, the fuel must be gasified and made into a product called synthesis gas (syngas) [9]. This is called Syngas fueled Chemical Looping Combustion and is endothermic in nature which requires the input of energy, supplied either from pure oxygen as a gasifying agent or supplied from the reactor itself [9]. If solid fuels are directly fed into the Solid fueled-CLC reactor, it can be further classified into two kinds: the in-situ Gasification Chemical Looping Combustion (iG-CLC) process and the Chemical Looping with Oxygen Uncoupling (CLOU) process [14]. In iG-CLC, the solid fuel is mixed with the oxygen carrier in the fuel reactor. The oxygen carrier then reacts with gasified products of the solid fuel, generated by H_2O along with CO_2 which act as gasifying agents that have fluidized (meaning caused a finely divided solid such as coal char to act as a fluid due to gas passing through it) the fuel reactor. The reactions that comprise this process are as follows:

$$Coal\ \ (Solid\ \ Fuel) \rightarrow Volatile\ \ matter + Char\ \ (\mathrm{C}) \qquad \text{(R3)}$$

$$Char\ \ (\mathrm{C}) + \mathrm{H_2O} \rightarrow \mathrm{H_2} + \mathrm{CO} \qquad \text{(R4)}$$

$$Char\ \ (\mathrm{C}) + \mathrm{CO_2} \rightarrow 2\mathrm{CO} \qquad \text{(R5)}$$

$$\mathrm{H_2} + \mathrm{CO} + Volatile\ \ matter + n\mathrm{Me}_x\mathrm{O}_y \rightarrow \mathrm{CO_2} + \mathrm{H_2O} + n\mathrm{Me}_x\mathrm{O}_{y-1} \qquad \text{(R6)}$$

$$\mathrm{H_2O} + \mathrm{CO} \rightarrow \mathrm{H_2} + \mathrm{CO_2} \qquad \text{(R7)}$$

$$\mathrm{Me}_x\mathrm{O}_{y-1} + 0.5\mathrm{O_2} \rightarrow \mathrm{Me}_x\mathrm{O}_y \qquad \text{(R8)}$$

FIGURE 5 [9]
Chemical reactions that detail the gasification of fuel and subsequent oxidation of the metal oxide in iG-CLC

Reactions (R3-R5) represent gasification of the fuel inside the fuel reactor. The combustion reactions are shown by (R6-R8) which shows the oxygen carrier undergoing the repeated cycle of oxidation-reduction that produces heat [9]. This reaction, while effective, is a slow process due to the gasification of the solid fuel into char. CLOU, on the other hand, skips this slow process by breaking an oxygen free from the oxygen carrier and then reacts with the fuel according to the following reactions:

$$2\mathrm{Me}_x\mathrm{O}_y \rightarrow 2\mathrm{Me}_x\mathrm{O}_{y-1} + \mathrm{O_2} \qquad \text{(R9)}$$

$$Coal\ \ (Solid\ \ Fuel) \rightarrow Volatiles + Char\ \ (\mathrm{C}) + \mathrm{H_2O} \qquad \text{(R10)}$$

$$Char\ \ (\mathrm{C}) + \mathrm{O_2} \rightarrow \mathrm{CO_2} \qquad \text{(R11)}$$

$$Volatiles + \mathrm{O_2} \rightarrow \mathrm{CO_2} + \mathrm{H_2O} \qquad \text{(R12)}$$

FIGURE 6 [9]
Chemical reactions that detail the gasification of solid fuel into combustible material in CLOU

Reaction (R9) shows oxygen being freed from the metal oxide and reactions (R10-R12) show the reaction of oxygen with volatiles and char that result from regular combustion [9]. The oxygen carrier is then re-oxidized in the air-reactor and undergoes reactions (R1) and (R2) to produce heat.

Reactor Systems

Since the yield of a CLC system depends on contact between the oxygen carrier and the fuel, the type of reactor is an important consideration for the CLC process [9]. The requirements for designing an effective and efficient CLC system are as follows: there must be adequate particle exchange between the FR and the AR to realize complete combustion of the fuel; the time of contact between the fuel and air should be sufficient to attain maximum conversion of fuel; high temperature and high pressure must be present to achieve a higher efficiency and makes CO_2 sequestration easier; and finally, there should be limited CO_2 leakage from the FR to AR [9]. These conditions can be met using any of the three previously listed reactors variants.

Two interconnected fluidized-bed, or moving bed reactors, are the most commonly used reactor variety, and consist of a high velocity riser as the AR and a low velocity bubbling fluidized bed as the FR [14]. In this kind of reactor, the conversion of fuel occurs in the FR, while the oxygen carrier is oxidized inside the AR. Moreover, there are two loop seals that prevent the leakage between the AR and FR. Most oxygen carriers require a high particle residence time for a good reaction to take place, so the choice of such reactors is often based on individual reaction characteristics [9].

Alternating packed or fluidized-bed reactors have dynamically operating fluidized-bed reactors. This kind of CLC design consists of a minimum of two reactors that work in parallel and provide a constant high temperature stream of gas to the turbine [10]. The process consists of alternate oxidation and reduction cycles in the two reactors, which are alternated with short periods of mild fluidization of the fuel bed after each cycle to return the temperature and gas concentrations back to normal [14]. The main advantage of this process lies in the ability to avoid the separation of gas and fuel particles due to the fluidization of the bed. However, the disadvantage of this process lies in the necessity to maintain high temperatures and a high flow gas system that must switch between the two reactors.

The last kind of reactor currently available is the rotating variety that is comprised of a doughnut shaped fixed bed which contains an oxygen carrier material which is rotated between sections where air and fuel are being fed radially outwards through the fixed bed [10]. A stream of inert gas is used to prevent mixing of the reacting gases. The disadvantage, however, is the unavoidable mixing of fuel gas and air [9]. The three reactor types each have their own favorable qualities, and each kind is dependent on the kind of oxygen carrier present.

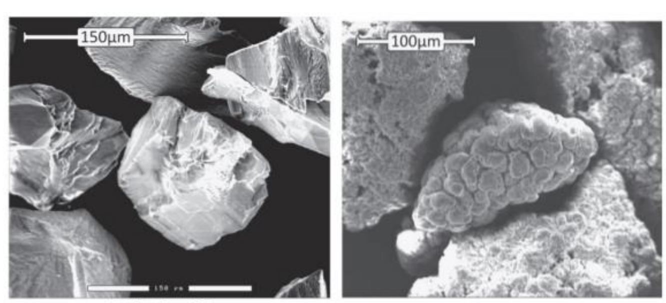
One of the most vital aspects of chemical looping is the oxygen carriers, or metal oxides, as they play a vital role in the process. Since they are at the heart of the chemistry that propagates CLC, selection of the appropriate oxygen carrier is one of the most important criteria for a good performance [12]. The attributes which are preferable in a metal oxide are as follows: it should be environmentally friendly; it should have appropriate thermodynamic properties of conversion of fuel into CO_2 and H_2O; it should have a high reactivity for both the oxidation and reduction steps; it should have proficient oxygen carrying capacity; reasonable durability to withstand many reactions; high melting points; readily able to fluidize; high mechanical strength to resist frictional stress; avoid collecting carbon so as to avoid interfering with CO_2 capture efficiency; must be at the particle size; must not collect into masses; and should be cost effective [9]. Since so much of chemical looping is dependent on the logistics of how metal oxides react in this dynamic process, details of this process can be found in the next section (See 'Metal Oxides: Type and Efficiency').

METAL OXIDES: TYPES AND EFFICIENCY

As one of the three main components required for chemical looping, metal oxides have seen many different improvements throughout the years. Originally, the reactions were carried out with materials such as copper, nickel, or cadmium oxides. Within the reactions, these are called the oxygen carriers (OC). They work by completing the loop between the two reactors present for the process. In figure 3, the reaction which takes place at the beginning of the process is shown. Air is introduced into the system which in turn oxidizes the selected OC. The result is an oxidized form of the carrier, which is then transported into the next part of the system. The second equation, figure 4, explains what happens in the next reactor. A fuel source is introduced, and it reduces the previously oxidized carrier. The OC then travels back, and the cycle continues [9].

For an OC to be selected, many things must be considered. First of all, it needs to have satisfactory thermodynamic properties in terms of conversion of the fuel source to CO_2 and H_2O [9]. For example, Fe-based oxygen carriers are cheap, non-toxic, and environmentally friendly, but have restrictions when it comes to thermodynamics. As the Fe-based OCs reach different oxidation states, CO_2 is lost, and the rate of the reverse reaction decreases. As a process based around its ability to internally convert fuel to energy, without exposure of outside additions, a reduction in reversibility results in a decrease of overall productivity and desirability [9].

In addition to thermodynamic issues, agglomeration tends to be a common problem among tested oxygen carriers [14]. As the oxides go through multiple cycles, solid particles begin to clump which reduces their ability to transfer oxygen. This phenomenon is observed with most unsupported metal oxides [15]. Therefore, when selecting a OC, tests are reviewed, and levels of agglomeration are recorded. The most favorable are the ones resulting in the lowest number of agglomerating particles. Figure 4 is included to provide a visual of agglomeration. The image on the left shows the particles before any reactions, while the one of the right shows the particles after 85h of operation [16].



(a) Fresh particles

FIGURE 7 [16]
SEM images of agglomerated ilmenite particles.

The most important characteristic of a suitable oxygen carrier is stability. It must be able to go through many oxidation and reduction cycles at high temperatures without breaking down. To date, the state-of-the-art oxygen carrier particles reported in most literature only remain effective to around 900 redox cycles [17]. At that point they begin to degrade. Chemical stress put upon the oxygen carriers from the redox reactions, coupled with the mechanical and thermal stress introduced from the process environment, produces the need for a much higher recyclability if industrialization is to be achieved[17]. While the chemical stress is dictated by the type of oxide, the choice of reactor and operating conditions affect the latter. Recent experiments have revealed an oxygen carrier which, at an efficiency of 3000 cycles, may help move further towards industrialization [9]. The experiments and chemistry of the particles will be detailed later in this section.

Since every oxide is going to have some type of issue, whether it be environmental concerns, or efficiency issues, no metal oxide is really considered the true solution to CLC. An article detailing the current status of chemical looping states that, “since its development has started, nearly a thousand of oxygen carriers have been tried and tested for CLC” [9]. Based upon this statistic, it is evident how difficult it actually is to find the perfect material to facilitate this revolutionary, green technology. Out of thousands of tests since 1954, none have improved the process enough for industrialization.

Currently, engineers and scientists have moved on from simple metallic oxides and have begun to discover ways to remedy some of the issues each individual oxide possess. This comes in the form of support materials. Support materials are additives which, when combined with metal oxides, increase the surface area for reaction, add mechanical strength and resistance to attrition, and also enhance the ionic conductivity of the OC [9]. Generally, the support materials come in the form of inert materials such as, SiO_2 or Al_2O_3. Most are prepared with a process called dry impregnation. First the support particles are heated at around 250°C for 2 hours to remove moisture [18]. They are then exposed to a warm and highly concentrated aqueous solution of metal nitrates. The volume of the nitrate solution is dependent on the volume of pores in the chosen support material. For example, SiO_2 has a pore volume of 1.86 cm^3/g, therefore the solution of metal nitrate would need to correspond to that value. After this, the oxygen carries are dried for 3 hours at 110°C, then go through a calcination process for 3 more hours at 500°C which removes the nitrates. This leaves you with the metal oxides in a powdered form. From there, the newly formed particles are sintered to acquire a solid form [18]. With the use of support materials, industrialization is becoming more of a reality.

Recent Breakthroughs

We may be closer to industrialization than we think. In a paper published on October 13th of 2017, engineers from The Ohio State University report their findings on a new method of extending the life of their oxygen carrier particles for chemical looping combustion [5]. Focused around the Iron-Titanium oxide, ilmenite ($FeTiO_3$), their research has discovered a composite oxygen carrier which exceeds all the other top options. On its own, ilmenite is considered to be an attractive choice due to its natural occurrence, low cost of production, and favorable reactivity with hydrocarbons [6]. In the short-term, ilmenite has an acceptable level of attrition, but begins to fail during prolonged redox cycles. This increased attrition level results from a segregation of ilmenite into both Fe-rich and Ti-rich phases, leading to a non-uniform distribution. A correlation between an uneven expansion rate of particles by 0.25-0.5% per cycle and a rapid decline in mechanical strength under 100 cycles presents an obvious problem as the process requires stability through a much higher number of cycles [17].

In the work mentioned at the beginning of this subsection, they produced a composite oxygen carrier which is comprised of an Al skeleton that encloses 65 mol% of oxidized ilmenite. With the addition of the skeleton, an increase in mechanical strength and attrition resistance are observed [17]. The skeleton is also able to utilize one of the properties which makes basic ilmenite undesirable. The segregation from $FeTiO_3$ to both Fe-rich and Ti-rich phases causes an increase in porosity, which on its own caused the oxides to break down after only a few cycles. With the skeleton present, the increased porosity, instead of inhibiting the reactions, enhances the redox reactivity. It also protects the metal oxide from the walls of the reactor [17].

Through a thermogravimetric analysis experiment, the composite oxygen carriers were put through 3000 cycles in a strong reducing and oxidizing environment at high temperatures [6]. At the end of the experiment the results were promising. With a measured average crushing strength of 120 MPa, the Al skeleton effectively helped to maintain the structural integrity of the carrier. When compared to another state-of-the-art carrier of Cu and alumina which measured an average of 66 and 39 MPa at only 800°C and 900°C respectively, this result is impressive [17]. The figure below shows a before and after view of the carriers. On the left, you see a group of solids (ilmenite with Al-skeleton), before any reaction has taken place. Then on the right, a carrier post-redox cycle is shown.

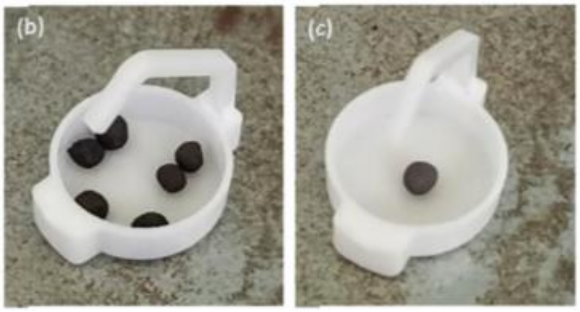


FIGURE 8 [17]
Before and after image of newly developed ilmenite oxide with Al-skeleton. Through 3000 cycles the shape and hardness of the particle is maintained.

Small scale tests reveal that the ilmenite oxide coupled with an Al-skeleton has the potential to be a novel oxygen carrier with a promising level of strength through many cycles. Considering that recyclability is one of the main issues blocking chemical looping, these particles developed by engineers at The Ohio State University are as close as we have gotten to a commercially applicable oxygen carrier for the CLC process. The last step involves carrying out more largescale tests to further assess the qualifications of these particles [17].

FUTURE OF CHEMICAL LOOPING: APPLICATION AS A STOPGAP TECHNOLOGY

Despite the plethora of articles and news on climate change, global warming, and all the other negative effects of greenhouse gas emissions, the fact of the matter is, there is not much that we can do to avoid it right now. As the world grows and more countries begin to industrialize, the cheapest and most effective way of extracting energy remains as the combustion of fossil fuels. They power our homes, our factories, and really, our entire lives. The other name for fossil fuels, unrenewable resources, effectively explains their issue on its own. Eventually our supplies will run out, leaving us without an efficient source of energy. Considering that they make up 67% of the world's total energy production, it is safe to say without them we would have a large problem on our hands.

One of the biggest, and most funded solutions to our shortening supply of fossil fuels are renewable energy sources. This includes things such as solar, wind, and hydroelectric power. One of the more promising sources of renewable energy, the sun, has the potential to provide a significant portion of our worlds future energy needs. Many improvements need to be made before this can become a reality. At around 20% efficiency and \$0.12-\$0.20 per kWh of energy, they are still far too inefficient and expensive to be considered competitive [19]. Wind and hydroelectric powers suffer from the same complications. Both require large areas of land for operation, harm the environment, and carry large production costs. A switch from fossil fuels to renewable energy needs to be made eventually but will not be possible until the proper levels of efficiency and cost are reached. It is estimated that we still have around 260 billion tons of recoverable coal, which is enough to last 235 years if we continue at our current consumption rate [19]. Based on this, we need not rush due to limited supply (assuming the problems within the renewable energy sector will be solved within 235 years). Greenhouse gas emissions remain the problem and sources of clean fuel production are the key to solving this.

This is where chemical looping comes into play. Not only would it allow us to continue to use our economically friendly, efficient, and abundant fuel sources, but it would almost help alleviate the problem. With a CO_2 capture rate of about 90%, worldwide implementation of CLC reactor systems would be revolutionary. Especially since the CO_2 concentration in the atmosphere has been rising since the beginning of the industrial revolution and currently sits at 43% higher than the concentration at that time [3]. The figure below displays that increase.

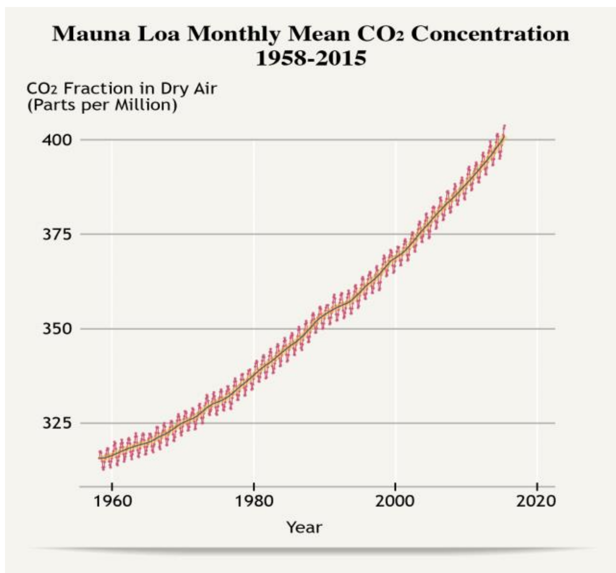


FIGURE 8 [3]
Steep increase of CO_2 concentration in the atmosphere beginning in 1960, and estimation of over 400 ppm by 2020.

The International Energy Agency estimated that by 2050, the cost of battling CO_2 emissions without the carbon sequestration method of CLC could be 70% higher than with it [3]. This fact relates towards the economic sustainability which we mentioned in the opening sections. Unless we combat this issue now, we will be paying for it in the future.

If we can solve the main limiting factor of CLC, a suitable metal oxide, we would be able to reach an efficiency which would facilitate a transition to CLC. This can only be achieved through continued research and funding of dedicated organizations and individuals.

Looking into the future, the looming of threat of a warming global climate will not disappear. The only solution is to change the way we live now. By transitioning to sustainable means of energy production, we have the power to prevent the inevitable crisis that will happen. Environmentally friendly technologies, like chemical looping combustion, will be the key to remedying these problems. Through the efforts of engineers today, work can be done to prevent future problems. The future of our society and the global environment can only be decided by the actions of humans today, and chemical looping can be one of the contributing factors that works towards solving these issues. If we play the cards right, it can be a sustainable technology which solves our issues now and our issues later. It will help alleviate the damages to our environment and prevent the destruction and displacement of people and societies around the world.

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