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DECARBONISING THE DRI FEED FOR EAF USING H_2

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Abstract

Direct reduction iron (DRI) is an alternate method for the processing of iron ore for the production of iron and steel. DRI produces high grade product, ~97% iron. Hot DRI (HDRI), can produce compacted briquettes which are easily transported. The output is a feedstock for Electric Arc Furnaces (EAF). DRI requires high grade iron ore (>67%) for reduction. The main process is the use of natural gas reforming to syngas, CO and H_2. The resultant gases can act as reductants for the raw feedstock. Over 90% of DRI is produced using natural gas.

$$Fe_2O_3 + 3CO \rightarrow 2Fe + 3CO_2$$

$$Fe_2O_3 + H_2 \rightarrow 2Fe + 3H_2O$$

The use of natural gas to generate the reductant gases greatly reduces the CO_2 emissions in preference to coal and coke. DRI is used extensively where natural gas prices are low, Middle East and North America, with India using DRI with cheap non-coking coal. The process is less commonly used in Europe.

If the reforming stage can be eliminated from the process, and the use of H_2 used as a reductant, then the products will high grade iron and emissions of water. The only potential CO_2 emissions would come from the iron ore. Investments in H_2 DRI, has been made by LKAB, Vale, Arcelor Mittal and ThyssenKrupp.

In 2018, 96% of the hydrogen production was still from fossil fuels using steam reforming of natural gas. CO_2 (scope 1 and scope 2) can be eliminated from the DRI processing or iron ore with the production of H_2 from renewable sources. Electrolysis of water to produce hydrogen from green electricity is a viable option, however the energy density of the hydrogen is equal or less than the energy required to produce the hydrogen with current technology, resulting in high cost H_2 and thus a cost increase in the production of green steel.

Introduction

Iron and steel manufacturing produces 7-8% of the annual global CO_2 emitted to the atmosphere, with Global emissions of 37 $GtCO_2eq$ [1], [2]. A method of reducing these emissions is the adoption of electric arc furnaces (EAF), where scrap steel can be reprocessed. There is not however sufficient quantities of high grade scrap steel available for all of the steel produced in EAF's [3], [4], [5]. To supplement the production, iron from ore can be used in an EAF. The iron from ore increases the mass of product able to be produced and can also be used as a method to increase the quality of steel from the EAF. To process the iron ore into a form that can be utilised in an EAF, the ore can be reduced in a direct reduction furnace (DRI). The ore for use in a DRI has to be of high grade, with a ~65% minimum iron content [6]. The iron ore is pre-processed for use in a DRI into either pellets or as lump ore. Sponge iron is produced from a DRI through the reduction of oxygen from the ore, with iron contents of the product between 85-97% [6], [7], [8]. DRI can be used to produce hot briquetted iron (HBI) and cold briquetted iron (CBI). HBI can be transferred to the EAF at ~650°C, making significant savings against the heating costs.

The processing of CBI and HBI is often used for long steel production in an EAF, whilst scrap steel is generally used to produce lower grade steel. Scrap steel tends to be cheaper than the use of iron ore however the scrap tends to contain higher percentages of undesirable materials and trace metals that are contraindicative for higher grade steels. The scrap steel requires going through a vigorous selection process to eliminate the high levels of undesirable materials and impurities that would affect the grade and quality of steel produced.

The reduction of iron ore in a DRI is often carried out using natural gas as a source of heat and as a reductant. Natural gas as a heat source is significantly cheaper than electricity. In the UK, natural gas is approximately one third of the price of electricity. Coal reduction is still used in some areas where coal is significantly cheaper, however this is becoming less common, where the coal is being replaced with natural gas. The practice of using coal produces higher levels of CO_2 emissions, therefore with emissions control taking effect across the globe, coals is becoming less prevalent. Whilst lower than from coal, the use of natural gas however still produces significant CO_2 emissions.

DRI operates below the melting point of iron, but still requires heating to ~800-1200°C, in the presence of a reductant [6], [8], [9]. The reductant often takes the form of syngas, a mixture of CO and H_2. Once the reduction has taken place, to achieve the grade of steel required, a carburization process is carried out to apply a controlled mass of carbon to the melt.

Reduction

$3Fe_2O_3 + CO + H_2 \rightarrow 2Fe_3O_4 + CO_2 + H_2O$
$Fe_3O_4 + CO + H_2 \rightarrow 3FeO + CO_2 + H_2O$
$FeO + CO + H_2 \rightarrow Fe + CO_2 + H_2O$

Carburization

$3Fe + CH_4 \rightarrow Fe_3C + 2H_2$
$3Fe + 2CO \rightarrow Fe_4C + CO_2$
$3Fe + CO + H_2 \rightarrow Fe_3C + H_2O$

The transfer of the products of DRI tends to be pyrophoric, and therefore needs to be transferred from the DRI to the EAF under an inert atmosphere. This is particularly important where HBI is produced, as the extra heat present in the sponge iron makes it more susceptible to spontaneous combustion in contact with oxygen [8]. HBI is normally transferred directly from the DRI to the EAF. Due to the high iron content, the produce of DRI is susceptible to oxidation and thus rusting if left unprotected, therefore the production of DRI does come with risk and time penalties if not processed into steel promptly.

The DRI process reduces hematite (from the iron ore) into magnetite and then magnetite and ferrous oxide into iron. Gangue is higher in sponge iron at ~5%, whilst from a blast furnace (BF) this tends to be only around 1% [8]. Higher gangue leads to larger quantities of slag in the melt. Whilst the slag is an integral part of the steel making process, as it helps to retain heat in the EAF and provides a medium for impurities from the melt to flocculate to, excess slag can have adverse effects. The excess slag can lead to less space for liquid steel and an excess of impurities to remove from the process. The increase in impurities may also lead to an increase in electricity needed for the melt, thus leading to increases in cost of steel production. The increase in impurities can also affect the chemical balance of the steel making process. [5], [8]

As the increase in scrap steel gathers pace and greater quantities of steel are required the use of ore-based metals becomes more imperative as a major part of the mix required in an EAF. The control of the carbon content within the steel making process is important. Whilst great efforts are made to initially reduce the carbon content within the raw materials and the mix, the controlled addition of carbon during the steel making if imperative to achieve the correct grade of steel.

Reduction gas production technology

Reduction gases have been produced through two main processes, heating of coal to produce coal gas and methane reforming, producing syngas. Steel in India is primarily produced from non-coking coal, whilst natural gas shaft reactors are commonly used in Asia where cheap natural gas is readily available.

Both methane reforming and syngas production are high carbon emitters.

Hydrogen production

Hydrogen production for the steel industry can come from a range of technologies. The established route is from methane steam reforming, whilst an adaptation of steam reforming, autothermal reforming has become established recently. [10] To use renewable energy, biomass gasification can be used from sustainable sources to produce hydrogen, and electrolysis from renewable sources of electricity is a method of producing hydrogen that can be used as a reductant for steel production.

Hydrogen methane reforming

This is the most common method of hydrogen production, and is overall, energy intensive, requiring approximately 206 kJ/mol of heat. [11]

$CH_4 + CO_2 \rightarrow 2CO + 2H_2$
$CH_4 + H_2O \rightarrow CO + 3H_2$

The carbon monoxide can be further treated in the water gas shift reaction to produce more hydrogen.

$CO + H_2O \rightarrow CO_2 + H_2$

The water gas shift reaction is mildly exothermic, releasing 41 kJ/mol of heat [11]. The process can also be used to produce ammonia, increasing the efficiency of the system. The energy consumption for the production has greatly decreases, with a tonne of ammonia now costing 27 GJ.

Autothermal reforming (ATR)

ATR is a similar process to steam reforming, however increased levels of O_2 re used for the process rather than just air. Through this process, the methane becomes partially oxidised. There are two different reaction pathways in ATR, there is the use of CO_2, and the use of H_2O. When reforming using CO_2, the ratio of H_2 to CO is 1:1, however when ATR uses steam for reforming the ratio of H2 to CO increases to 2.5:1.

Green hydrogen

When electricity is used as a heat source, the replacement through the use of hydrogen from electrolysis is counterintuitive, as the energy required to produce hydrogen is more than the energy produced from the hydrogen. The production of green hydrogen using wind, solar, hydroelectric or hydrothermal can be used during off peak times, then the use of cheaper electricity can be an effective method of producing hydrogen.

Hydrogen has an energy density of 120MJ/kg, which is equivalent to 33.6 kWh/kg. To produce hydrogen from pure water, the electrical energy required for electrolysis is 35.8 kWh/kg, giving an efficiency of 94% of the electrolyser. These figures do not take account of heat, electrolysis rotation and compression of gases, which brings the efficiency of electrolysis down to 70-80%. It is anticipated the efficiency will reach 86% by 2030 [12].

The production of hydrogen from pure water also produces ~8 times more oxygen than hydrogen by mass. The oxygen can be used for industrial processes. Therefore, whilst purely based on hydrogen production the cost analysis is high, when the production of oxygen is included, the cost value becomes more appealing. To compliment the production costs, there are no greenhouse gases produced, therefore the cost of production will not be subjected to carbon taxation.

Biomass gasification

The production of hydrogen from biomass can follow a similar gasification process as for coal, where the biomass is subject to heat during pyrolysis in low oxygen atmosphere, then partial oxidation to produce further hydrogen. Biomass has high moisture content, as such high levels of heating is required to dry the biomass before pyrolysis. Syngas is further produced during reforming. Due to the high levels of heat required efficiencies can be as low as 35-50%. [13], [10]. ½

Table 1. Reactions that can take place during biomass gasification

Reaction method	Reactions
Pyrolysis	$C_6H_{10}O_5 \rightarrow 5CO + 3H_2 + CH_4$ $C_6H_{10}O_5 \rightarrow 5CO + 5H_2 + C$
	$C_6H_{10}O_5 + 1/2O_2 \rightarrow 6CO + 5H_2$
Oxidation	$C_6H_{10}O_5 + O_2 \rightarrow 5CO + 5H_2 + CO_2$ $C_6H_{10}O_5 + O_2 \rightarrow 3CO + 5H_2 + 3CO_2$
Reforming	$C_6H_{10}O_5 + H_2O_2 \rightarrow 6CO + 16H_2$ $C_6H_{10}O_5 + 3H_2O_2 \rightarrow 4CO + 8H_2 + 2CO_2$ $C_6H_{10}O_5 + O_2 \rightarrow 3CO + 5H_2$

Table 2 Advantages and disadvantages of biomass gasification

Advantages	Disadvantages
Sustainable CO_2 emissions	High moisture content
Use of residual crop increases agricultural value	Production of tars
Replacement of fossil fuels	Undesirable products: corrosive
Secondary solid products	

Electrolysis

Electricity required to produce one tonne of green energy steel requires 3.5MWh (90kg of hydrogen). Global DRI production was 108MT, and to produce hydrogen from renewable energy to supply DRI would require 459 TWh of electricity.

There are three main three main types of electrolysis

Polymer electrolyte membrane (PEM)
Using PEM, water is electrochemically spilt into hydrogen and oxygen. Figure 1 shows the principal operation of a PEM electrolyser. At the anode, oxygen is produced, while at the cathode hydrogen is the product. Water is pumped through the system at the anode, and hydrogen protons are transferred through the membrane to the negative side. Electrons are produced at the anode which are fed through the external circuit to provide power for the process. PEM typically operates at 80-90% efficiencies and produces hydrogen at 99.99% purity.

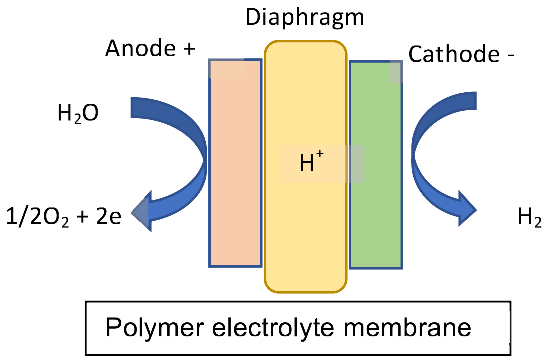

Figure 1 Principle of PEM electrolysis

Alkaline water electrolysis (AWE)
AWE is a well-established technology, with systems into the megawatts range, which operate at temperatures of 30-80°C. At the cathode hydroxyl ions are produced at the cathode which transfer through the diaphragm from an alkaline solution of KOH and NaOH. H_2 is produced at the cathode, whilst O_2 is delivered at the anode. The H_2 produced at the cathode combines with the hydroxyl, which can transfer through the diaphragm under the influence of electricity and is emitted at the anode as an O_2 molecule. Alkaline water electrolysis typically operates at efficiencies of 70-80%. Figure 2 highlights the basic operating principals of an AWE system.

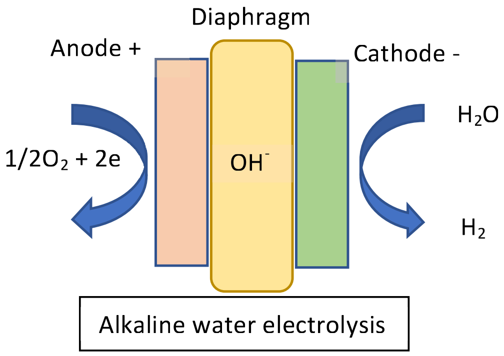

Figure 2 Principle of operation of an AWE

Solid oxide electrolysis (SOE)
The SOE system is a highly efficient system of hydrogen electrolysis production, however, operates at high pressures and temperatures of 1000°C, however there are some laboratory scale systems operating between 500-850°C. The technology is still mainly at laboratory scale but produces efficiencies of 90-100%. Hydrogen is produced at the cathode and oxygen ions pass through the diaphragm. At the anode oxygen is produced with the electrons released. Figure 3 shows the principal parts of an SOE system.

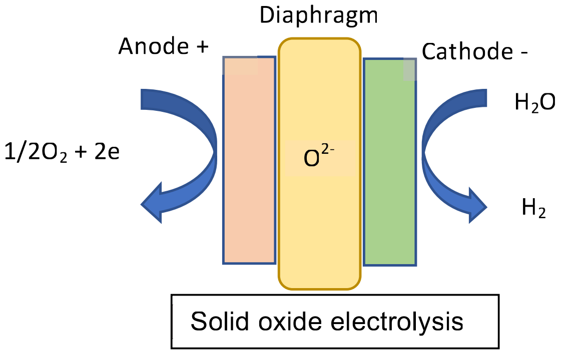

Figure 3 Principle of operation of an SOE

Table 3 is used to show the advantages and disadvantages of the three types of electrolysers. The SOE shows the highest level of efficiencies, however the technology is still not at industrial level. The PEM has high efficiencies and produces a high purity product.

Process	Advantages	Disadvantages
PEM	High efficiency, 80-90% High purity product 99.99%	New technology Low durability High costs
AWE	Established technology Energy efficiency 70-80% Non noble catalysts	Low current density Low purity of product Low systems
SOE	High efficiency 90-100% Non noble catalyst at high operating pressure	Laboratory scale only with low durability

Table 3 Advantages and disadvantages of the three electrolysers

Summary

To reduce carbon emissions from the steel industry, a move from traditional incorporated steel sites, and the adoption of EAF technology is essential. EAF technology however still produces ~0.6tCO_2/t liquid metal. The use of hydrogen as a reductant to replace syngas, in DRI to produce a feedstock for EAF is a viable option for the steel industry. The hydrogen would reduce the emissions from a DRI to almost zero carbon. The established route for hydrogen production is through methane steam reforming, however there is still an inherent carbon emission tariff. The use of the electrolysis of water to produce hydrogen and oxygen has a net zero scope 1 emissions of CO2. There are several electrolysis technologies commercially and under development. PEM offers a commercially established route with relatively high efficiencies at 80-90% and purities of 99.99%, which are suitable for most applications. AWE provides a solution with efficiencies of 70-80%, whilst SOE has high efficiencies of 90-100% however is still only available at laboratory scales.

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