Article

Lowering the carbon footprint of steel production using hydrogen direct reduction of iron ore and molten metal methane pyrolysis

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Abstract: Reducing emissions from the iron and steel industry is essential to achieve the Paris climate goals.A new system to reduce the carbon footprint of steel production is proposed in this article by coupling hydrogen direct reduction of iron ore (H-DRI) and natural gas pyrolysis on liquid metal surface inside a bubble column reactor.If grid electricity from EU is used,the emissions would be 435 kgCO_2/tls without considering methane leakage from the extraction,storage and transport of natural gas.Solid carbon, produced as a by-product of natural gas decomposition,finds applications in many industrial sectors,including as a replacement for coal in coke ovens.Specific energy consumption (SEC) of the proposed system is approximately 6.3 MWh per ton of liquid steel(tls).It is higher than other competing technologies,3.48 MWh/tls for water electrolysis based DRI,and,4.3-4.5 MWh/tls for natural gas based DRI and blast furnace-basic oxygen furnace (BF-BOF) respectively.Utilization of large quantities of natural gas,where the carbon remains unused, is the major reason for high SEC.Preliminary analysis of the system revealed that it has the potential to compete with existing technologies to produce CO_2free steel,if renewable electricity is used.Further studies on the kinetics of the bubble column reactor,H-DRI shaft furnace,design and sizing of components,along with building of industrial prototypes are required to improve the understanding of the system performance.

Keywords: Hydrogen;Methane pyrolysis,Direct reduced iron;Industrial decarbonization;Iron and steel;Electric Arc furnace

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1. Introduction

It is essential to decarbonize all sectors of the energy system to meet the goals of the Paris agreement.Industrial sector consumes one-third of the primary energy resources and releases one-quarter of the energy related greenhouse gas emissions. Energy intensive industries(EII),like,iron and steel, cement, chemicals, non-ferrous metals,paper and pulp etc are more difficult to decarbonize than other sectors of the energy system like electricity generation,buildings,transport, as emissions are caused from use of fossil fuel for combustion,as feed stock and for industrial processes [1].EII's can be decarbonized by introducing innovative process technologies as an alternative to existing processes or by applying CCUS to existing technologies and using renewable energy as an alternative to process energy [2,3].

Iron and steel sector is responsible for 7% of the total CO_2 emission,and, 16% of the total industrial emission of CO_2 globally[4].Steel is a versatile material,and finds application in buildings, transport,packaging,shipping,infrastructure etc.Steel demand is stated to increase trend until 2050 [5,6].Steel is produced through the primary (reduction of iron ore) or the secondary route (from scrap recycling).Limited availability of scrap and demand for special grades of steel,which can not be produced from steel recycling units,point towards an increased demand for steel produced through the primary route in the future.Present primary steel-making process,BF-BOF route has an emission intensity of approximately 1870 kgCO_2/tls [7] [4].Majority of the emissions in an integrated steel plant come from the blast furnace (61%) and coke making plant (27%)[8].

In order to reduce the emissions from the iron and steel industry, breakthrough process technologies need to be developed.With incremental changes in the existing technologies,the steel industry would fail to achieve the emission reduction targets [9].Techno-economic feasibility of three innovative steel production technologies,blast furnace with carbon capture and storage(BF-CCS),iron ore electrolysis or electrowining(EW) and hydrogen direct reduction of iron ore (H-DRI),were evaluated by [6],based on the material and energy flows for the production of one tonne of crude steel.In their analysis,they found H-DRI,as the most attractive option,economically and environmentally.

One of the earliest works on H-DRI was done in the early 1930's.Properties of the iron produced from direct reduction of iron oxide with hydrogen was evaluated experimentally at a lab scale[10].High production cost of hydrogen and availability of cheaper alternatives stalled further development of the technology.There is a renewed interest in the hydrogen economy among researchers,policy makers and industry,on the back of declining prices of renewable electricity systems [11–13].H-DRI offers an added advantage of providing flexibility to the electricity grid through large scale hydrogen storage,produced from water electrolysis,which is essential for a 100% renewable generator based electricity grid of the future [14].Hydrogen,as an energy carrier has application in various sectors of the energy system,which are otherwise difficult to decarbonise.The cost of producing hydrogen from renewable electricity could fall 30% by 2030 as a result of declining costs of renewable energy and the scaling up of hydrogen production[12].In a recent study,done by researchers at Technical university of Munich and Stanford University,it is stated that cost of hydrogen produced from renewable electricity has decreased to €3.23kg^{-1} and will further decrease to €2.50kg^{-1} in Germany and Texas [15] within the next decade.Use of green hydrogen and ammonia in the iron and steel sector,through the H-DRI route has the potential to reduce emissions by 2.3 gigatonnes of carbon dioxide per year ($GtCO_2/y$) [1].

Steep reduction in electrolyser costs and availability of cheap renewable electricity are necessary for adoption of water electrolysis based H-DRI-EAF route for steel production.Although,there has been substantial progress in both,use of green hydrogen for steel production,to replace the BF-BOF process,would not be economically feasible before late 2030's [6].Given the impending climate crisis,there is an urgent need to take immediate action to reduce emissions from the steel industry.During the transition period of fossil fuel based electricity generation to renewable based electricity system,use of hydrogen,derived from natural gas could accelerate the transition towards H-DRI and pave the path for use of green hydrogen in the future.Methane pyrolysis,could act as a bridge technology for the hydrogen future [11] as it generates hydrogen without emitting CO_2[16].A new system for H-DRI production and CO_2 free hydrogen production is proposed in this article,by combining natural gas pyrolysis on liquid metal surface inside a bubble column reactor and hydrogen direct reduction of iron ore coupled with an EAF for steel production.The concept of the system along with the relevant literature is described in section 2.In section 3,the proposed system is described.Discussions based on preliminary investigations of the systems based on its mass and energy balance and CO_2 footprint are presented in section 4.These discussions are followed with the concluding remarks in section 5.

2. Concept

At present,direct reduced iron (DRI) is produced by reacting solid iron oxide with hydrocarbon based reducing gases [17,18].Reduction reactions occurs below the melting temperature of iron (1535°C).The technology has been deployed commercially and five percent of the total global steel is produced through the DRI route [19].Lower capital investment and space requirements,and, lower complexity in design and operation make it easier to build and operate a DRI plant.With recent increase in cheap shale gas production,there has been an up surge in installation of DRI plants .Majority of the DRI plants,are based on MIDREX [19] and HYL[20] technologies.In the commercial installations reduction of iron ore is carried out with a mixture of carbon monoxide and hydrogen produced from steam methane reforming[21,22].Reduction reactions occurring inside the shaft furnace are depicted in

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Equation 1-2 [22].
Exothermic reduction of Hematite by CO:

$$Fe_2O_3(s) + 3\,CO(g) \longrightarrow 2\,Fe(s) + 3\,CO_2(g) \tag{1}$$

Endothermic reduction of Hematite by H_2:

$$Fe_2O_3(s) + 3\,H_2(g) \longrightarrow 2\,Fe(s) + 3\,H_2O(g) \tag{2}$$

Natural gas is converted to a mixture of CO and H_2 using steam methane reforming (SMR).The reaction is endothermic and has a reaction enthalpy of 206 $kJmol^{-}1$ [23,24],as shown in equation 3.

$$CH_4(g) + H_2O(g) \longrightarrow CO(g) + 3\,H_2(g) \tag{3}$$

Countries with large reserves of natural gas such as Saudi Arabia, Qatar, USA(shale gas),Iran have deployed the technology for steel production [19].The DRI produced from the vertical shaft furnace can either be fed to an EAF as hot DRI or cooled and briquetted for transport.Addition of briquetted DRI in the EAF reduces the dependence on scrap and improves the quality of the steel produced [25][26][27].Emissions from the DRI-EAF route,using natural gas SMR for syngas production is approximately 1269 $kgCo_2/tls$,which is lower than 1870 $kgCo_2/tls$ [7]from the BF-BOF route,but,still quiet high.Specific energy consumption of 4.3 MWh/tls is almost similar to that of the BF-BOF route [7].Many studies have proposed using CCUS with SMR for CO_2 free H_2 production,however,carbon capture technology is still not commercialized.Transport and storage of captured CO_2 also poses engineering challenges as well social acceptance issues.It is easier to collect, store and transport solid carbon than gaseous or liquid CO_2.Carbon capture,also increases the specific energy consumption of the process.

2.1. Hydrogen direct reduction of iron ore

In H-DRI,pure hydrogen is used,as the reducing gas.The DRI is fed to an electric arc furnace (EAF) for steel production.If the hydrogen is produced through electrolysis of water using cheap and abundantly available renewable electriciy,then the emissions can be reduced significantly.This system can reduce the carbon remissions from steel production by 85% [28].Three different types of steel pellets,with varying surface area were tested using thermogravimetric analyzer by [29].They found that the reduction reaction occurs in three distinct steps,where hematite is first converted to magnetite,then wustite and finally iron.The longest step is the conversion of wustite to iron.It was observed during the experiments conducted on coarse,sintered and nano powdered samples,that solid state diffusion is the rate limiting step and the reaction rate is lowered even if the initial area of the sample is higher.The reactions are depicted in equations 4-6.Reaction is endothermic and the reaction enthalpy is 99.5 $kJmol^{-}1$

$$3\,Fe_2O_3(s) + H_2(g) \longrightarrow 2\,Fe_3O_4(s) + H_2O(g) \tag{4}$$

$$x\,Fe_3O_4(s) + (4\,x\text{-}3)\,H_2(g) \longrightarrow 3\,Fe_xO(s) + (4\,x\text{-}3)\,H_2O(g) \tag{5}$$

$$Fe_xO(s) + H_2(g) \longrightarrow x\,Fe(s) + H_2O(g) \tag{6}$$

With $x = 0.95$

Industries have shown interest in the H-DRI technology and many pilot plants are being constructed in Europe.Luossavaara-Kiirunavaara Aktiebolag (LKAB), Svenskt Stål AB (SSAB) and Vattenfall along with Swedish energy agency are building three pilot plants for Hydrogen direct reduction of iron ore under the HYBRIT project in Sweden [30].The projects will demonstrate production of DRI,hydrogen from renewable electricity, fossil free pellets and hydrogen storage.Under the SALCOS project [31],on-site production of hydrogen using green electricity at a steel facility is being investigated. The project has close ties with GrInHy2,which is an EU-funded project,where solid oxide electrolysers are being used to produce hydrogen, by using renewable electricity and waste heat from the industry [32].30 MW of wind electricity will be generated and coupled with proton exchange membrane electrolysers for green hydrogen production under the Windh2 project [33].Voestalpine,which has recently commissioned a natural gas based DRI plant in Texas,USA is participating in H2future project,where 6 MW of PEM electrolysers are being installed for green hydrogen production [34].Tata steel Europe,Nouryon and the port of Amsterdam are partnering to develop the largest green hydrogen cluster in Europe[35].

Techno-economic evaluation of H-DRI system using water electrolysis for hydrogen production revealed,that,feasibility of H-DRI based on water electrolysers depends on availability of cheap and abundant renewable electricity,and, drastic reduction in electrolyser costs [5,14,36].According to estimates made in the HYBRIT [30] project,application of H-DRI technology at all Swedish iron plants could reduce Sweden's emissions by 10% ,and, at the same time,increase demand for renewable electricity by 15 TWh.

2.2. Methane pyrolysis

During the transition to renewable based electricity generation systems,natural gas based hydrogen production technologies can be deployed to reduce emissions from steel production plants.Arcelormittal,the largest steel producer in the world, is investing in a H-DRI unit with production capacity of 100,000 tonnes/year at its Hamburg plant.Hydrogen of 95% purity will be produced by separation from the top gas of the existing DRI plant by pressure swing adsoprtion [37].Infrastructure built for grey hydrogen ,produced from top-gas of natural gas based shaft furnace,will expedite the integration with green hydrogen in the future.Excess hydrogen produced from natural gas can be stored,and,used to power stationary fuel cells to provide flexibility to the grid.This can provide additional revenue and expedite the integration of renewable energy systems to the grid.

Methane pyrolysis is introduced in this study as an alternative to steam methane reforming and water electrolysis for hydrogen production.Methane pyrolysis is the process of decomposing methane into solid carbon and hydrogen by heating the natural gas to temperature of 1200 °C to 1500 °C in the absence of oxygen [38].The reaction is endothermic,74.6 kJmol^-1 is the heat of the reaction,which much lower than the SMR process.Thermal energy is needed raise the temperature of the incoming methane stream to the reaction temperature.

$$\mathrm{CH_4} \longleftrightarrow \mathrm{C\,(s)} + 2\,\mathrm{H_2(g)} \tag{7}$$

Thermal energy from different sources can be added to the reactor ,including solar thermal, electrical,nuclear,micro-wave, plasma [39].Thermo-catalytic reduction of methane can be carried out at temperature lower than 1000°C.Various catalysts have been investigated by researchers.Metallic catalysts like Ni-SiO_2,Ni-Fe_2O_3,Ni-Mn,Ni-Fe,Fe-Al_2O_3 have been used.Carbonaceous catalysts like activated carbon and carbon black have also been investigated for the production of hydrogen from methane pyrolysis[39].Deposition of carbon on the surface of the catalysts reduces their activity [38–41] and can clog the fluid bed and packed bed reactors commonly used for thermo-catalytic conversion of methane to hydrogen and carbon.Finding efficient solutions to removal of carbon from the catalyst surface is an active area of research and solutions like steam and air purging,heating,frequent change of catalysts and other solutions are being explored.

2.2.1. Liquid metal reactor for methane pyrolysis

Using a liquid metal bubble column reactor solves the problem of carbon deposition as carbon is insoluble in molten metal and can be easily scraped off from top of the molten metal surface.57% CH_4 conversion rate was achieved by bubbling natural gas through mott porous metal filters,in a bed of either tin or tin and silicon carbide at 750°C by [42].Liquid metal coolants from fourth generation nuclear reactors were considered as the heat source.Molten tin was used as the heat transfer metal by [43].They found that molten tin does not have any catalytic impact but inhibits production of intermediate products. Molten tin was used in a quartz glass-steel bubble column reactor by [44],to conduct experimental studies on decomposition of methane.Maximum hydrogen yield of 78% was achieved during the experiments.Only 1.5% intermediate products were formed during all experimental runs.Liquid metal temperature,gas flow rate and residence time were found to be the most important factors affecting hydrogen production.Carbon formed during the reaction was found to be completely separated on the top surface of the liquid metal.Trace amounts of carbon nano-tubes(CNT) were formed at the quartz glass reactor wall.Small quantity of carbon particles were transported with the off-gas stream.Effect of inlet gas dilution was evaluated in the study,by mixing the inlet stream with nitrogen.In their earlier work,the researchers had achieved a conversion efficiency of 30% [45].A process set-up,for industrial production of hydrogen was proposed by [40],using molten iron in the bubble column reactor and using an electric heater to produce molten metal.By conducting a techno-economic analysis,the authors estimated that hydrogen can be produced at 1.72 $kg^{-}1$,with a natural gas price of \$3 $MMBTU^{-}1$.A new system for production of H_2 using methane pyrolysis in a liquid metal bubble column reactor coupled with a DRI shaft furnace and EAF system has been proposed.

3. System description

Different components of the proposed system are depicted in figure 1.Hydrogen,which is used as the reducing agent,in the DRI shaft furnace,is produced using methane pyrolysis in a molten metal bubble column reactor,based on the system design proposed by [40].Natural gas is used as the source of methane.Amount of methane in natural gas varies with the source.Some pre-treatment steps might be necessary to improve the methane concentration and remove impurities from the natural gas stream.Methane,is decomposed into solid carbon and hydrogen by passing it through a molten metal bubble column reactor.The reaction is endothermic and requires $74.6kJmol^{-}1$ of energy.Molten metal has to be maintained at a temperature of 1500°C to 1700 °C to ensure complete conversion of methane to hydrogen and carbon.Temperature and gas residence time have the highest impact on conversion rate inside the reactor.Advantage of molten metal reactor instead of catalytic bed converters,is the ease in separation of solid carbon from the surface of the molten metal.Carbon deposition on the surface of catalysts reduces their catalytic activity,cause mechanical degradation and lead to clogging of the reactor leading to frequent down times.It is assumed that the molten metal acts only as a heat transfer media and has no catalytic effect on the reaction.While tin, bismuth,copper,iron etc have bee used for experimental investigation in the recent times,we propose the use of steel as the molten metal in the integrated system,owing to its lower cost and ease of integration in the system. In the integrated system,molten steel produced in the EAF can be fed directly inside the reactor,through an intermediate storage.The liquid metal can be pumped through ceramic pumps [46] or through gravity by placing system components at different elevations.Instead of directly feeding the molten metal into the reactor,which might disrupt continuous operations,the reactor,can be designed as a jacketed reactor.Molten metal can flow through the jacket and provide the sensible heat and reaction energy for complete decomposition of incoming methane stream in the reactor continuously.In this configuration,molten salts like lithium chloride,potassium chloride could also be used inside the reactor.Molten steel,exiting the reactor,is sent for further processing steps like casting,rolling etc.Operating temperature of the EAF will have to be higher than the normal operating temperature,to account for the heat supplied to the reactor.This will lead to an increase in the electricity consumption and operating cost(faster deterioration of graphite electrodes and refractory lining owing to higher operational temperatures) of the EAF but will substantially reduce the capital cost of the system.In a standalone methane pyrolysis system,electric heating system contributes to 77% of the capital cost [40].

Methane,enters the reactor from the bottom part of the reactor,gas bubbles rise through the molten metal and undergo decomposition.The bubbles contain the solid carbon particle, hydrogen,unreacted methane and other products inside them.Solid carbon,hydrogen,methane and the other products are released at the top of molten metal surface.Carbon is insoluble in the molten metal and can be removed easily.Mechanism similar to the one used to remove impurities dissolved in foam on the molten steel surface inside the EAF can be used to remove the carbon particles from the metal surface.The hot carbon is collected in the bubbling carbon bed.Incoming stream of natural gas can be passed through the carbon bed,which pre-heats the methane and removes impurities.Carbon also acts a reducing agent.Hydrogen stream, exiting from the top of the reactor may contain trace amounts of carbon and unreacted methane.They can either be separated from the hydrogen stream by using a pressure swing adsorption system, or fed into the direct reduction shaft furnace,as carbon and methane are both reducing agents for iron oxide to metallic iron conversion.It will result in production of small quantities of CO_2 but will reduce the system costs.Outgoing hydrogen stream from the reactor is at a higher temperature,1200°C-1500°C than the optimal temperature required for direct reduction of iron ore,which is 800 °C[28].Sintering of iron ore pellets occurs at higher temperatures,which can reduce the rate of reduction substantially as it prevents diffusion of hydrogen inside the solid pellets.The high temperature hydrogen stream can be used in the pelleting plant,and,for pre-heating the iron ore,which will improve the overall efficiency of the system and reduce the CO_2 footprint.

Pre-heated iron ore pellets enter the DRI shaft furnace from the top at 800°C.Impurities in the pellets should not be more than 5% to 7%.The DRI shaft furnace is a counter flow solid gas reactor,where iron ore pellets from the top react with hydrogen stream entering from the bottom of the reactor.The reduction reaction is endothermic and requires 99.5 kJ$mol^{-}1$ of energy.The reaction enthalpy is transferred from the hydrogen stream to the reactants. Diffusion rate of hydrogen in the pellets,heat transfer and chemical reaction at the reaction sites are important parameters to design a shaft furnace with optimal reduction rate and minimum residence time of the reactants for industrial production.Size and geometry of the pellets and temperature of the inlet gas have a strong influence on the reaction rate.While stoichiometric requirement for conversion of 1 ton of iron ore to metallic iron is approximately 54 kg of hydrogen,in practice a higher flow rate of hydrogen needs to be maintained to ensure higher diffusion rate of hydrogen for a higher reaction and metallization rate.The ratio of actual flow rate of hydrogen to stoichiometric flow rate of hydrogen required for the reduction reaction is called lambda λ[14].Metalization rate,is defined as the ratio of metallic iron leaving the shaft furnace in the iron stream.The iron stream contains metallic iron along with FeO,which needs to be reduced inside the EAF.Metalization rate achieved in a H-DRI shaft furnace is quiet high,up to 94% to 96%.Experimental studies have shown that the rate of iron ore reduction reaction is higher with pure hydrogen than with traditionally used syn gas(mixture of CO and H_2 [28].This would lead to a more compact design of the shaft furnace,which can lead to reduced capital costs and lower heat losses from the shaft furnace,owing to a smaller surface area for heat transfer. The waste gases or exhaust stream of the H-DRI shaft furnace is composed of unreacted hydrogen and water produced as a by product of the reduction reaction.Typically,the exhaust gases in a DRI shaft furnace exit the furnace at a temperature of 275°C to 400 °C [22].Temperature and composition of the waste gas stream is dependent on the mass flow rate(λ) and temperature of the inlet gas as well as the temperature of the iron ore pellets entering the shaft furnace.The exhaust gases can be passed through a ventury scrubber,where hydrogen is separated from water or through a pressure swing adsorption system,as depicted in 2.Hydrogen,collected from the waste stream can either be used in the pellet plant or fed back to the shaft furnace.

Metallic iron or sponge iron or hot direct reduced iron with a metallic content of 94%-96% enters the EAF at a temperature of 600°C to 700 °C.The DRI contains 5% impurities, which need to be separated in the EAF.While the EAF can operated with 100% Hot DRI,there is a possibility of adding steel scrap.This requires some changes in the operation of the EAF, such as an additional natural gas burner,as the scrap enters the EAF at an ambient temperature.A more detailed techno-economical analysis needs to be done to understand the optimal operational parameters.Temperature inside the electric arc furnace is raised up to 1750°C to ensure melting of metallic iron.Heat is supplied by an electric arc, produced by graphite electrodes.Dolomite and lime,up to 50 kg/tls [27],are added in the EAF to remove the impurities contained in the DRI and to maintain the basicity of the system as the impurities contained in the DRI are oxides of silicon, manganese and aluminium and can cause damage to the refractory lining of the EAF.Carbon,from the reactor in small quantity,10 kg/tls [27],can be added in the EAF to reduce the remaining FeO in the DRI and to produce CO,which assists in froth formation for impurities removal and increasing the heat transfer rate inside the EAF.This in turn,increases the life of the electrode.Graphite,is a by-product of the methane pyrolysis and can be used to manufacture graphite electrodes on-site for the EAF.

4. Discussions

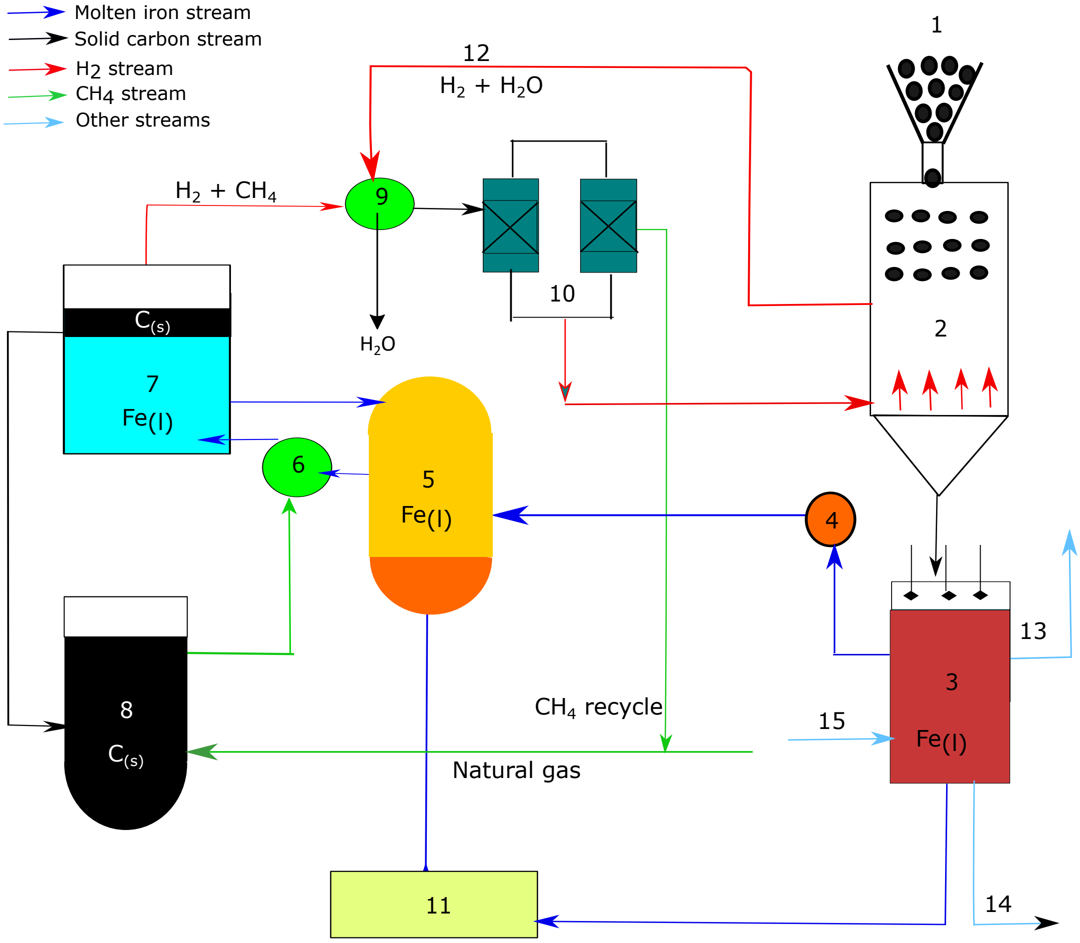
Preliminary calculations on the mass,energy and emissions of the system for one ton of liquid steel production have been carried out.The values have been calculated based on the stoichiometric coefficients of the reactions,and,should be considered as indicative values.A detailed analysis based on the chemical equilibrium and reaction kinetics would provide more accurate information about the system performance.They are presented under the sub-sections 4.1,4.2and 4.3 respectively.Possible applications of the carbon produced in methane pyrolysis are discussed in subsection 4.4.

4.1. Mass balance

Amount of hydrogen required for the production of 1 ton of liquid steel (tls) is approximately 54 kg.Considering a λ value of two,this value increases to 108 kg/tls.Natural gas required for producing 108 Kg of H_2 in the liquid metal bubble column reactor is 433 kg.Amount of liquid metal inside the reactor will depend on the production capacity,reduction rate, heat transfer coefficients and carbon removal mechanism.Considering 5% impurities in the system,approximately 1503 kg of iron ore is required to produce 1 ton of steel in the H-DRI-EAF system.A high metallization rate of 94% is expected to be achieved in the H-DRI.85 kg of FeO is transferred to the EAF along with the DRI.Considering a λ value of two,the waste stream is composed of 161 kg of water/steam and 54 kg of unused hydrogen.In the electric arc furnace 50 kg/tls of lime and dolomite are added to remove impurities.10 kg of carbon is added per ton of liquid steel.35 Nm^3/tls of oxygen is added into the system for the formation of CO and oxidation of other impurities.Composition of the EAF waste gases depends on the operational parameters,chemical equilibrium etc.Mass flow rate of molten metal from the EAF to the reactor would depend on the reactor design,heat transfer rate,molten metal inside the reactor,optimal reactor temperature etc.

4.2. Energy consumption

Energy required to heat the iron ore pellets from ambient temperature to a temperature of 800°C is approximately 300 KWh.Energy input inside the shaft furnace depends on the hydrogen inlet temperature and λ value,as depicted in figure 2.Approximately 400-450 KWh/tls of electric energy is consumed in the electric arc furnace.This value will increase,when the molten metal is transferred from the EAF to the reactor.Based on the calculations done by [40],8.6 MWh of electricity is required to produce 1 ton of H_2.Considering a λ value of two,930 KWh of electricity is required to produce 108 kg of hydrogen.Transferring the molten metal produced in the EAF into the pyrolysis reactor can reduce the energy consumption of the system.To quantify the reduction in electricity consumption a more detailed analysis of the system is needed, taking heat transfer coefficient,system design and reaction kinetics into consideration.



1	Iron ore pellets
2	Direct shaft furnace
3	Electric arc furnace
4	Hot metal pump
5	Molten iron storage tank
6	Bubble lift pump
7	Reactor
8	Bubbling carbon bed
9	Product cooling
10	Pressure swing adsorption unit
11	Steel processing unit
12	DRI waste gas stream
13	EAF waste gas stream
14	EAF slag
15	Carbon,lime ,oxygen and dolomite

Figure 1. Hydrogen direct reduction of iron ore from hydrogen produced from methane pyrolysis on molten metal surface.Hydrogen is produced by passing pre-heated natural gas from 7.Incoming natural gas stream is passed through 8, and is pumped to the reactor by 6, where liquid steel stored in 5, also enters.Hydrogen stream exiting the reactor is passed through 9,where 12 from the DRI is also mixed.The mixture is passed through 10.Purified hydrogen enters).Iron ore pellets enter the shaft furnace at 1.The hot DRI is transferred to 3.Part of the molten metal is pumped using 4 to the liquid metal storage in 5.Molten steel exits the EAF in 14.Exhaust gases from the EAF exit through 13.

Total energy consumption or the specific energy consumption (SEC) for production is approximately 6.3 MWh/tls.Majority of the input energy comes in the form of natural gas.The SEC value is higher than 3.48 MWh/tls for $\lambda = 1.5$,for a H-DR EAF system coupled with an electrolyser,as reported by [14,36].It is also higher than the SEC of BF-BOF and DRI-EAF(using natural gas) of 4.3 MWh/tls. The higher SEC,based on the preliminary calculations,could be because of the unused carbon in the CH_4.A higher mass flow rate of hydrogen inside the shaft furnace of $\lambda = 2$ has been considered in the present work to ensure a higher reduction and metallization rate.However,the SEC value could be significantly reduced by heat integration and optimization of the system.

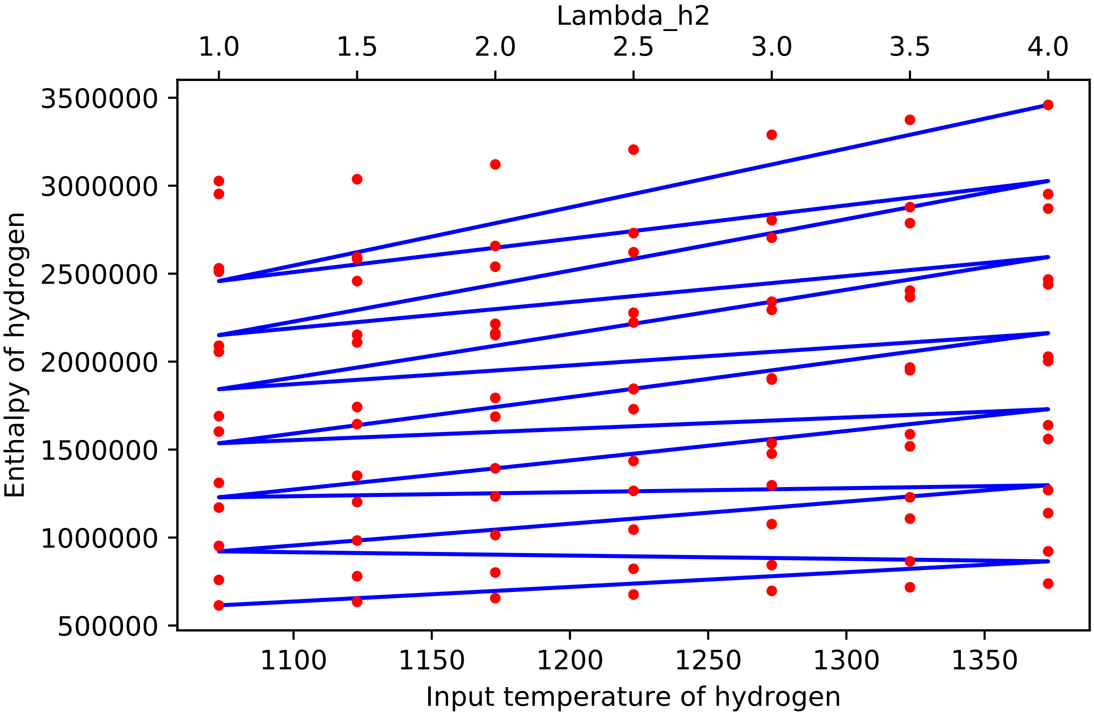


Figure 2. Variation of input enthalpy(kJ) with input temperature and flow rate.It can be seen that the enthalpy entering the shaft furnace increases with increased temperature of the hydrogen stream.It also has a positive correlation with the lambda value.Red dots represent the lambda value and the blue lines depict the change in enthalpy in kJ

4.3. CO2 footprint

The CO_2 footprint of the system stems from the use of electricity in the EAF and heating of the molten metal.Emission arising from production of one ton of liquid steel in different EU countries through the proposed system is compared with other production technologies and is depicted in 3.Methane pyrolysis,has the lowest carbon footprint among comparable technologies and can help steel industry reach its CO_2 emission reduction goals.Grid emissions factors for different countries have been taken from [47–49].Electricity consumption of the water electrolysis route is taken from [14].Emission values for the BF-BOF and natural gas based DRI route are taken from [7].If grid electricity from EU is used,the emissions would be 495 $kgCO_2$/tls.Emissions from water electrolysis route would be approximately 1030 $kgCO_2$/tls.The emissions for both technologies would be much lower in countries with low grid emission factors like Sweden and Norway.

Although, methane leakage from the extraction,storage and transport of natural gas has not been considered,it can have a considerable impact on overall emissions.Recent studies have revealed that emissions from methane leakage are higher than what had been previously reported in the literature[50,51].Shale gas production can release upto 12% of the total production as methane into the atmosphere.Earlier estimated values were close to 1.5%-1.8%.Global warming potential(GWP) of methane is hundred times higher than that of CO_2[51].Methane leakage rates vary with geographies and source of natural gas,a thorough life cycle analysis should be done before selecting a technology for hydrogen production.

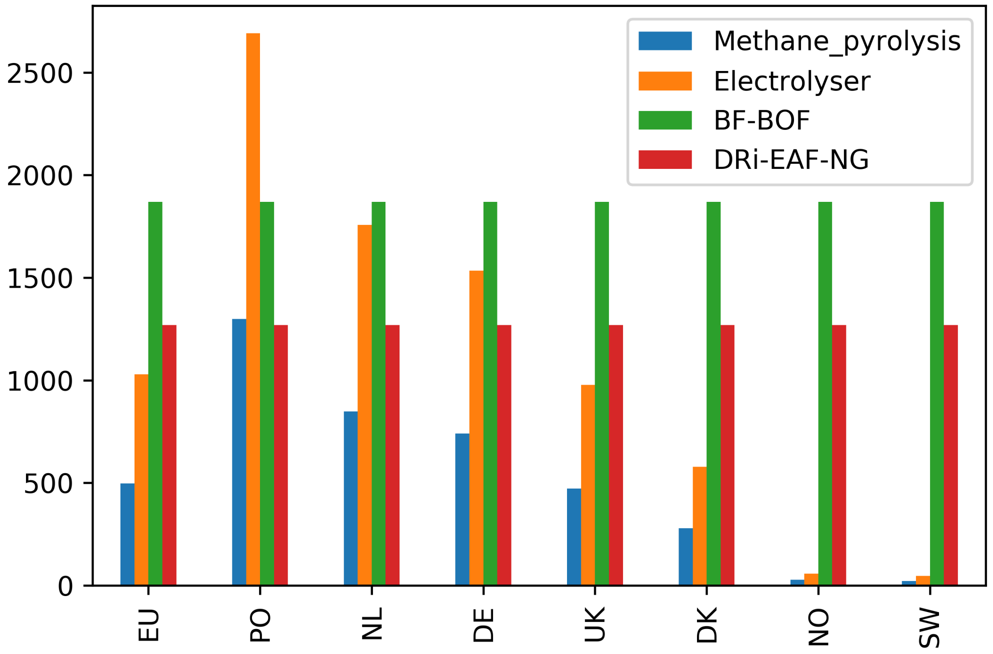


Figure 3. CO_2emission from the production of 1 ton of liquid steel represented in $kgCO_2$/tls.Methane pyrolysis and H-DRI-EAF route are compared with emissions from water electrolysis based route.Emissions from the BF-BOF and natural gas based DRI-EAF route are also shown.Fixed value of 1870 $kgCO_2$/tls for BF-BOf and 1269 for natural has based DRI-EAF has been taken.Although the value for DRI-EAF $kgCO_2$/tls route will vary with grid emission factor.(EU=European Union,PO=Poland,NL=Netherlands,DE=Germany,UK=United Kingdom,DK=Denmark,No=Norway,SW=Sweden)

4.4. Solid carbon utilization

Utilizing carbon produced in the pyrolysis process is an area of active research as it can have a positive effect on the economic feasibility of the process.Some companies are producing carbon black commercially from methane pyrolysis.Monolith materials is using the electrical plasma technology to produce carbon black from natural gas/shale gas.Clean hydrogen produced from the plant is used to power a 125 MW boiler,at Nebraska public power district to produce green electricity [12].Three tons of solid carbon is produced per ton of hydrogen produced in the reactor.This translates to production of 32.4 kg/tls.Classification of the carbon produced in the pyrolyser is important to find relevant applications.Approximately,10 kg/tls of carbon is required in the EAF for reduction of remaining FeO in the DRI and for production of CO in the EAF.Needle coke,produced in the reactor can be used for making the electrodes of the EAF.BASF,Linde group and ThysenKrupp are undertaking a project,to produce from hydrogen from methane pyrolysis,and combining it with CO_2 to produce syn gas,which is an important raw material for the chemical industry.Carbon produced during methane pyrolysis will be used to replace coal in coke plants in integrated steel plants [52], which could reduce their emissions significantly.The remaining carbon can be in the form of carbon black (CB),graphite,carbon fibres,carbon nanotubes(CNT).CB has application in production of tyres,inks,high performance coatings and plastics.It is manufactured at by partial oxidation of aromatic hydrocarbons,producing significant quantity of CO_2 emissions.It has a commercial value of \$0.4-\$2 per kg [53].Graphite, finds application in lithium ion batteries.Carbon fibres, have numerous applications in the aerospace,automobile,sports and leisure,wind turbine, textile industries owing to their high strength and light weight.They can cost anywhere between \$25 to \$113 [53].Small quantities of CNT's can be produced in the pyrolyser.They have application in polymers, plastics,electronics and batteries.CNT's could have a market price as high as \$2-\$5 /gram[54].

5. Conclusion

A new system for the production of green steel has been proposed in this work.Methane pyrolysis in molten metal bubble column reactor has been considered for the first time for production of H_2 required for reduction of iron ore reduction in the shaft furnace.Use of molten metal produced in the electric arc furnace in the pyrolysis reactor can reduce capital and operational costs of the system substantially.Preliminary investigations indicate that the proposed system has the potential to reduce the carbon footprint of steel production significantly.The system has a high specific energy consumption,owing to the use of large quantities of natural gas,where the carbon remains unused.Solid carbon produced in the pyrolysis process can be used in the EAF and sold to different industries to generate additional revenues.If used in the coke ovens,it can reduce the use of coal in the BF-BOF process and bring emissions down.

Based on the initial analysis,coupling of methane pyrolysis and H-DRI-EAF system appears to be promising alternative to CO_2 free steel making.It warrants more attention from the research community and industry.Most components of the proposed system,barring the EAF have not been commercially deployed and very little information is available about their performance and costs.Impact of different parameters on the overall performance of the system in terms of throughput,economics,efficiency need to be studied in detail.Many other configurations to couple methane pyrolysis with H-DRI-EAF systems are possible and should be investigated.Use of molten metals with catalytic properties can reduce the operating temperature and reduce operational costs.Design of components for optimal system performance,based on chemical equilibrium and reaction kinetics is required to get more insights about the techno-economic feasibility of the system. A detailed techno-economic analysis of the methane pyrolysis based hydrogen reduction system,along with its comparison with other technology options will be presented in future works.

Author Contributions: For research articles with several authors, a short paragraph specifying their individual contributions must be provided. The following statements should be used "conceptualization, X.X. and Y.Y.; methodology, X.X.; software, X.X.; validation, X.X., Y.Y. and Z.Z.; formal analysis, X.X.; investigation, X.X.; resources, X.X.; data curation, X.X.; writing–original draft preparation, X.X.; writing–review and editing, X.X.; visualization, X.X.; supervision, X.X.; project administration, X.X.; funding acquisition, Y.Y.", please turn to the CRediT taxonomy for the term explanation. Authorship must be limited to those who have contributed substantially to the work reported.

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Abbreviations

The following abbreviations are used in this manuscript:

DRI	Direct reduced iron
H-DRI	Hydrogen direct reduced iron
EAF	Electric arc furnace
BF-BOF	Blast furnace basic oxygen furnace
SMR	Steam methane reforming
BASF	Badische Anilin und Soda Fabrik
SSAB	Svenskt Stål AB
LKAB	Luossavaara-Kiirunavaara Aktiebolag
MMBTU	Metric Million British Thermal Unit
CB	Carbon black
CNT	Carbon nano tube
SEC	Specific energy consumption
TLS	Ton of liquid steel
kgCO$_2$	Kilogram of carbon dioxide
kg	kilogram
kJ	KiloJoule
KWh	Kilowatthour
MWh	Megawatthour
$	US Dollar
€	Euro

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