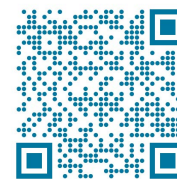




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Alternative reductants for the Blast Furnace process and catalytic treatments of exhaust gases: A review

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ABSTRACT

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Blast Furnace (BF) process is dominant in the ironmaking industry in the World. Growing demand for steelmaking raw materials results in fast consumption of fossil fuels, which are required for the BF operation and also serve as reducing agents. To lower the carbon footprint and achieve sustainable development, as well as circular economy, there is an increased need for using alternative reducing agents for BFs, such as waste plastics, bio-based materials etc. Those materials can be recycled or upcycled by utilization in BF process. Catalytic recycling/upcycling of exhaust gases was proposed, as it could be highly profitable, and, as well lower the carbon footprint of the BF process.

Keywords: Blast Furnace, Alternative reductants, Waste plastics recycling, Catalytic treatments, Carbon neutrality.

1. Introduction

Nowadays, a fast increasing demand for the iron and steel industry products results in fast iron ores and fossil fuels consumption. The iron and steel industry has a very important role in economic status of a country shaping. There is a growing trend in this industry, which is a matter of concern because the high-grade iron ores are depleted rapidly (Roy et al. 2020). Since large amounts of fossil fuels are, as well, used in ironmaking processes, there are carbon peaking and carbon neutrality goals, which have been urgently applied in order to solve the great problems between the use of resources and the environmental protection (Zhang et al. 2023). Blast furnace (BF) ironmaking is the dominant process in the world for providing steelmaking raw materials. In BF operation, coke is typically used as a reductant for iron ores in order to produce pig iron, which is further processed to obtain various types of cast irons and steels. Therefore, utilization of alternative reducing agents, including plastic wastes as sources of C is an extensively researched topic (Daniel et al 2022, Bazaluk et al 2022, Ghanbari et al. 2015, Mazhandu et al. 2020, Al-Moftah et al. 2021, Tang et al. 2021).

Large amounts of different plastic wastes, hard to recycle, upcycle or degrade, continuously grow. Less than 20 % of plastic waste in the world is recycled and the rest is discarded to landfills or oceans, or incinerated in power plants. Lack of recycling or upcycling of such

plastics results in forming of microplastics, which ends up in human food chain, and also causes other serious environmental problems (Zhao et al. 2022, Jing et al. 2021). Plastic wastes that contain polyvinyl chloride (PVC) or fluoropolymers, that are a source of Cl and F, so when this waste is burned or treated improperly, it leads to formation of highly toxic dioxins and furans (Mazhandu et al. 2020, Zhao et al. 2022, Morita et al. 2024). In Instructions on best available techniques and best practices for the environment (Kamberović et al. 2024) that refer to Stockholm Convention on Persistent Organic Pollutants, Article 5 and Annex C, dioxins and furans (PCDD/PCDF), hexachlorobenzene (HCB), pentachlorobenzene (PeCB) and polychlorinated biphenyls (PCB) present persistent/long-term bioaccumulative compounds which have long-distance mobility and are all documented as toxic. Almost all living beings and humans are exposed to them. Such compounds are formed unintentionally and released into the environment in thermal processes in which organic matter and Cl are used. Some industrial sources with very high formation and release of those pollutants are waste incinerators, sintering plants in iron and steel making and other. Open burning of waste, burning in sites where landfills are located, installations for burning wood and other biomass fuels also present sources of PCDD/PCDF, HCB, PeCB and PCB release. Since separation of plastic waste contaminated by chlorinated and fluorinated plastic is challenging, those plastics can be dechlorinated or defluorinated according to methods that were proposed by Jiang et al. (2021) and Morita et al. (2024). The necessity of recycling or upcycling plastic wastes, without forming dioxins and furans, resulted in a variety of

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research, with goals of minimization of environmental and health impacts, as well as establishing circular economy. Plastic wastes mainly contain C, H, O and N and such wastes most commonly include polyethylene terephthalate (PET), polystyrene (PS), polypropylene (PP), polycarbonate (PC) and polyphenylene oxide (PPO). It is particularly hard to treat mixed plastic wastes, especially if contaminated by PVC (Zhao *et al.* 2022, Jing *et al.* 2021). Zhao *et al.* (2022) have written an excellent detailed review on topic of conventional and emerging technologies for treatment of plastics wastes, especially focusing on upcycling plastics. However, this paper did not deal with using plastics in BF process. Some of widely and on a large scale applied conventional technologies, such as landfilling, mechanical reprocessing and incineration, have recycling limits. Landfilling: space use, gaseous products like CH₄ and CO₂ and aquifer contamination. Mechanical reprocessing: mechanical stability decreases. Incineration: emissions of CO₂ and toxic pollutants. Thermochemical conversion to high value products is promising from aspects of environment, health and economy. As an example, pyrolysis, often in combination with catalytic decomposition, can enable production of almost pure H₂ and high-value carbon nanomaterials. Gasification can be applied to obtain synthesis gas (CO + H₂), as high-energy source, but it is very sensitive to contaminants. In order to reduce upcycling costs, some new technologies, such as compatibilization and depolymerization, have emerged. Compatibilization involves addition of compatibilizer (usually multicomponent polymers) to non-miscible plastic blends and it has a potential to turn plastics to higher value products with reduced costs. Depolymerization includes use of selective catalysts to depolymerize plastics to monomers (which are obtained from fossil sources) and production of new polymers from those monomers. Depolymerization has not yet been investigated in industrial conditions. One of new technologies for upcycling plastics is microwave-assisted pyrolysis, where microwaves can uniformly heat a material, and a common product of the technology is bio-oil. It can contain up to 96 % of gasoline. As well, halogenated plastics can be treated this way. Conventional gasification can be improved in a new way by using plasma and supercritical water. Thermal plasma gasification produces higher synthesis gas yield (up to 82 vol.% of CO and 95 vol.% of H₂), smaller tar content and higher efficiency in energy use, compared to conventional gasification. In addition, plasma-assisted gasification reliably destroys dioxins, furans and benzo(a)pyrene. Supercritical water is a solvent and a catalyst in plastics gasification process. This process can also include a metal-oxide based catalysts and it can enable about 98 % efficiency of carbon gasification. There are also emerging technologies for plastic wastes upcycling. For example, biochemical conversion via micro-organisms may degrade PE to ethylene glycol, or PET and PS to CO₂ and other products (Zhao *et al.* 2022). CO₂ can be used, for example, in catalytic reforming reactions (Ghanbari *et al.* 2015). Biochemical conversion technology has significant limitations – costly, time-consuming and can produce microplastics. Photoreforming involves sunlight, water and a photo-catalyst. It is a promising method due to low costs and simplicity and it is applied for production of H₂ or acetic acid from plastics, but results in low selectivity and yield of products. This technology is challenging because of low water solubility, complex structure and general non-biodegradability of plastic wastes. Some other emerging technologies are: hydrogenolysis, glycolysis, catalytic processing, etc. Hydrogenolysis is performed with a catalyst (like Ru-based) to obtain value added diols. Glycolysis degrades polymer with glycols, by use of catalysts, to obtain many highly valued products than plastics, like bis(2-hydroxyethyl)terephthalate. Catalytic processing can upcycle PET to fiber-reinforced plastics, bisphenol A based polycarbonate to functionalized cyclic carbonate, amorphous carbon from treated plastic wastes to flash-graphene, graphene film or carbon nanotubes from plastic wastes and other. When using conventional catalysts in plastics treatment, more research is needed to prevent a catalyst deactivation caused by metal sintering and coke generation (Zhao *et al.* 2022). As an example of catalyzed plastics treatment in order to achieve circular

economy, Jing *et al.* (2020) had developed the direct upgrading of mixtures of aromatic plastic wastes to arenes by utilizing a Ru/Nb₂O₅ catalyst. Arenes are highly valuable chemicals, mainly obtained from fossil fuels, and are used for production of aromatic plastics and fibers. The catalyst had superior performance and gave excellent monomers yield (95.2 %), together with high selectivity for arenes (87.1 %). However, some limitations are present: solid-solid contact between the catalyst and plastics is challenging, so there is a need for advanced solvent system; H₂ is used as a reducing agent, so renewable H₂ sources like alcohols and acids are needed to decrease process complexity and costs; to improve overall economic efficiency, high-performance noble metal catalysts need to be explored.

For all the stated reasons, in BF ironmaking process, it is necessary and challenging to find solutions that enable the following: minimization of adverse environmental impacts, achieving positive effects considering sustainable development, recycling or upcycling of C bearing wastes, C footprint lowering and circular economy building. The current review deals with investigation of possibilities of utilizing different alternative reductants for iron ores in BFs operations, such as plastics and bio based materials instead of a part of coke. As well, catalytic treatments of exhaust gases from BFs were proposed.

2. Alternative reductants instead of a part of coke and coal in BF iron production

Trinkel *et al.* (2015) have investigated influence of the use of waste plastics as an alternative reductant in an Austrian BF (Voestalpine Stahl GmbH) to an additional input of Hg, Cd, Zn and Pb into the process, for a period of 4 years. Waste plastics originated from end of life vehicles (light fraction after shredding). Amount of used plastics in the Austrian BF have doubled from 17 to 35 kg/t HM at a period of time from 2007 to 2011, respectively. The amount of heavy metals imputed by use of plastics in the BF during that period remained almost constant for Hg, Pb and Cd, or increased slightly for Zn. It can be noted that content of heavy metals from waste plastics has significantly declined over the years. Use of such plastics waste in BF is only important for Cd and Hg, and for them, plastics input contribute to about 81 % and up to 44 % of the whole input, respectively. Considering Zn and Pb, plastics contributes less than 14 % of the whole input. After a proper treatment of output streams in the ironmaking plant, major amounts of all those metals are landfilled: Cd – more than 95 %, Hg – about 90 %, Pb – about 60 % and Zn – approximately 34 %. On the basis of the obtain investigation results, it can be concluded that the use of waste plastics in BF does not influence emissions of Hg, Cd, Pb and Zn into the environment under real process conditions and loadings. The concentrations of those metals in the cleaned top gas and in waste water are not affected by use of waste plastics at an amount of 35 kg/t HM. Mazhandu *et al.* (2020) have written a review article describing advantages and disadvantages of use of waste plastics as alternative reductants to coke for iron production in BF. Plastics are mostly hydrocarbons and they contain about three times more H₂ than pulverized coke, which makes it better reductant in terms of environment and economy. Energy savings are a result of higher calorific value. As well, they have fewer impurities and, therefore, less dioxins and furans are released in the ironmaking processes. The addition of 2 wt.% of plastic to the coke reduces CO₂ emissions by 2 %. Moreover, production of synthesis gas (H₂ + CO) from the plastics and its subsequent injection through the BF tuyeres lowers the CO₂ by 7 %. When utilizing plastics in BF process (there are several ways of it), 30 % of CO₂ emission lowering can be achieved and iron production costs are lower, as well. The recommended plastics content in coke is 30 to 40 wt.%. There are also disadvantages when using certain types of plastics. As mentioned before, halogenated plastics need to be dehalogenated before use in BF, since, for example, chlorides and fluorides are very corrosive and also, their emission can lead to formation of highly toxic dioxines and furans. PVC pre-treatment results in higher costs. Plastic wastes cannot totally replace the coke in BF due to lack of mechanical strength and they do not have the required gas permeability. The presence of too much Zn in plastics leads to operational problems in BF. Single use facemasks (left after Covid-19 pandemic) that were used in the study of Daniel *et al.* (2022) are usually

produced from polypropylene fabric. To produce granular material suitable for production of cold bonded briquettes, first, coarsely cut masks were mixed with GCI coal fines and charcoal, with wt.% ratio of 20:80. The mixture was made physically and then heated to 250 °C for 1 h in air. Hot mixture was stirred. After cooling down, it was ball milled at 500 rpm for 5 min. The whole powder passed through sieve and particles were <250 µm, and parts of nose wire did not pass the sieve. Wires can be used as additional Fe source for BF. C and H₂ content from mask plastics can reduce Fe oxides and match the raceway of BF conditions. The previously obtained granular material is a good candidate for direct injection in BF tuyeres. Moreover, facemasks treated GCI coal shows improved gasification reactivity and it could have use in enhancing coal reactivity throughout BF injection. This could make cheaper and less reactive coals more attractive for the injection process or possibly increase the maximum injection rate, with no undesirable effects on furnaces operation. The granular material made of masks, GCI coal and charcoal is also appropriate for storage and transport, especially by conveyer belt, where no airborne powder hazard is generated. In addition, CaCO₃ is used as filler for polypropylene, so when polypropylene is combusted in oxidizing conditions, ash residue is primarily composed of CaO and CaCO₃. That ash is not a major problem for iron and steel making from the viewpoint of the K, Na and Zn introduction, which is very undesirable. In general, there are certain limitations when using facemasks in iron making. Since they are made of fibrous plastics, pulverization to suitable sizes is particularly challenging because of high ductility of such materials, relatively low softening temperature and, in addition, conventionally milled plastic waste has low density, so because of that, storage and transport are also very challenging (Stewart *et al.* 2022). For BF processes, bio-based materials can be injected through tuyeres, in the form of lump bio-coke, or as a C source at the Fe ore sinter plant. In the research of Bazaluk *et al.* (2022), wood pellets were used as biomass for BF. Pellets were ground to a particle size of <3 mm. Carbonization of mixtures of ground pellets and coke was performed in laboratory, at 950 and 1100 °C. At both temperatures, the yield of biocoke lowers with an increase of wood pellets content that is higher than 5 wt.% in coke. The reason for this is high content of volatile compounds in starting biomass. Also, at the higher carbonization temperature, the yield of coke and biocoke decreases. However, with a decrease in final carbonization temperature, together with an increase of biomass content (more than 5 wt.%), overall properties of charcoal pellets with biocoke for BF utilization deteriorate, and those are the limitations. The conclusion is that, for BF purposes, 5 wt. % of biomass pellets in coke can be used and it is an optimal content. Ghanbari *et al.* (2015) used mathematical programming to optimize design and operation of integrated systems for steelmaking. Integrated system includes BF, BOF – basic oxygen furnace and a methanol production plant, in case that methanol is produced from exhaust gases. Gases originating from coke oven, BF and BOF are mainly consisted of CO, H₂ and CH₄, which can be utilized as a fuel in a power plant in iron and steel production or for heating of hot stoves and slab reheating furnaces in rolling mills. BF top gas (primarily composed of N₂, CO, CO₂, H₂O and H₂) could be recycled and used as reducing agent. Before injection, CO₂ separation is required. As mentioned before, those gases could be used for methanol production. The authors studied effects of utilizing different fuels in ironmaking, such as: oil, natural gas, pulverized coal, coke oven gas, charcoal, and torrefied biomass. Special focus was on use of torrefied biomass (mild pyrolysis at 200 to 320 °C) in order to reduce emissions from the system. Integration of torrefied biomass enables 60 % decrease of CO₂ emissions from primary steel production, although further investment is needed. For the BF, an upper limit of all the fuels listed above was 120 kg/t_{hm}. For the integrated system, the highest net present value (2.57 G\$) is obtained with torrefaction, great level of recycling of preheated top gas and O₂ injection. Also, lowest costs are reported for the system with torrefaction and highest for combined coke oven gas and natural gas due to requirement of external coke and no methanol synthesis. The lowermost net present value (1.90 G\$) is gotten when using combination of coke oven gas and natural gas as supplementary fuel. The minimum CO₂ emission (0.29 t_{CO₂/t_s) is achieved with torrefaction, while the lowest value (0.73 t_{CO₂/t_s) for fossil fuel utilization is for the integrated system with oil. Charcoal use in the integrated system reduces CO₂ emission by 45 %. The assessed optimal process conditions for the torrefaction are as follows. First step is drying of biomass with starting moisture content of 40 % to obtain moisture of 15 % at 167 °C. Then, that biomass is torrefied in reactor}}

at 227 °C for 30 min. Considering torrefied biomass, charcoal and pulverized coal systems, costs of liquid steel producing are all within 10 US\$/t_s. In general, there are limitations for using biomass as alternative reducing agents for BFs or as an energy source. Biomass has contaminants and low heating values, and therefore it is a problematical fuel from the aspects of wide-ranging resources and waste streams. Al-Moftah *et al.* (2021) have considered Subcoal™ for BF ironmaking alternative reductant or as a fuel for power generation. Subcoal™ is a product made of non-recyclable waste – mixture of paper and plastics left after passing through municipal refuse processing industrial facilities. Thermal decomposition kinetic study for different treatments of this waste was carried out. *E_a* values for combustion were lowest compared to gasification and pyrolysis. Combustion *E_a* values were 76.74 ± 15.4 kJ/mol and 71.0 ± 4.4 kJ/mol for both Ozawa Flynn Wall and Kissinger-Akshira-Sonuse model free methods, respectively. Subcoal™ has great content of C and H₂, which means it could be suitable as an alternative reductant for BF ironmaking, either by direct injection through tuyeres after milling or by pre-gasification and feeding directly into the BF that way. Tang *et al.* (2021) have made carbon composite briquettes (CBB) for use in BF. They developed a model for simulated laboratory conditions and predicted CBB reaction behavior in actual BF. The CBB reaction behavior is essential for the enhancement of BF efficiency due changing of ore reduction and coke gasification in the upper part of BF. The CBB had the wt.% composition of: C – 20.30, Fe₃O₄ – 29.70, FeO – 39.70, Fe – 1.57 and gangue – 8.73. The starting materials for CBB preparation were hematite, quartz (as an additive for enhancement of briquette strength) and coal fines. Weight percent ratio was: hematite, quartz and coal fines of 67:3:30. Cellulose (2 wt.%) was added as a binder, and moistened mixture was pressed under 15 MPa. The samples were dried, hardened by heat treatment and, finally, held at 800 °C for 30 min. For the prediction of CBB reaction behavior in actual BF, the CBB charge operation was presupposed to be conducted in BF of 2500 m³ with 6250 t/hm per day productivity. CBB is mainly charged by complete mixing with ore burden. Gasification of C from CBB starts at 577 °C. At temperatures from 700 to 827 °C, CCB added both CO and CO₂ to the BF gas, showing that the CCB underwent its full self-reduction. At temperatures from 827 to 877 °C, the reduction of iron-oxide is nearly complete. The CBB utilization becomes efficient for BF energy savings after 800 °C due to suppressing gasification of the coke and increasing of the sinter reduction. The conclusion in this research is that it is preferred to charge CBB in the area near BF mid-radius. In addition, 10 wt.% of CBB in the sinter does not considerably change the phenomena in BF furnace, while large content of 30 wt.% can be a limitation due to significant impacts to those phenomena.

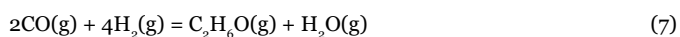
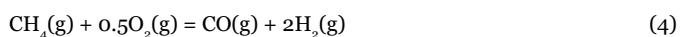
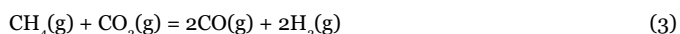
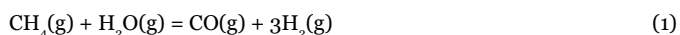
As a summary of this chapter, advantages and limitations of utilization of different reductants for BF operation, as well as of using of different fuels for steelmaking facilities, are presented in [Table 1](#)

3. Catalysis of exhaust gases from ironmaking

Exhaust gases from ironmaking facilities could be recycled, either as fuel for power plants, or by catalysis and subsequent injection in BF, due to a content of reductants such as CO and H₂. To achieve use in BF, it is necessary to increase content of CO and H₂, as well as lower the content of N₂ and remove CO₂ from the system.

Therefore, in this chapter, there are several examples of catalysts utilization in order to treat exhaust gases from ironmaking plants.

Residual gases from coke oven, BF and BOF are mainly composed of CO, H₂ and CH₄ and they can be utilized as fuel for a power plant. Available gases from the plant can also be used for heating purposes or, as an example, for methanol synthesis and this requires appropriate plant units. In order to treat coke oven gas containing CO₂ to produce more H₂, technologies that can be applied are: steam methane reforming, CO₂ reforming (dry reforming) and partial oxidation reforming. Those technologies can be also used in order to gasify CH₄ for the production of more H₂. The stated technologies require a heterogeneous catalyst. Low pressure steam is used for heating and also for internal use in the plant, as an example, for steam methane reforming. The dominant reforming reactions, in general, are presented by reactions 1 to 8 (Ghanbari *et al.* 2015).



Reaction (2) is the side reaction of steam CH_4 reforming. CH_3OH (gas and liquid phase) are presented in reactions (5) and (6). Dimethyl ether ($\text{C}_2\text{H}_6\text{O}$) is a side reaction that is produced from catalytic reactions between CO , CO_2 and H_2 . Generation of $\text{C}_2\text{H}_6\text{O}$ is 2 wt.% of CH_3OH production in the side reaction. (Ghanbari et al. 2015) High resistance to C deposition, and therefore deactivation, is a necessary property of any catalyst for reforming processes. As an example, C deposition in the CO_2 methane reforming cannot be eliminated, but it can be significantly reduced by high dispersion of small catalytically active particles and promoting of the catalyst. It is important to use or develop catalyst supports based on ceramics or other, that possess high controlled open porosity which would enable good dispersion of active particles (Al-Fatesh et al. 2021, Nikolić et al. 2022, Nikolić et al. 2023). Ou et al. (2021) have investigated Ni/perovskite catalysts for obtaining of H_2 by steam CH_4 reforming. Perovskite materials are considered as the most promising catalyst supports, considering improvement of activity, stability and selectivity. The authors prepared catalysts on different perovskites, including Ni/LaAlO_3 and $\text{Ni/La}_{0.7}\text{Mg}_{0.3}\text{AlO}_{3.8}$, where La in LaAlO_3 is partially substituted with 0.3 moles of Mg. The wt.% of Ni and support was 1:10. That substitution enhances catalytic activity and significantly improves C deposition resistance

of Ni-based catalysts. In addition, $\text{Ni/La}_{0.7}\text{Mg}_{0.3}\text{AlO}_{3.8}$ exhibits outstanding performance in CH_4 reforming. The activity test was carried out for 3 h, while stability test lasted 35 h. Reforming temperature was 650°C . Ni/LaAlO_3 shown CH_4 conversion of 67.55 % and H_2 yield of 51.31 %. $\text{Ni/La}_{0.7}\text{Mg}_{0.3}\text{AlO}_{3.8}$ enables CH_4 conversion of 72.08 % and H_2 yield of about 56.44 %. Addition of non-toxic Mg also lowers the cost of catalyst. Al-Fatesh et al. (2021) have studied Ni-based catalysts with well-defined mesoporous structure for the dry methane reforming (CO_2 reforming) to obtain synthesis gas. The catalysts were supported on $\text{La}_2\text{O}_3+\text{ZrO}_2$. Also, the Ni in catalysts was promoted by 1 wt.% of Gd, Ga, Cr and Ca. Compared to all the other catalysts in this work, the sample with Cr exhibited the best performance due to high mesoporosity, high dispersion of small Ni particles and promoting. CH_4 and CO_2 conversions were about 83% and 88%, respectively. H_2/CO ratio was near 1 and the catalyst had satisfying stability. Kim et al. (2019) have researched CO_2 reforming (dry reforming) of coke oven gas by using Ni-based catalysts supported on different oxides and with various Ni loadings. A simulated coke oven gas had the following composition (%): $\text{H}_2 - 55.57$, $\text{CO}_2 - 2.56$, $\text{CH}_4 - 28.04$, $\text{N}_2 - 5.84$ and $\text{CO} - 7.99$. The CO_2 was added for the catalytic reaction (at 800°C for 12 h), where CO_2/CH_4 ratio was 1.2:1. The CH_4 conversions were from 86.0 to 88.1 % for 15 wt.% $\text{Ni/MgO-Al}_2\text{O}_3$ and 87.6 % for 15 wt.% $\text{Ni/Al}_2\text{O}_3$. Also, the 15 wt.% $\text{Ni/MgO-Al}_2\text{O}_3$ shown the highest CH_4 and CO_2 conversion because of high Ni dispersion, great surface area and strong basicity. Stability of this catalyst was conducted for 50 h, and there was not observed noticeable catalyst deactivation. That catalyst had superior performance. Fazlikeshteli et al. (2023) researched catalysts for low-temperature partial oxidation of CH_4 to produce synthesis gas. Their work included the following catalysts: monometallic Pd/CeO_2 and Ni/CeO_2 systems, as well as bimetallic Pd-Ni/CeO_2 , that were synthesized by mechanochemical and conventional incipient wetness impregnation routes. Much better performances were achieved for bimetallic catalysts than for monometallic. The highest catalytic performances were obtained for the Pd-Ni/CeO_2 catalyst prepared by ball milling in the partial CH_4

Table 1. Advantages and limitations for using of different reducing agents for BF operation and for using of different fuels for steelmaking facilities

Alternative reductant	Advantages	Limitations	Ref.
Waste plastics for BF	<ul style="list-style-type: none"> - The use of waste plastics in BF does not influence emissions of Hg, Cd, Pb and Zn into the environment under real process conditions and loadings - The concentrations of Hg, Cd, Pb and Zn in the cleaned top gas and in waste water are not affected by use of waste plastics at an amount of 35 kg/t HM 	<ul style="list-style-type: none"> - Limited to 35 kg/t HM 	(Trinkel et al. 2015)
Waste plastics for BF	<ul style="list-style-type: none"> - About three times more H_2 than pulverized coke - Higher calorific value than coke - Fewer impurities so less dioxins and furans are released - Production of $\text{H}_2 + \text{CO}$ from the plastics and use of the gas in BF through the tuyeres - Up to 30 % of CO_2 emission decrease and lower costs of iron production - Content in coke up to 30 to 40 wt.% 	<ul style="list-style-type: none"> - When there is PVC in the waste, it needs to be de-chlorinated to prevent formation of dioxins - Pre-treatment results in higher costs - When there is too much Zn, it causes operational problems in BF 	(Mazhandu et al. 2020)
Single use facemasks for BF (waste plastics)	<ul style="list-style-type: none"> - Obtaining of granular material that could be directly injected through BF tuyeres - Facemasks treated GCI coal have an improved gasification reactivity - Granular material is suitable for storage and transport 	<ul style="list-style-type: none"> - Challenging pulverization to suitable sizes - Challenging storage and transport of conventionally milled plastic waste 	(Stewart et al. 2022)
Carbonized wood pellets for BF	<ul style="list-style-type: none"> - Can be injected through tuyeres 	<ul style="list-style-type: none"> - Only 5 wt.% can replace coke - High content of volatile compounds in the starting biomass 	(Bazaluk et al 2022)
Torrefied biomass as the most promising reductant/fuel in the research, for BF and steelmaking plants	<ul style="list-style-type: none"> - Minimal CO_2 emission (0.29 tCO_2/t) compared to other bio-based reductants and lower costs for iron and steel production - 60 % decrease of CO_2 emissions from primary steel production in the integrated system 	<ul style="list-style-type: none"> - Biomass has contaminants and low heating values, so it is a problematical fuel from the aspects of wide-ranging resources and waste streams - Not tested in actual BF or steelmaking plant 	(Ghanbari et al. 2015)
BF top gas	<ul style="list-style-type: none"> - Can be recycled in order to synthesize methanol 	<ul style="list-style-type: none"> - CO_2 separation is required 	(Ghanbari et al. 2015)
Subcoal™ (made of non-recyclable waste) as a reductant for BF or as a fuel for power generation	<ul style="list-style-type: none"> - Great content of C and H_2 - Direct injection through tuyeres after milling or by pre-gasification and feeding directly into the BF by direct injection 	- /	(Al-Moftah et al. 2021)
Carbon composite briquettes (CBB) for BF	<ul style="list-style-type: none"> - Efficient for BF energy savings after 800°C due to suppressing gasification of the coke and increasing of the sinter reduction - 10 wt.% of CBB in the sinter does not considerably change the phenomena in BF 	<ul style="list-style-type: none"> - 30 wt.% of CBB in the sinter can be a limitation due to significant impacts to phenomena in BF 	(Tang et al. 2021)

oxidation. At only 550 °C, Pd-Ni/CeO₂ catalysts (various metal contents) have exhibited CH₄ conversion levels from 62 to 75%, selectivity for H₂ from 64 to 66%, selectivity for CO from 19 to 24% and synthesis gas yield from 52 to 64%. Optimal preparation parameters and contents for the Pd-Ni/CeO₂ catalyst were: ball milling at 50 Hz for 20 min and only 0.12 wt.% of Pd and 1.38 wt.% of Ni. As well, outstanding metal dispersion over CeO₂ was achieved for that catalyst. Moreover, activity tests were conducted for 100 h at 550 °C. After 40 h, performance of the optimal catalyst reached steady state for both CH₄ conversion and synthesis gas obtaining. That catalyst also had superior stability – deactivation rate was almost zero (0.01 % × h⁻¹) due to less C deposition. Deng and Adams (2020) have conducted techno-economic analysis of a new process to produce methanol from coke oven and blast furnace gases, including CO₂ capturing and using. This work, in addition, takes into account removal of thiophene (C₄H₄S) and other S compounds. Authors proposed a process that significantly shortens desulphurization by utilization of CO₂ steam reforming at 800 °C, with the use of Ni/MgO-Ce_{0.8}-Zr_{0.2}-O₂ catalyst. The process can enable production of about 179 ktonne of methanol per year. The method spends 0.75 kg of coke oven gas and 0.73 kg of CO₂ from blast furnace gas for 1 kg of synthesized methanol. Achieved carbon efficiency is 72 %. Waste heat is used for steam production, where about 52 % of the feed energy is converted to methanol. Recovered thermal energy from methanol production system adds up to 85 %. Thus, it was concluded that methanol production in iron making plants is highly profitable.

On the basis of existing knowledge, this paper proposes utilization of waste plastics as an alternative reductant for BFs, together with a catalytic unit(s) for recycling of exhaust gases by reforming processes. Waste plastics was selected due to particularly large quantities all over the World, and, on the other hand, only small amounts are recycled or upcycled. Exhaust gases from BF processes have a suitable composition for several recycling possibilities that include catalytic treatment. Catalytic reforming of the exhaust gases could, for example, convert the gases to the synthesis gas (CO + H₂) that would subsequently be used as a reducing agent for BF, or convert them to methanol, which is highly profitable, etc. Such treatment(s) will be a topic of future studies.

4. Conclusions

The growing production trend in ironmaking industry results in fast increase in consumption of iron ores, as well as fossil fuels, which are utilized in BFs as a fuel and as reductants. Utilization of alternative reductants is necessary in order to lower the carbon footprint and to achieve sustainable development and circular economy. Those reductants include waste plastics, waste bio-based materials and similar carriers of C and H₂. Utilization of those wastes for BF process enables their recycling or upcycling. This paper proposes use of waste plastics as a reductant in BF, since there is a large amount of this waste and only about 20 % is recycled/upcycled. To additionally lower the carbon footprint of the BF process and achieve more profit, in this paper, catalytic recycling/upcycling of exhaust gases was proposed, since top gas from BF, as well as exhaust gases from the whole ironmaking plant, have a suitable composition such treatments. Resulting products of catalytic reforming are, for example, synthesis gas (CO + H₂), which is a high energy fuel and an excellent reductant, or methanol, that enables high profitability when it is produced in ironmaking plants. Suitable catalysts are solid, usually based on economically favorable Ni or Ni with a very small amount of Pd and are commonly supported on different metal-oxides, such that enable high dispersion of catalytically active matter and increased basicity. Catalytic reforming of BF top gas will be a topic of future research.

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