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A review of thermochemical processes and technologies to use steelworks off-gases

Wilmar Uribe-Soto[a,b], Jean-François Portha[a,b,*], Jean-Marc Commenge[a,b], Laurent Falk[a,b]

[a] *Université de Lorraine, Laboratoire Réactions et Génie des Procédés, UMR 7274, Nancy F-54001, France*
[b] *CNRS, Laboratoire Réactions et Génie des Procédés, UMR 7274, Nancy F-54001 France*

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ABSTRACT

The steel industry is the main generator of CO_2 among the different industrial sectors. That is why efforts are being made to reduce or avoid CO_2 emissions by process optimisation or by Carbon Capture and Storage (CCS) processes. In the steel production by blast furnace technology, three main off-gases are generated, namely the Blast Furnace Gas (BFG), the Coke-Oven Gas (COG) and the Basic Oxygen Furnace Gas (BOFG). Many processes and technologies can be identified for their use, depending on the volume and composition of the steelwork off-gases. In the present work, a review and an analysis of several alternatives proposed during last years to use these off-gases are carried out, with a particular focus on thermochemical processes. Three main alternatives are considered: the thermal use of the gases, the recovery of valuable compounds for selling and the synthesis of a high-added value product. The possible implementation of these alternatives may conduct to improvements in energy efficiency of the steel making process with subsequent reduction of CO_2 emissions.

1. Introduction

Global warming, due to greenhouse gases (GHG) such as CO_2 or CH_4, is perhaps one of the most important issues which humanity has to deal with. To tackle this problem, the capture and storage or the utilisation of carbon can be applied when the produced quantity of carbon dioxide is sufficiently high, such as, for example, in power plants, cement works or steelworks. The steel industry is precisely the main generator of CO_2 among the different industrial sectors [1]. This industry is responsible for 30% of the whole industrial emissions [2] corresponding to 6% of CO_2 emissions from total anthropogenic sources in the world [3]. That is why efforts are being made to achieve the reduction of CO_2 emissions in the steel industry. The first attempt includes improving energy efficiency of process, which minimizes the consumption of the primary reducing agent and fuel (coke or natural gas) as well as electricity. The main routes and technologies to produce steel are presented in this introduction.

The steelmaking process is a very complex process comprising several steps in configurations that depend on target products, investment capacity, available raw materials and energy sources. However, there are two basic methods for steel production [4]:

- primary route: steel is produced from iron ore extracted out from mines,
- secondary route: steel is produced from scrap (recycled steel).

The main difference between the two methods is that the recycled steel can be directly melted to produce new steel (usually using an electric arc furnace). Thereby, iron ore, which is a mixture of iron oxide (with an iron content of about 60%), must first be reduced to iron by means of a reducing agent (mainly coke, and much less widespread natural gas or H_2). For the primary route, three different processes have been developed: the integrated route including a Blast Furnace (BF) and a Basic Oxygen Furnace (BOF), the smelting reduction process and the direct reduction process (Fig. 1). The integrated route is the most widespread in the world, used in over 50 countries and representing 73.4% of world steel production for 2013 [5].

The use of coal, biomass, used lubricating oils and even plastic waste as a substitute for a portion of the coke has also been considered [7–9]. This allows the reduction of CO_2 emissions through the reduction of the coke consumption. Many other alternative technologies to the BF have been proposed. A comparison of these new technologies by comparison with the BF process is proposed by Hasanbeigi et al. [10].

Regarding the BF process, another improvement has been studied: the Top Gas Recycled Blast Furnace (TGRBF). In this case, pure oxygen instead of air is used, to obtain a BFG free of N_2. CO_2 from the off-gas is then removed, so that a stream rich in carbon monoxide is fed back to the BF. In this way, a reduction in coke consumption is achieved which implies a reduction in GHG emissions [11]. The CO_2 stream resulting is

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[*] Corresponding author at: Université de Lorraine, Laboratoire Réactions et Génie des Procédés, UMR 7274, Nancy F-54001, France.
E-mail address: jean-francois.portha@univ-lorraine.fr (J.-F. Portha).

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Nomenclature

ATR	Auto-Thermal Reforming
BF	Blast Furnace
BFG	Blast Furnace Gas
BOFG	Basic Oxygen Furnace Gas
CAP	Chemical absorption process
CMR	Combined Methane Reforming
CCS	Carbon Capture and Storage
CCU	Carbon capture and utilisation
CHP	Combined heat and power (cogeneration)
CPO	Catalytic Partial Oxidation
COG	Coke oven gas
DMC	Dimethyl carbonate
DME	Dimethyl ether
DMR	Dry methane reforming
GHG	Greenhouse gases
GP-MEOH	Gas-phase methanol unit
GSP	Gas Separation Unit
IGCC	Integrated gasification combined cycle
IRR	Internal Rate of Return
HTS	High temperature shift
LCA	Life Cycle Assessment
LHHW	Langmuir-Hinshelwood-Hougen-Watson (isotherm model)
LHV	Lower heating value
LP-MEOH	Liquid-phase methanol unit
LTS	Low temperature shift
MEOH	Methanol purification unit
MSP	Membrane Separation Process
MTBE	Methyl tert-butyl ether
MTS	Medium Temperature Shift
MR	Methane Reforming
POR	Partial Oxidation Reforming
PSA	Pressure Swing Adsorption
SMR	Steam methane reforming
Syngas	Synthesis gas
TGRBF	Top Gas Recycled Blast Furnace
TRL	Technology Readiness Level
TSA	Temperature swing adsorption
WGSR	Water-Gas Shift Reaction
WSP	Water separation

either sent for use in other processes (after purification), or sent to a Carbon Capture and Storage (CCS) system. CO_2 emissions can be reduced by 5–10% by using the TGRBF, by 25–30% when using a CCS and up to 60% for the combination TGRBF - CCS, compared to the conventional use of BF [12]. As a part of the European research project ULCOS (Ultra-Low CO_2 Steelmaking) [13], this technology has been considered as a relevant alternative among others. However, some major obstacles have compromised the TGRBF fulfillment. The major challenges include: the cost of production and operation of the proposed processes, the fall of the economic value of CO_2 quota levels and the social acceptability of CCS, with more and more European countries taking forward measures against this practice. Worldwide carbon reduction program and new CO_2 breakthrough technologies for energy saving and CCS in steel making processes are reported elsewhere [14].

In the solutions previously discussed, the main effort is made to reduce CO_2 emissions or to trap it in an underground geological formation. However, it must be considered that most of the chemicals used in our society operate with carbon as a central element and that these chemicals are produced from nonrenewable fossil sources (coal, crude oil, natural gas, etc.). In this case, the CO_2 should be seen as a carbon source that may be transformed into products with high added value [15]. There are also other applications in which CO_2 can be used directly without chemical conversion. This is the case, for example, for CO_2 use as a solvent under supercritical conditions or the use in the carbonated drinks industry. In both cases (using CO_2 with or without chemical conversion), one talks about the CO_2 valorisation, implying that we are facing a changing paradigm in how to consider CO_2 [15].

In the steel production process, considering the primary integrated

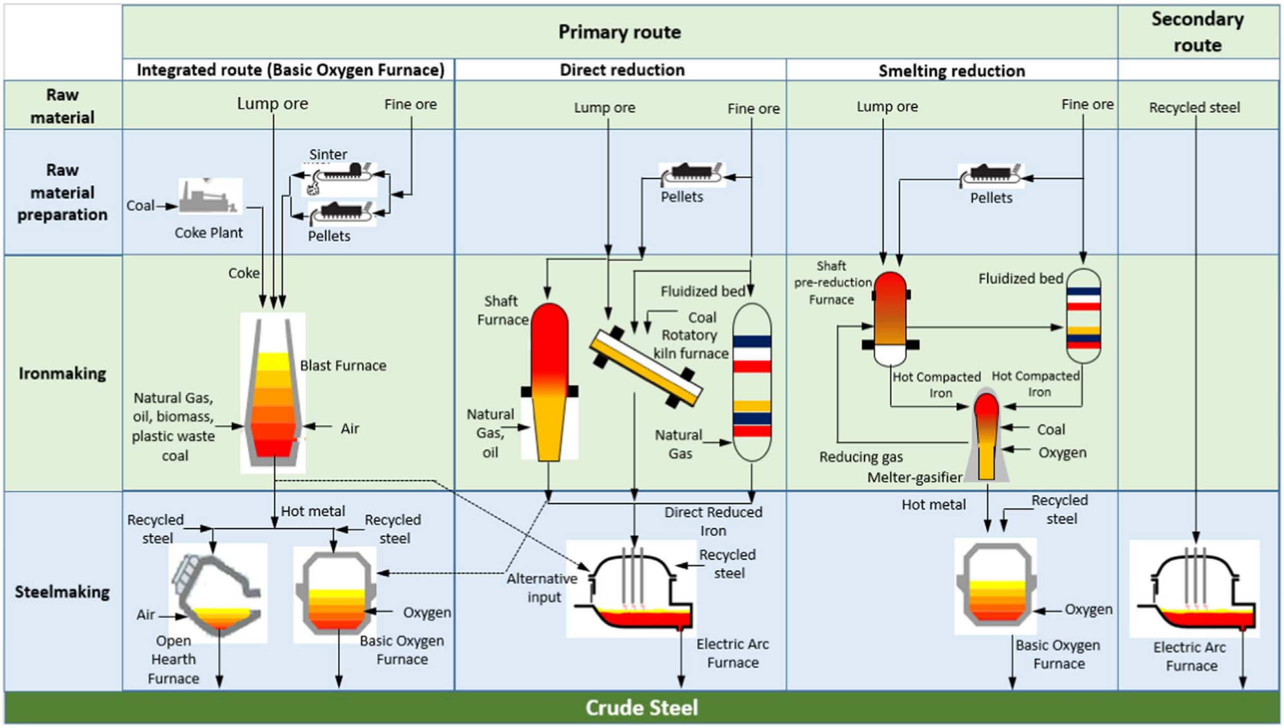

Fig. 1. Production routes to make steel, adapted from Birat [6].