Techno-economic analysis of a process for CO_2-free coproduction of iron and hydrocarbon chemical products

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HIGHLIGHTS

- A CO_2-free integrated iron and hydrocarbon process utilizing molten salt electrolysis is proposed.
- Partial oxidation of natural gas alkanes using a liquid metal halide ($FeCl_3$) as the oxidising agent.
- Generates a high-value electrolysis feedstock through leaching the iron ore with inorganic acids.
- Metallic halide feedstock is regenerated through the coproduction of reduced iron.
- Process economics are competitive with low imposed carbon prices.

GRAPHICAL ABSTRACT
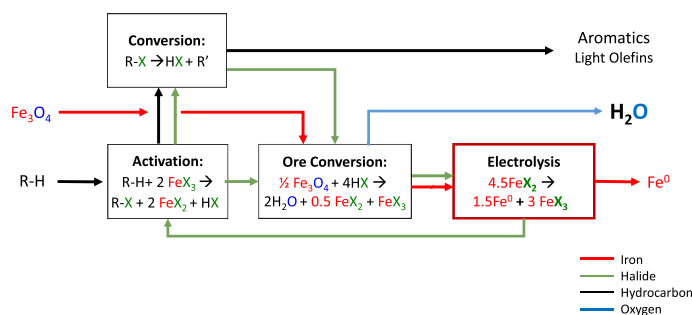
ABSTRACT

The economics of an integrated iron and hydrocarbon process utilizing molten salt electrolysis to produce 1850 kilotonnes per annum (kta) of reduced iron and 500 kta of higher hydrocarbons is presented. Capital and operating cost models based on Aspen Plus V8.6 sizing data were used to generate cash-flow and production costs for the proposed scheme. The process economics are most strongly dependent on the natural gas and electricity prices. The capital cost estimates include high contingency costs to reflect the higher investment risk for a first-of-a-kind (FOAK) process. At a carbon price of less than US $30/$tCO_2$e, the process is competitive with traditional blast furnace smelting. Areas where a more complete understanding is needed of the barriers to the deployment of this technology are identified.

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1. Introduction

Industrial manufacturing is a cornerstone of the global economy. It is a significant challenge for large producers of metals and chemicals to remain cost competitive whilst simultaneously lowering emissions and maintaining process energy and feedstock efficiency [1,2]. Manufacturing industries are responsible for approximately 30% of global CO_2 emissions and iron and steel pro-

duction is the largest industrial source of direct CO_2 emissions estimated to be about 6–7% of the total global anthropogenic CO_2 [3].

The carbon intensity of different iron and steel production routes varies considerably, ranging from 0.4 tCO_2/t crude steel for scrap/electric arc furnaces (EAFs), 1.7–1.8 tCO_2/t crude steel for integrated blast furnace (BF) basic oxygen furnaces (BOFs) to 2.5 tCO_2/t crude steel for coal-based direct reduced iron (DRI) processes [3]. Of these, the integrated BF-BOF route is the most widely used, accounting for approximately 70% of the world crude steel production in 2010 [4]. The majority of the emissions (~1.8 tCO_2/t crude steel average) come from the high temperature reduction of iron ore which today occurs through the oxidation of carbon feedstocks (e.g. coke) [5].

The production of metallic iron requires the chemical reduction of ores. Replacing coke as a reducing agent for the oxide ores with less carbon intensive feedstocks including natural gas, hydrogen (sourced from fossil fuels), or biomass have been investigated [6,7]. However, these methods have limited economic viability or unacceptable secondary environmental consequences and in some cases simply pass the emissions upstream [8].

Significant reduction in CO_2 emissions (>50% of current emissions) is achievable through carbon capture and storage (CCS) [9]. The deployment of CCS technologies within an integrated steel mill is technically feasible and has been the subject of significant research [7,9–11]. Indeed, CCS represents the largest portion of emissions reductions in the International Energy Association (IEA) emission reduction roadmaps for the iron and steel industry [1]. The complexities of integration, the high cost and energy penalty associated with capture from relatively dilute flue gas streams and the uncertainties of geological sequestration, mean that CO_2 avoidance costs for 50% emissions reductions and higher have been estimated in excess of US $74/$tCO_2$ avoided for current best available technologies [9].

An alternative is to electrochemically reduce the iron oxide as is done for other metal oxide ores. This is not currently economically feasible due to the high temperatures (>1500 °C) required for iron ore reduction [12]. Chemical upgrading of iron ore through leaching to facilitate low temperature electrolysis of iron has also been investigated but prohibitively high processing costs have inhibited its development in industry [13,14].

Olefins such as ethylene and propylene represent the largest volume of organic chemicals produced globally. In contrast to iron produced by reduction of oxide ores, the production of olefins requires partial oxidation of hydrocarbon carbon feedstocks. The most common processes require heating alkanes to very high temperatures and 'cracking' them in the presence of steam. Additional chemistry allows the production of a variety of important commodity chemicals including alcohols, aromatics, and a diverse range of high value hydrocarbons [15]. Natural gas and methane hydrates are likely to provide abundant low cost light alkanes as feedstocks for organic chemicals for decades [16,17]. The CO_2 emissions result from the large quantities of energy required for modern olefin processing. Several hundred million tonnes of CO_2 each year are released to produce olefins [16]. Hydrocarbon processing and the chemical industry as a whole account for 17% of industrial CO_2 emissions (5.5% global CO_2 emissions) [2].

Efforts to use light alkanes to produce olefins and aromatics by selective partial oxidation and oxidative coupling of methane (OCM) using limited oxygen have been ongoing [18]. These catalytic processes have been identified as providing the largest potential for greenhouse gas emissions reductions in the IEA chemical industry roadmaps [2]. Despite decades of investigation, fundamental chemical limitations and practical challenges in catalysis remain and there is no evidence an economically competitive process is possible [19–23]. It has not been possible to demonstrate sustained high reaction rates of oxygen

with light alkanes without producing large quantities of carbon oxides.

Partial oxidation of methane and other light alkanes using alternative oxidants such has halogens has been demonstrated and operated in pilot plants [24–26]. Reactions of halogens including chlorine and bromine with methane or other light alkanes generate alkyl-halide intermediates which are readily transformed into olefins and aromatic products. The process technology is an alternative to the conventional steam cracking and dehydrogenation processes. For methane, the methyl-halide intermediate undergoes the same types of chemical transformations as methanol to form olefins (methanol-to-olefins [27]) or aromatics (methanol-to-aromatics [28]). The main challenges to widespread commercialization of the halogen-based processes are the costs of recycling stoichiometric quantities of corrosive hydrogen halides which are used to regenerate the halogen and the thermal management of the exothermic reactions [29,30].

We propose a unique process that couples the reduction of iron ore with the partial oxidation of natural gas alkanes to co-produce iron and organic chemicals. Iron ore is upgraded by reaction with hydrogen chloride and the iron chlorides electro-reduced to the iron product. The oxidized iron chlorides are used for reaction with methane to produce the methyl-chloride intermediates. These are subsequently converted to hydrocarbon chemical products and the hydrogen chloride reused. No CO_2 is produced. The integrated process overcomes the limitations of the conventional iron ore electrolysis and methane partial oxidation processes using halogens through:

- Substitution of the pure halogen for a liquid metal halide ($FeCl_3$) as the oxidising agent to advantageously manage the exothermic heat load;
- Leaching iron ore with the inorganic acid (HCl) generated as a by-product to create a higher-value iron feedstock to an electrolyser (eliminating the major feedstock cost for leaching on the iron side);
- Regeneration of the iron chloride feedstock via the production of reduced iron from electrolysis (eliminating the major regeneration cost of the halogen).

It is generally expected that a price will be placed on atmospheric carbon emissions at some time [31]. This will significantly impact both the iron and chemical industries and may have far reaching economic consequences for infrastructure, construction, transport, advanced manufacturing and consumer products [19]. In this paper we examine the techno-economics of a production process that co-produces iron and hydrocarbon products and makes use of process integration and process intensification for overall efficiency and economic gains. Specifically, we address the following questions: What are the estimated capital and operating costs of the integrated process? What are the sensitivities of the costs to the major process uncertainties? What cost of carbon dioxide (CO_2 price) would be needed for such a process to be economically competitive with present commercial processes?

1.1. Process description

A simplified process flow diagram of the proposed coupled process is shown in Fig. 1. Methane from pre-treated natural gas is supplied to the ferro-chlorination reactor, where the facile reaction of methane with molten ferric chloride to produce ferrous chloride, hydrogen chloride and methyl chloride occurs (Eq. (1)). Chlorination of methane using redox active chlorinated molten salts is expected to reduce the exothermic heat load of the chlorination reaction due to the endothermic Cl^- evolution reaction [32]. The relatively small heat load is managed through absorption into a