

# Fuel saving, carbon dioxide emission avoidance, and syngas production by tri-reforming of flue gases from coal- and gas-fired power stations, and by the carbothermic reduction of iron oxide

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## Abstract

Flue gases from coal, gas, or oil-fired power stations, as well as from several heavy industries, such as the production of iron, lime and cement, are major anthropogenic sources of global CO<sub>2</sub> emissions. The newly proposed process for syngas production based on the tri-reforming of such flue gases with natural gas could be an important route for CO<sub>2</sub> emission avoidance. In addition, by combining the carbothermic reduction of iron oxide with the partial oxidation of the carbon source, an overall thermoneutral process can be designed for the co-production of iron and syngas rich in CO. Water-gas shift (WGS) of CO to H<sub>2</sub> enables the production of useful syngas. The reaction process heat, or the conditions for thermoneutrality, are derived by thermochemical equilibrium calculations. The thermodynamic constraints are determined for the production of syngas suitable for methanol, hydrogen, or ammonia synthesis. The environmental and economic consequences are assessed for large-scale commercial production of these chemical commodities. Preliminary evaluations with natural gas, coke, or coal as carbon source indicate that such combined processes should be economically competitive, as well as promising significant fuel saving and CO<sub>2</sub> emission avoidance. The production of ammonia in the above processes seems particularly attractive, as it consumes the nitrogen in the flue gases.

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## 1. Introduction

Flue gases discharged by fossil fuel burning power stations are major anthropogenic sources of atmospheric greenhouse gases, contributing 47% of the annual world carbon dioxide emissions, which in 1990 amounted to  $5.6 \times 10^6$  ton of carbon [1,2]. In addition, several heavy industries, such as the conventional production of

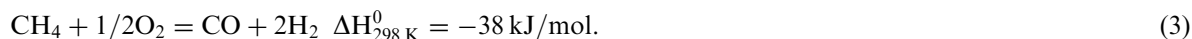
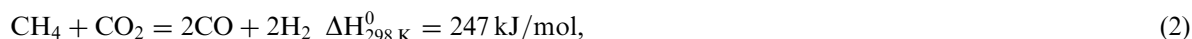
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### Nomenclature

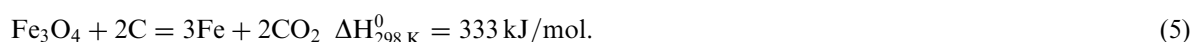
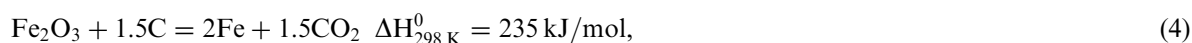
FT	Fischer–Tropsch
$\eta$	exergy efficiency
C(gr)	carbon graphite
DRI	direct reduction iron
HHV	high heating value
MSR	methane-steam reforming
NG	natural gas
WGS	water-gas shift
Ton	metric ton

metals from their ores, of syngas from natural gas, and of lime and cement from limestone, contribute together about 10% to the total annual anthropogenic CO<sub>2</sub> emissions to the atmosphere, derived mostly from the combustion of fossil fuels for high-temperature process heat and from various process reactions [3]. CO<sub>2</sub>-free alternatives to the above technologies are often associated with either environmental or safety concerns (e.g. hydroelectric or nuclear power), or with limitations due to cost or applicability (e.g. solar, wind or biomass power generators). Recently, a new concept of “tri-reforming” was proposed and experimentally demonstrated for the utilization of the power station flue gases for syngas production, without the need for an upstream air separation unit. The high-temperature reaction of the flue gases with natural gas results in the combined H<sub>2</sub>O/CO<sub>2</sub> reforming (Eqs. (1) and (2)) and partial oxidation (Eq. (3)) of methane [4,5]:



In such a combined process, most of the CO<sub>2</sub> content of the flue gases would be consumed by the CO<sub>2</sub> reforming reaction (Eq. (2)). The syngas produced could then be converted to hydrogen, methanol (a precursor for polymers), dimethyl carbonate (an automobile fuel additive and intermediate to polycarbonates), dimethyl ether (a fuel additive and aerosol propellant), or hydrocarbons, hence providing a long-term or temporary sink for carbon [2a,3]. Another important target product could be ammonia, the production of which involves about 3% of the world energy consumption [6]. The purpose of the present work is to define the thermodynamic constraints for applying the tri-reforming of power station flue gases and the carbothermic reduction of iron oxide to the production of syngas suitable for ammonia, hydrogen, and methanol syntheses, to determine the extent of CO<sub>2</sub> emission avoidance and fuel saving thus achieved, and to assess the economic consequences of the large-scale industrial production of these chemical commodities. Due to the uncertainties inherent in the proposed new technology, it is not justified to provide more detailed economic evaluations. The analysis follows a similar approach previously applied to determine the mitigation of CO<sub>2</sub> emissions from the reduction of metal oxides to metals, or the calcination of limestone to lime, by combining each of these processes with the reforming/partial oxidation of natural gas, thus co-producing syngas and metals or lime. Such processes were shown experimentally to proceed without added catalysts [7–9].

The production of iron from its ores involves energy-intensive carbothermic processes that contribute 5.4% to the anthropogenic worldwide CO<sub>2</sub> emissions [4,5]. The net reactions can be represented by



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