Available online at www.sciencedirect.com
SCIENCE DIRECT®
Catalysis Today 115 (2006) 170–178
CATALYSIS TODAY
www.elsevier.com/locate/cattod

Thermoneutral tri-reforming of flue gases from coal- and gas-fired power stations

M. Halmann [a,*], A. Steinfeld [b,c]

[a] Weizmann Institute of Science, Department of Environmental Sciences and Energy Research, Rehovot 76100, Israel
[b] ETH-Swiss Federal Institute of Technology Zurich, Department of Mechanical and Process Engineering, 8092 Zurich, Switzerland
[c] Solar Technology Laboratory, Paul Scherrer Institute, 5232 Villigen, Switzerland

Abstract

The treatment of flue gases from fossil fuel fired power stations by tri-reforming with natural gas or by coal gasification could become an attractive approach for converting the CO_2, H_2O, O_2, and N_2 contained in these flue gases via syngas processing into useful products, such as methanol, hydrogen, ammonia, or urea. The present study determines the constraints for achieving such thermochemical reactions under conditions of thermoneutrality, by reacting the flue gases with water, air, and natural gas or coal at 1000–1200 K. The implications of such reactions are examined in terms of CO_2 emission avoidance, fuel saving, economic viability, and exergy efficiency.

Keywords: Methanol; Carbon dioxide; Coal; Gasification; Exergy; Flue gases; Fuel saving; Greenhouse gas; Hydrogen; Methane; Methanol; Natural gas; Power stations; Syngas; Thermoneutral; Reforming; Urea

1. Introduction

Fossil fuel based power stations contribute about 47% to the world CO_2 emissions [1]. There exists an urgent need to mitigate these emissions, preferably by their conversion to useful products [2]. One attractive approach is the tri-reforming of flue gases by reaction with natural gas in the presence of catalysts, in which the CO_2, H_2O, and O_2 contained in the flue gases react with added CH_4 to form syngas, a reaction which was experimentally confirmed using a variety of catalysts [3–5]. Syngas is a versatile intermediate to important products such as methanol, hydrogen, and ammonia [6]. The addition of CH_4 is required to realize the CO_2-reforming reaction,

$$CH_4 + CO_2 = 2CO + 2H_2, \quad \Delta H^\circ_{298\,K} = 247\,kJ/mol \tag{1}$$

The addition of H_2O is necessary to promote both the steam-reforming and the water–gas shift reactions,

$$CH_4 + H_2O = CO + 3H_2, \quad \Delta H^\circ_{298\,K} = 206\,kJ/mol \tag{2}$$

$$CO + H_2O = CO_2 + H_2, \quad \Delta H^\circ_{298\,K} = -41.5\,kJ/mol \tag{3}$$

The addition of air is needed to provide sufficient O_2 for the exothermic partial oxidation of CH_4 (Eq. (4)),

$$CH_4 + \frac{1}{2}O_2 = CO + 2H_2, \quad \Delta H^\circ_{298\,K} = -35.7\,kJ/mol \tag{4}$$

in order to compensate for the endothermic reforming reactions (Eqs. (1) and (2)), thus achieving an overall thermoneutral reaction. Instead of natural gas, coal, biomass, or other carbonaceous solid materials may be used to perform the reduction of CO_2. This is actually the long-known process of coal gasification. At 1300 K, the gasification proceeds at reasonable rates in the absence of added catalysts—possibly the catalysis is provided by minerals contained in the coal ash. It depends mainly on the strongly exothermic oxidation of carbon,

$$C + O_2 = CO_2, \quad \Delta H^\circ_{298\,K} = -393.5\,kJ/mol \tag{5}$$

combined with the endothermic C-gasification reactions,

$$C + CO_2 = 2CO, \quad \Delta H^\circ_{298\,K} = 172.4\,kJ/mol \tag{6}$$

Abbreviations: HHV, high heating value; LH_2, liquid hydrogen; MSR, methane-steam reforming; NG, natural gas; Ton, metric ton; WGS, water–gas shift

* Corresponding author. Tel.: +972 89 344 124; fax: +972 89 344 124.
E-mail address: m.halmann@weizmann.ac.il (M. Halmann).

0920-5861/$ – see front matter © 2006 Elsevier B.V. All rights reserved.
doi:10.1016/j.cattod.2006.02.064

$$C + H_2O = CO + H_2, \quad \Delta H^{\circ}_{298\,K} = 131.3\,kJ/mol \tag{7}$$

In the present work, the thermochemical constraints have been determined for achieving these tri-reforming and gasification reactions under conditions of thermoneutrality, in the temperature range of 1000–1200 K. Three cases have been studied: (a) the tri-reforming of flue gases from coal-fired power stations by natural gas; (b) the tri-reforming of flue gases from gas-fired power stations by natural gas; (c) the treatment of flue gases from coal-fired power stations by coal gasification. In cases (a) and (b), the reactant mixtures are chosen to result in a H_2/CO molar ratio suitable for methanol synthesis. For economy, air is added instead of pure oxygen. The advantage of this is in avoiding the cost of oxygen separation from air, but this obviously results in increased reactor volumes. Also, it is assumed that the power station flue gases had been pre-treated for removal of SO_X and NO_X contaminants, and that fly ash and other dust had been removed by filters or electrostatic precipitators. Thermochemical equilibrium calculations were performed using the NASA CET85 program code [7]. Thermoneutrality was determined using the data in the NIST Chemistry web-book [8]. Carbon was taken as representative of coal for the thermochemical calculations. The incoming added reactants are assumed to have been preheated by heat exchange with the outgoing gas stream from the tri-reforming or coal gasification reactor. These reactions proceed with adequate rates in the temperature range of 1000–1200 K only in the presence of catalysts [5], but have been demonstrated to proceed without added catalysts at above 1500 K in a solar furnace [9,10]. The presence of large concentrations of N_2 in the reactant mixtures obviously affects the rates of the reforming reactions. However, the partial oxidation of methane by air to syngas had been reported with CH_4–O_2–N_2 (2:1:4) using lanthanide ruthenium oxide catalysts, achieving almost complete conversion to CO and H_2 at 1050 K and atmospheric pressure [11]. The H_2O/CO_2 mixed reforming of CH_4 was compared with the partial oxidation of CH_4 over Mg-supported noble metals using gas feeds of either CH_4–O_2–N_2 (3.6:1.8:7.2) or CH_4–H_2O–CO_2–N_2 (2.7:1.8:0.9:7.2) [12]. High conversion rates were achieved by passing CH_4–CO_2–N_2 (10:10:80) over a Rh-modified catalyst at 873 K [13]. Therefore, the presence of N_2 should not be an obstacle to the tri-reforming reaction. A series of Ni catalysts have also been tested for the tri-reforming of flue gases, among which Ni/MgO and Ni/MgO/CeZrO were found to be very effective for the conversion of CO_2 [5]. Syngas containing nitrogen is particularly useful for ammonia synthesis, and air–natural gas mixtures are used in industrial ammonia production.

The purpose of this study is to clarify to what extent the treatment of power station flue gases by tri-reforming or coal gasification may mitigate CO_2 emissions, with the costs substantially offset by the production of useful products, but also to show the limits raised by the ability of the markets to absorb the huge amounts of the products thus formed, as well as the limits given by the size of the currently proved reserves of natural gas or coal. The selection of thermoneutral reaction conditions was made to achieve tri-reforming or coal gasification of flue gases with or without very small external heat supply.

2. Coal-fired power stations: tri-reforming with natural gas

Flue gases released from coal-fired burners of power stations are composed mainly of CO_2, H_2O, O_2, and N_2, in the average ratio of 13:9:4:74 parts by volume [3]. Adding to this CH_4, H_2O, and air (20, 11, and 24 parts) results in a mixture of $13CO_2$–$20H_2O$–$9O_2$–$20CH_4$–$93N_2$. The thermochemical equilibrium composition of the above initial mixture as a function of temperature is shown in Fig. 1. At 1000 K and 1 atm, the overall reaction can be represented by the equation,

$$\begin{aligned} 13CO_2 + 20H_2O + 9O_2 + 20CH_4 + 93N_2 &= 12.79CO_2 \\ &+ 18.30H_2O + 20.12CO + 41.49H_2 + 0.09CH_4 + 93N_2 \end{aligned} \tag{8}$$

in which the product H_2/CO molar ratio equals 2.06, suitable for methanol and Fischer-Tropsch syntheses. The endothermicity of the reaction at 1000 K described in Eq. (8) is only 3.0 kJ per mol CO_2 in the original flue gas.

2.1. Methanol production

The CO_2 emissions derived from a conventional 45%-efficient 500 MW coal-fired power plant are reported to be 0.75 ton CO_2/MWh [14]. Thus, the annual emissions are 3.29×10^6 ton CO_2 (or 74.7×10^9 mol). By the tri-reforming reaction, according to Eq. (8), 98.4% of the flue-gas CO_2, or 3.24×10^6 ton, would be released. Also, according to Eq. (8), the molar ratio of CO produced in the syngas by the tri-reforming reaction, relative to the CO_2 content of the original flue-gas would be 1.55. Assuming 90% overall yield in the conversion of the CO in the syngas into methanol, the annual production of methanol would be 104.2×10^9 mol, or 3.33×10^6 ton methanol. This production represents 8.5% of the current worldwide capacity for methanol [15a].

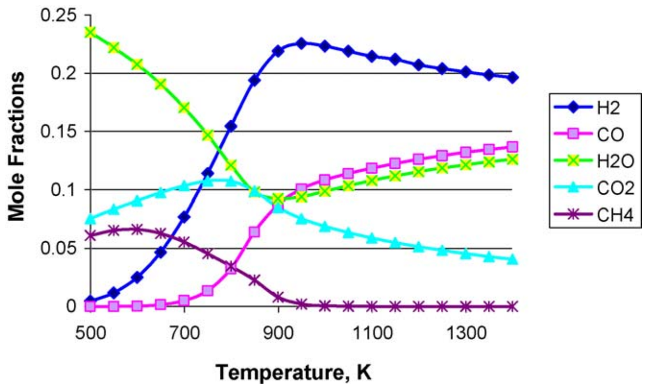

Fig. 1. Mole fractions vs. temperature for flue-gas from coal-fired burners + added CH_4 + H_2O + air. Initial CO_2–H_2O–O_2–N_2–CH_4 = 13:20:9:93:20.

2.1.1. CO_2 emission avoidance by methanol production

The conventional methanol production via MSR results in the release of 0.837 ton CO_2/ton methanol [16], or of 2.79×10^6 ton CO_2 for the production of 3.33×10^6 ton methanol. Thus, the total CO_2 emissions from the untreated flue-gas and from the conventional methanol production would be 6.08×10^6 ton CO_2/year. The overall CO_2 emission avoidance by applying the tri-reforming reaction followed by methanol synthesis, relative to the conventional processes, would be 46.7%.

2.1.2. Fuel saving in methanol production

For the annual production of 3.33×10^6 ton methanol by tri-reforming of the flue gas from the above coal-fired burner, the required amount of NG according to Eq. (8) would be 114.9×10^6 kmol CH_4, or 102.4×10^6 GJ (based on its HHV of 0.891 GJ/kmol). For comparison, the total fuel consumption for methanol synthesis via conventional MSR is 44.5 GJ/ton methanol [18a], or 148.2×10^6 GJ for producing the same amount of methanol. Therefore, the fuel saving by tri-reforming followed by methanol production, relative to the conventional production of methanol, would be 30.9%.

2.1.3. Economics of methanol production

Considering the very high cost of natural gas, this is usually the largest cost item in syngas production. The present very preliminary estimate is unable to provide details on the other costs (capital, operation and maintenance). The production of 3.33×10^6 ton methanol by tri-reforming of the flue gas from the above coal-fired burner would require 102.4×10^6 GJ (or 96.9×10^6 MMBTU) of NG. At the current (April 2005) NG price of US$ 6.73/MMBTU [19], the fuel cost would be US$ 652×10^6, or US$ 196/ton methanol. Adding to this an estimated US$ 30/ton for the conversion of NG to methanol, the total expected cost would be US$ 226/ton methanol. The current (May 2005) market price is US$ 316/ton methanol [15b].

2.2. Hydrogen production

The molar ratio of syngas in the tri-reformed flue-gas relative to the CO_2 in the original flue-gas is $(H_2 + CO)/CO_2 = 4.74$ (see Eq. (8)). Assuming 90% yield in the water–gas shift of CO to H_2, the resulting molar ratio H_2/CO_2 would be 4.58. For the 45%-efficient 500 MW coal-fired power plant, emitting annually 3.29×10^6 ton CO_2 (or 74.7×10^9 mol) CO_2, the expected H_2 production is 342×10^9 mol, or 0.685×10^6 ton H_2. Such an amount would add 0.15% to the current annual worldwide production of 446×10^6 ton H_2 [20].

2.2.1. CO_2 emission avoidance in hydrogen production

Hydrogen production by conventional MSR, not including the conversion to liquid hydrogen, was reported to cause the emission of 9.21 ton CO_2/ton H_2 [17]. Thus, the production of 0.685×10^6 ton H_2 would result in the emission of 6.31×10^6 ton CO_2. The total CO_2 emission from the conventional H_2 production and from the untreated flue-gas would be 9.60×10^6 ton CO_2. From Eq. (8), the molar ratio of $(CO + CO_2)$ in the treated flue-gas relative to the CO_2 in the original flue-gas is 2.53. Therefore, the CO_2 emission from the 500 MW coal-fired burner after tri-reforming and water–gas shift would be 189.1×10^9 mol, or 8.32×10^6 ton CO_2. The CO_2 emission avoidance by tri-reforming followed by H_2 production, relative to the conventional separate processes, would be 13.3%.

2.2.2. Fuel saving in hydrogen production

For producing 0.685×10^6 ton H_2 by tri-reforming, the total required amount of NG would be 102.4×10^6 GJ (see Section 2.1.2). Conventional H_2 production by MSR requires 602 GJ/ton H_2 [2b], or 412×10^6 GJ for producing the same amount of H_2. The fuel saving by tri-reforming followed by H_2 production would be 75.2%.

2.2.3. Economics of hydrogen production

The annual production of 0.685×10^6 ton H_2 by tri-reforming of flue gas from the 500 MW coal-fired boiler would require a total input of 102.4×10^6 GJ (or 96.9×10^6 MMBTU). At the NG price of US$ 6.73/MMBTU, the fuel cost would be US$ 652×10^6, or US$ 0.95/kg H_2. This cost is significantly below the reported price of US$ 2.40/kg of gaseous H_2, or US$ 4–5/kg of LH_2 [20].

2.3. Ammonia and urea production

The hydrogen annually produced as described in Section 2, i.e. 0.685×10^6 ton (or 342×10^9 mol), could be converted to ammonia. In this case only partial separation of H_2 from N_2 would be necessary to remove excess N_2 and achieve a molar ratio $H_2/N_2 = 3$. Assuming 90% yield in the ammonia synthesis, the expected annual production would be 205×10^9 mol NH_3, or 3.49×10^6 ton. Such an amount represents 2.3% of the current (2005) world capacity for ammonia. Modern ammonia plants are being designed to produce 1.1×10^6 ton NH_3/year or more, and are commonly integrated with the production of urea (mainly for slow release fertilizers), thus consuming a large part of the CO_2 formed in the process [21]. Industrial urea production occurs, via an ammonium carbamate intermediate, according to an overall exothermic reaction [2c,18b],

$$2NH_3 + CO_2 = NH_4{-}OCONH_2 = H_2NCONH_2 + H_2O \qquad (9)$$

According to Eq. (9), 205×10^9 mol NH_3 would bind 102.5×10^9 mol, or 4.51×10^6 ton CO_2, and, assuming 100% yield, would produce annually 102.5×10^9 mol, or 6.16×10^6 ton urea. This represents 5.1% of the (2005) world urea demand of 120×10^6 tons. The predicted annual growth in demand for urea is about 3%, while the predicted growth in capacity is 1.5% [18b,21]. The expected demand thus exceeds the capacity.

2.3.1. CO_2 emission avoidance in ammonia and urea production

The conventional production of ammonia by MSR and WGS requires 35–41 GJ of NG/ton NH_3, resulting in the release of 2.2 ton CO_2/ton NH_3 [18c,21]. Therefore, the conventional production of 3.49×10^6 ton NH_3 would require about 136.0×10^6 GJ of NG, and would release 7.68×10^6 ton CO_2. The total CO_2 emissions from the untreated flue gas and from the conventional NH_3 production would be 10.97×10^6 ton/year. The predicted CO_2 emission avoidance would be 24.2%. Considering the part of ammonia converted to urea, the overall CO_2 emissions, both from the conventional and the tri-reforming processes, would be much smaller. The net emission from a 500 MW coal-fired burner, after tri-reforming, WGS, ammonia synthesis, and urea processing would be 3.81×10^6 ton CO_2. Production of the same amount of urea via conventional ammonia synthesis, along with the untreated flue gas, would release 6.46×10^6 ton CO_2. The emission avoidance by tri-reforming for urea synthesis would be 41%.

2.3.2. Fuel saving in ammonia and urea production

The production of 3.49×10^6 ton NH_3 via tri-reforming would require 102.4×10^6 GJ of NG, as for the production of methanol or hydrogen (see Section 2). Since the conventional production of the same amount of ammonia by MSR would require 136.0×10^6 GJ of NG, the fuel saving by tri-reforming would be 24.7%. The same extent of fuel saving can be expected for the production of urea via flue gas tri-reforming.

2.3.3. Economics of ammonia production

The production of 3.49×10^6 ton NH_3 via tri-reforming require 102.4×10^6 GJ of NG (or 96.9×10^6 MMBTU). At a NG price of US$ 6.73/MMBTU, the fuel cost for production of this amount of ammonia would be US$ 652×10^6, or US$ 187/ton NH_3. Adding US$ 33/ton for the conversion of NG to ammonia, the total production cost would be US$ 220/ton NH_3, which is below the current market price of about US$ 290/ton NH_3 [21].

3. Gas-fired power stations: tri-reforming with natural gas

The average composition of flue gas from NG-fired burners is CO_2–H_2O–O_2–N_2 (9:19:2.5:69.5 parts by volume) [3]. Adding NG and air (15 and 19 parts, respectively), the condition of thermoneutrality is met at 1100 K and 1 atm pressure by the reaction,

$$9CO_2 + 19H_2O + 6.8O_2 + 15CH_4 + 85.6N_2 = 8.71CO_2 + 17.89H_2O + 15.29CO + 31.1H_2 + 0.003CH_4 + 85.6N_2 \quad (10)$$

At this temperature, the ratio H_2/CO is 2.03, as required for methanol or Fischer-Tropsch syntheses. The endothermicity is 3.2 kJ per mol of CO_2 in the original flue gas. The thermochemical equilibrium compositions at 1 atm pressure in the temperature range 500–1400 K is presented in Fig. 2.

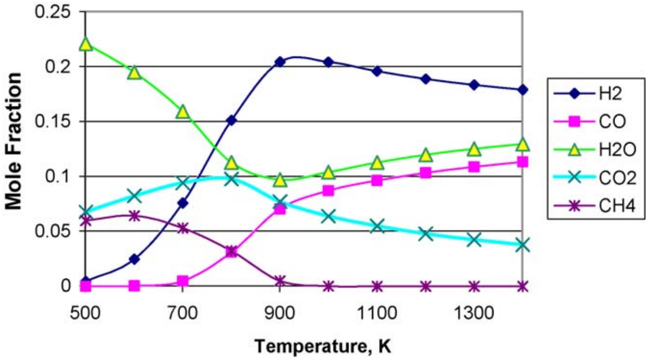

Fig. 2. Mole fractions vs. temperature for flue-gas from gas-fired burners + added CH_4 + air. Initial CO_2–H_2O–O_2–N_2–CH_4 = 9:19:6.8:85.6:15.

3.1. Methanol production

CO_2 emissions from a modern 49%-efficient 400 MW NG-fired power plant are 0.42 ton CO_2/MWh [14], totaling 1.47×10^6 ton CO_2/year (or 33.4×10^9 mol). According to Eq. (10), 96.8% of the original flue gas CO_2, or 1.42×10^6 ton, would be released by the tri-reforming reaction. The molar ratio of CO formed in the tri-reforming reaction to the CO_2 in the original flue gas would be 1.70. Assuming 90% overall yield in the conversion of CO into methanol, the annual production would be 51.1×10^9 mol, or 1.635×10^6 ton methanol. This amount represents 4.15% of the current world capacity for methanol [15a].

3.1.1. CO_2 emission avoidance by methanol production

The conventional production of 1.635×10^6 ton methanol would result in the release of 1.37×10^6 ton CO_2 (see Section 2). The total CO_2 emissions from the untreated flue gas and from the conventional methanol production would be 2.84×10^6 ton CO_2/year. Thus, the CO_2 emission avoidance by tri-reforming of the flue gas followed by methanol synthesis, relative to the conventional processes, would be 50.0%.

3.1.2. Fuel saving in methanol production

For the production of 1.635×10^6 ton methanol/year by tri-reforming the flue gas from the above gas-fired burner, the required amount of NG according to Eq. (10) would be 55.7×10^6 kmol CH_4, or 49.6×10^6 GJ (based on its HHV of 0.891 GJ/kmol). By conventional methanol synthesis, the total fuel consumption would be 72.8×10^6 GJ (see Section 2). Thus, the predicted fuel saving by tri-reforming followed by methanol synthesis is 31.8%.

3.1.3. Economics of methanol production

The production of 1.635×10^6 ton methanol by tri-reforming of flue gas from the gas-fired burner would require 49.6×10^6 GJ, or 47.0×10^6 MMBTU. At the NG price of US$ 6.73/MMBTU [19], the fuel cost would be US$ 316×10^6, or US$ 193/ton methanol. Adding US$ 30/ton for the conversion of NG to methanol, the total expected cost would be US$ 223/ton, significantly below the current market price of US$ 316/ton methanol [15b].

3.2. Hydrogen production

According to Eq. (10), the molar ratio of syngas in the tri-reformed flue gas relative to CO_2 in the original flue gas is $(H_2 + CO)/CO_2 = 5.15$. Assuming 90% yield in the WGS of CO to H_2, the resulting H_2/CO_2 ratio would be 4.98. For the 49%-efficient 400 MW NG-fired power plant emitting annually 33.4×10^9 mol CO_2, the predicted H_2 production is 166.5 $\times 10^9$ mol, or 0.33×10^6 ton H_2. This amount represents 0.075% of the current world production of H_2 [20].

3.2.1. CO_2 emission avoidance by hydrogen production

The conventional production of 0.33×10^6 ton H_2 would result in the release of 3.04×10^6 ton CO_2. The total CO_2 emission from conventional H_2 production and from the untreated flue gas would be 4.51×10^6 ton CO_2/year. According to Eq. (10), the molar ratio of $(CO + CO_2)$ in the tri-reformed flue gas relative to the CO_2 in the original flue gas is 2.67. Thus, the total CO_2 emission after the tri-reforming and WGS is 3.92×10^6 ton/year. The CO_2 emission avoidance by tri-reforming followed by H_2 production, relative to the separate production of H_2, would be 13.1%.

3.2.2. Fuel saving in hydrogen production

For the production of 0.33×10^6 ton H_2 by tri-reforming, the required amount of NG would be 49.6×10^6 GJ (see Section 3.1.2). In the conventional production of the same amount of H_2, the total fuel consumption would be 199×10^6 GJ (see Section 2). The fuel saving by tri-reforming followed by H_2 production would then be 74.9%.

3.2.3. Economics of hydrogen production

The production of 0.33×10^6 ton H_2 would require 49.6×10^6 GJ (or 46.9×10^6 MMBTU) of NG. At a NG price of US\$ 6.73/MMBTU, the annual fuel cost would be US\$ 316×10^6, or US\$ 0.96/kg of gaseous H_2. This cost is lower than the reported price of US\$ 2.40/kg of gaseous H_2, or US\$ 4–5/kg of LH_2 [20].

3.3. Ammonia and urea production

From the 49%-efficient 400 MW gas-fired power plant, tri-reforming of the flue gas is expected to produce annually 0.33×10^6 ton H_2 (or 166.5×10^9 mol), while utilizing 49.6×10^6 GJ of NG, and releasing 3.92×10^6 ton CO_2 (see Section 3.2). Assuming 90% yield, the amount of NH_3 which could be produced from this H_2 would be 99.9×10^9 mol, or 1.70×10^6 ton NH_3, representing 1.1% of the current world capacity for ammonia [21]. If this ammonia is converted to urea, the annual production would be 49.95×10^9 mol, or 3.0×10^6 ton urea (2.5% of the world demand), while binding 49.95×10^9 mol, or 2.20×10^6 ton CO_2.

3.3.1. CO_2 emission avoidance and fuel saving in ammonia production

The conventional production of 1.70×10^6 ton NH_3 by MSR would require an input of 66.3×10^6 GJ of NG, and would release 3.74×10^6 ton CO_2. The sum of CO_2 emissions from the untreated flue gas and from the conventional ammonia production would be 5.21×10^6 ton CO_2. The CO_2 emission avoidance by tri-reforming relative to the conventional processes would be 24.8%. The corresponding fuel saving would be 25.2%. After tri-reforming of flue gas from the 400 MW NG-fired burner, WGS, ammonia synthesis, and urea processing, the net emissions would be 1.72×10^6 ton CO_2. The sum of emissions from the untreated flue gas and from urea produced via conventional ammonia synthesis would be 3.01×10^6 ton CO_2. The CO_2 emission avoidance by tri-reforming relative to the conventional processes would then be 42.9%.

3.3.2. Economics of ammonia production

The production of 1.70×10^6 ton NH_3 via tri-reforming require 49.6×10^6 GJ of NG (or 47.0×10^6 MMBTU). At a NG price of US\$ 6.73/MMBTU, the fuel cost for production of this amount of ammonia would be US\$ 316×10^6, or US\$ 186/ton NH_3. Adding US\$ 33/ton for the conversion of NG to ammonia, the total production cost would be US\$ 219/ton NH_3, while the current market price is about US\$ 290/ton NH_3 [21].

4. Coal-fired power stations: flue gas treatment by coal gasification

Adding to the flue gas of a coal-fired power station with an average composition (in moles) $13CO_2–9H_2O–4O_2–74N_2$ a mixture of coal, steam, and air in the ratio 40:11:33.2 will result in a mixture of $13CO_2–20H_2O–11O_2–40C–100.2N_2$. Taking carbon instead of coal, the thermochemical equilibrium composition of this initial mixture at 1 atm pressure as a function of temperature is shown in Fig. 3. At 1200 K and 1 atm, the overall reaction is represented by the equation,

$$13CO_2 + 20H_2O + 11O_2 + 40C + 100.2N_2 = 10.12CO_2 + 4.88H_2O + 42.9CO + 15.1H_2 + 100.2N_2 \quad (11)$$

The reaction described in Eq. (11) is slightly exothermic: $\Delta H = -4.2$ kJ per mol of CO_2 in the original flue gas. The resulting H_2/CO molar ratio is only 0.35, which is too low for methanol synthesis.

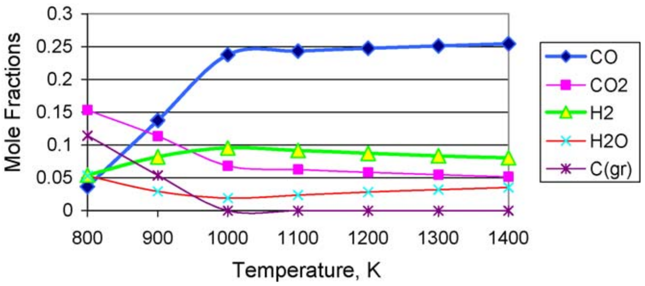

Fig. 3. Mole fractions vs. temperature for flue-gas from coal-fired burners + added $C + H_2O$ + air. Initial $CO_2–H_2O–O_2–N_2–C = 13:20:11:100.2:40$.

4.1. Methanol production

Assume again the case of the flue gas from a 45%-efficient 500 MW coal-fired power plant emitting annually 3.29×10^6 ton CO_2 (or 74.7×10^9 mol). By coal gasification, according to Eq. (11), 77.8% of the flue gas CO_2, or 2.56×10^6 ton, would be released. The water–gas shift reaction needed to bring the H_2/CO in the syngas to the molar ratio 2 would change the CO_2–CO–H_2 ratio of Eq. (11) to 33.67:19.33:38.67. The molar ratio of CO thus formed in the syngas relative to the CO_2 content of the original flue gas would be 1.49. Assuming 90% overall yield in the conversion of this CO into methanol, the annual production would be 100.2×10^9 mol, or 3.21×10^6 ton methanol. This represents 8.1% of the current world capacity for methanol.

4.1.1. CO_2 emission excess or avoidance by methanol production

The total amount of CO_2 released annually from the above power plant, both by the tri-reforming and by the water–gas shift reaction, would be 193.5×10^9 mol, or 8.51×10^6 ton CO_2. The CO_2 emission by the conventional production via MSR of 3.21×10^6 ton methanol would amount to 2.68×10^6 ton CO_2. Therefore, the total CO_2 emissions from the untreated flue gas and from the conventional methanol production would be 5.97×10^6 ton CO_2/year. The *excess* of CO_2 emission in methanol production from tri-reformed flue gas relative to the conventional process plus untreated flue gas would be 29.8%. A more valid comparison would be with conventional syngas production by coal gasification, followed by methanol production. Such a process would release at least twice the amount of CO_2 emitted by MSR, or at least 5.36×10^6 ton [17]. Including the emission from the untreated flue gas this would amount to 8.65×10^6 ton CO_2. In this case, the avoidance of CO_2 emission, relative to the conventional process plus untreated flue gas, would be 1.6%.

4.1.2. Fuel saving in methanol production

The annual production of 3.21×10^6 ton methanol by coal gasification with the flue gas from the above coal-fired burner would require 229.8×10^9 mol (229.8×10^6 kmol), or 2.76×10^6 ton coal (see Eq. (11)). Taking as the HHV of coal the value for graphite, i.e. 0.3935 GJ/kmol, the fuel input of the flue gas treatment would be 90.4×10^6 GJ (or 85.5×10^6 MMBTU). The conventional production of the same amount of methanol via MSR would require 142.8×10^6 GJ [18a–c]. The fuel saving, relative to the conventional production of methanol, is 36.7%.

4.1.3. Economics of methanol production

The production of 3.21×10^6 ton methanol from the above flue gas by coal gasification would require 2.76×10^6 ton coal. At an average coal price (in Australia, January 2005) of US$ 54.79/ton [22], the fuel cost would be US$ 151.2×10^6, or US$ 47.11/ton methanol. Adding to this US$ 30/ton for the conversion of syngas to methanol, the total estimated cost would be only US$ 77/ton methanol, much below the current market price of US$ 316/ton methanol [15b].

4.2. Hydrogen production

From the flue gas of a 45%-efficient 500 MW coal-fired power plant, emitting annually 3.29×10^6 ton CO_2 (or 74.7×10^9 mol), coal gasification according to Eq. (11) (assuming 90% yield in the water–gas shift of CO to H_2) would result in the production of 308.6×10^9 mol, or 0.617×10^6 ton H_2, which represents 0.14% of the current world production.

4.2.1. CO_2 emission excess or avoidance by hydrogen production

The conventional production of 0.617×10^6 ton H_2 by MSR would result in the emission of 5.68×10^6 ton CO_2. The total emission from the conventional H_2 production and from the untreated flue gas would be 8.97×10^6 ton CO_2. From Eq. (11), the total CO_2 emission after coal gasification and water–gas shift would be 304.7×10^9 mol, or 13.41×10^6 ton CO_2. The *excess* of CO_2 emission by tri-reforming followed by H_2 production, relative to the conventional processes would be 33.1%. If coal gasification is used for the conventional production of the above amount of H_2, the emission of CO_2 would be twice as large, or 11.36×10^6 ton, and together with the untreated flue gas would come to 14.65×10^6 ton. In this case, the extent of CO_2 emission avoidance would be 8.5%.

4.2.2. Fuel saving and economics in hydrogen production

For producing 0.617×10^6 ton H_2 from flue gas by coal gasification, the fuel requirement would be 90.4×10^6 GJ, or 2.76×10^6 ton coal. The conventional production of the same amount of H_2 by MSR would require 371.4×10^6 GJ. The fuel saving in H_2 production by flue gas treatment through coal gasification would be 75.7%. The fuel cost would be only US$ 151.2×10^6, or US$ 0.25/kg H_2, which is significantly lower than the reported price of US$ 2.40/kg of gaseous H_2 [20].

4.3. Ammonia and urea production

Assuming 90% yield in the ammonia synthesis from the flue gas of the 500 MW coal-fired power plant, the expected annual production would be 185.2×10^9 mol, or 3.15×10^6 ton NH_3, which represents 2.0% of the current world capacity. If this ammonia would be converted to urea, it would result in the production of 92.6×10^9 mol, or 5.56×10^6 ton urea (4.6% of the world demand), while binding 92.6×10^9 mol, or 4.07×10^6 ton CO_2, and emitting 9.34×10^6 ton CO_2.

4.3.1. CO_2 emission excess or avoidance and fuel saving by ammonia and urea production

The conventional production by MSR of 3.15×10^6 ton NH_3 would require an input of 122.9×10^6 GJ, and would release 6.93×10^6 ton CO_2. The total emissions from the untreated flue gas and from the conventional NH_3 production would be 10.22×10^6 ton CO_2. The total CO_2 emission after flue gas coal gasification and WGS would be 13.4×10^6 ton CO_2 (see Section 4.2). The emission *excess* by coal gasification relative to the conventional processes would be 23.7%. The fuel saving by flue gas coal gasification versus the conventional process by MSR would be 26.4%.

If coal gasification is used for the conventional production of syngas for ammonia, the energy use would be 165.9 GJ/ton NH_3, and the emission would be 16.7 ton CO_2/ton NH_3, amounting to 522.6×10^6 GJ and 52.61×10^6 ton CO_2 for the above production of NH_3 [21]. Along with the untreated flue gas, the total emissions would be 55.90×10^6 ton CO_2. In this case, the flue gas coal gasification would result in a fuel saving of 82.7% and an emission avoidance of 76.0% relative to the conventional production of ammonia by coal gasification.

The total CO_2 emission from the conventional production of 5.56×10^6 ton urea via MSR, together with that of the untreated flue gas, would be 6.15×10^6 ton CO_2. The expected *excess* of CO_2 emission for urea production by coal gasification of flue gases vs. the conventional process would be 34.2%.

4.3.2. *Economics of ammonia production*

The production of 3.15×10^6 ton NH_3 by flue gas coal gasification would require 2.76×10^6 ton coal (see Section 4.2), which at a coal price of US\$ 54.79/ton would amount to US\$ 151.2×10^6, or US\$ 48/ton NH_3. Adding US\$ 33/ton for the conversion of syngas to ammonia [21], the total production cost would be US\$ 81/ton NH_3, which is significantly lower than the current market price of about US\$ 290/ton NH_3.

5. Exergy efficiency

Exergy, also called thermodynamic availability, represents the theoretical optimum work that can be performed as a result of the change of the state of a system to that of an equilibrium state [23]. The exergy efficiency η exergy is here defined by the ratio of the theoretical maximum work output that can be extracted from the products (i.e., the ΔG of their complete combustion) to the heats of combustion (HHV) of the reactants, all calculated at 298 K. Values of ΔG for the full oxidation of H_2(g) to H_2O(l), of CO(g) to CO_2(g), of CH_3OH(l) to CO_2(g) and $2H_2O$(l), and of NH_3(g) to $0.5N_2$(g) and $1.5H_2O$(l) are 237, 257, 706, and 340 kJ mol^{-1}, respectively. The HHV of CH_4 and C(graphite) are 890.8 and 393.5 kJ mol^{-1}, respectively. The exergy efficiencies thus obtained for the production of methanol, hydrogen, and ammonia by tri-reforming of flue gases according to Eqs. (8), (10) and (11) are all in the range of 70–78%.

6. Discussion and conclusions

Table 1 summarizes the estimated CO_2 emission avoidance or excess, fuel saving, exergy efficiency, and % of world capacity for products obtained by flue gas treatment with either tri-reforming by natural gas, or by coal gasification. The predictions of CO_2 emission avoidance are particularly large for methanol and urea production from tri-reformed flue gases from both coal- and gas-fired power stations, amounting to 47 and 50% for methanol, and to 41 and 43% for urea, respectively. Very high fuel savings, of the order of 75%, are estimated for hydrogen production from tri-reformed flue gases from both coal- and gas-fired power plants. Preliminary evaluations indicate favorable economics, particularly for the flue gas treatment by coal gasification, however at the cost of relatively high CO_2 emissions.

In order to appreciate the large amounts of NG consumed in the tri-reforming reaction, it is worthwhile to consider the fraction of the world resources of NG required. The process (as described in Section 2.1) on the flue-gases from a 500 MW

Table 1
Predicted CO_2 emission avoidance or excess, fuel saving, and exergy efficiency, for products obtained by flue-gas treatment with either tri-reforming by natural gas, or by coal gasification

Flue-gas treatment	Product	% CO_2 emission avoidance	% Fuel saving	% Exergy efficiency	% World capacity
Coal					
Tri-reforming[a]	Methanol	46.7	30.9	71.7	8.5
Tri-reforming[a]	Hydrogen	13.3	75.2	73.8	0.15
Tri-reforming[a]	Ammonia	24.2	24.7	70.5	2.3
Tri-reforming[a]	Urea	41.0			5.1
Natural gas					
Tri-reforming[a]	Methanol	50.0	31.8	72.7	4.2
Tri-reforming[a]	Hydrogen	13.1	74.9	74.1	0.075
Tri-reforming[a]	Ammonia	24.8	25.2	70.8	1.1
Tri-reforming[a]	Urea	42.9			2.5
Coal					
Coal gasification[a]	Methanol	−29.8	36.7	78.0	8.1
Coal gasification[b]		1.6			
Coal gasification[a]	Hydrogen	−33.1	75.7	78.6	0.14
Coal gasification[b]		8.5			
Coal gasification[a]	Ammonia	−23.7	26.4	75.2	2.0
Coal gasification[b]		76.0	82.7		
Coal gasification[a]	Urea	−34.2	26.4		4.6

World capacity (%) is for products from flue gas of a 500 MW coal-fired or a 400 MW gas-fired power plant.

[a] Flue-gas treatment relative to syngas production by conventional MSR.

[b] Flue-gas treatment relative to syngas production by coal gasification.

coal-fired burner would consume 0.0016% of the world proved natural gas reserves, which in 2004 stood at 173×10^{12} m^3 (or 6100×10^{12} cu.ft., or 7.72×10^{12} kmol CH_4) [24a]. The global anthropogenic emissions of CO_2 amount to about 29×10^9 ton, of which about 30% are from large industries such as fossil-fuel fired power stations, cement production, and steel plants [25]. Assume that 1% of these industries would convert their flue gases by the tri-reforming process. In this case, 90×10^6 ton (2.05×10^{12} mol) CO_2 would be converted to syngas. The NG required for this process, according to Eq. (8), would be 3.15×10^{12} mol. This would amount to 0.04% of the proved reserves of NG. For tri-reforming the flue gases from a 400 MW NG-fired burner (as described in Section 3.1), the consumption of NG would amount to 0.0008% of the proved reserves. Such processes could therefore be attractive only for regions with abundant supplies of natural gas. Using coal gasification (as described in Section 4.1) would consume 0.0003% of the world coal resources, estimated at 0.98×10^{12} ton [24b].

The actual technical realization of the coal gasification of flue gases could be by a modified blast furnace, as described for syngas production by coal gasification coupled with natural gas reforming [26]. An additional aspect will be to assure sufficient demand for the products from the syngas produced. Syngas is an important intermediate to chemicals and synthetic fuels, and also serves as reducing gas in the production of sponge iron in the metallurgical industry. Major current markets for methanol are formaldehyde (35.5%, mainly for polymers), various chemicals and solvents (30.8%), methyl-*tert*-butylether (the fuel additive MTBE, 27.4%), and acetic acid (6.4%). Most of these uses, except for MTBE, are long-term sinks for carbon [2a]. When methanol is used as an automobile fuel, it would replace an equivalent amount of gasoline fuel. The production of ammonia seems particularly attractive, as it would consume part of the nitrogen. Ammonia production accounts for about 3% of the world energy consumption [18c]. The expected future worldwide demand for ammonia is predicted to outstrip capacity. Thus, the market could probably absorb the added production. The predominant use of ammonia, about 84%, is for its application as fertilizer, mainly as urea [21]. In this application of urea, the carbon would presumably be consumed by the crop, or would be incorporated in the soil/water bicarbonate–carbonate pool, which could be a long-term sink for carbon. An important future use for ammonia could be in ammonia fuel cells for automobile or stationary power sources [27]. Experimental lab work is required for determining the kinetics and catalysis of the reforming and coal gasification reactions.

References

[1] IPCC, Intergovernmental Panel on Climate Change, Cambridge University Press, 2001.

[2] (a) M. Halmann, M. Steinberg, Greenhouse Gas Carbon Dioxide Mitigation: Science and Technology, Lewis Publishers, Boca Raton, Florida, 1999, p. 368;
(b) M. Halmann, M. Steinberg, Greenhouse Gas Carbon Dioxide Mitigation: Science and Technology, Lewis Publishers, Boca Raton, Florida, 1999, p. 232;
(c) M. Halmann, M. Steinberg, Greenhouse Gas Carbon Dioxide Mitigation: Science and Technology, Lewis Publishers, Boca Raton, Florida, 1999, p. 266.

[3] C. Song, Tri-reforming: a new process for reducing CO_2 emissions, Chem. Innovat. 31 (2001) 21–26.

[4] C. Song, Tri-reforming: a novel concept for CO_2 conversion to syngas with desired H_2/CO ratio using flue gas of power plants without CO_2 separation, in: Proceedings of the Seventh International Conference on Carbon Dioxide Utilization (Abstracts), October 12–16, Seoul, Korea, (2003), pp. 121–122.

[5] C. Song, W. Pan, Tri-reforming of methane: a novel concept for catalytic production of industrially useful synthesis gas with desired H_2/CO ratios, Catal. Today 98 (2004) 463–484.

[6] M. Halmann, A. Steinfeld, Methanol, hydrogen, or ammonia production by tri-reforming of flue gases from coal- and gas-fired power stations, in: Proceedings of the ECOS2004 Conference, July 7–9, Guanajuato, Mexico, (2004), pp. 1117–1128.

[7] S. Gordon, J.B. McBride, NASA SP-273, NASA Lewis Research, Cleveland, OH, 1976. A PC version prepared by T. Kappauf, M. Pipho, E. Whitby for E.A. Fletcher at the University of Minnesota was used in the present study.

[8] National Institute of Standards and Technology, NIST Standard Reference Database, Thermodynamic Data, Chemistry Webbook, http://webbook.nist.gov.

[9] D. Trommer, F. Noembrini, M. Fasciana, D. Rodriguez, A. Morales, M. Romero, A. Steinfeld, Hydrogen production by steam-gasification of petroleum coke using concentrated solar power I. Thermodynamic and kinetic analyses, Int. J. Hydrogen Energy 30 (2005) 605–618.

[10] J.K. Dahl, A.W. Weimer, A. Lewandowski, C. Bingham, C. Bruetsch, A. Steinfeld, Dry reforming of methane using a solar-thermal aerosol flow reactor, Ind. Eng. Chem. Res. 43 (2004) 5489–5495.

[11] A.T. Ashcroft, A.K. Cheetham, J.S. Foord, M.L.H. Green, C.P. Grey, A.J. Murrell, P.D.F. Vernon, Selective oxidation of methane to synthesis gas using transition metal catalysts, Nature 344 (1990) 319–321.

[12] D.Y. Quin, J. Lapszewicz, X.Z. Jiang, Comparison of partial oxidation and steam-CO_2 mixed reforming of CH_4 to syngas on MgO-supported metals, J. Catal. 159 (1996) 140–149.

[13] T. Inui, Rapid catalytic reforming of methane with CO_2 and its application to other reactions, Appl. Organometal. Chem. 15 (2001) 87–94.

[14] J. Bugge, S. Kjaer, R. Blum, High-efficiency coal-fired power plants development and perspectives, in: Proceedings of the ECOS2003 Conference, June 30–July 2, Copenhagen, Denmark, (2003), pp. 1349–1354.

[15] (a) See: Methanol Institute, http://www.methanol.org;
(b) Methanex Corp., http://www.methanex.com.

[16] M. Werder, A. Steinfeld, Life cycle assessment of the conventional and solar thermal production of zinc and synthesis gas, Energy 25 (2000) 395–409.

[17] See: http://www.nap.edu/books/030909/1632/html/; The Hydrogen Economy: Opportunities, Costs, Barriers, and R&D Needs (2004), National Academy of Engineering, also: http://www.dotynmr.com/pdf/doty_H_2Price.pdf.

[18] (a) Ullmann's Encyclopedia of Industrial Chemistry, fifth ed., VCH Publ., Weinheim, Germany. H. Hiller, et al., Gas production A12 (1989) 289.;
(b) Ullmann's Encyclopedia of Industrial Chemistry, fifth ed., VCH Publ., Weinheim, Germany. J.H. Meesen, H. Petersen, Urea A27 (1996) 335.;
(c) Ullmann's Encyclopedia of Industrial Chemistry, fifth ed., VCH Publ., Weinheim, Germany. H. Bakemeier, et al., Ammonia A2 (1985) 143.
(d) H. Bakemeier, et al. Ammonia A 2 (1985) 143.

[19] May 2005. Source: International Herald Tribune.

[20] Hydrogen Cost and Worldwide Production, March 2002, U.S. Office of Transportation Technologies, see: http://www.ott.doe.gov/facts/archives/fotw205.shtml.

[21] I. Rafiqul, C. Weber, B. Lehmann, A. Voss, Energy efficiency improvements in ammonia production–perspectives and uncertainties, Energy 30 (2005) 2487–2504;
See also: Potash Corporation, http://www.potashcorp.com/npk_markets/industry_overview/nitrogen, and Brunei Fertilizer Project, http://www.incitecpivot.com.au/download/BruneiconsortiumPresentation.pdf.

[22] See: The World Bank, Commodity Price Data, http://sitesources.worldbank.org.

[23] I.L. Leites, D.A. Sama, N. Lior, The theory and practice of energy sav ing in the chemical industry: some methods for reducing thermodynamic irreversibility in chemical technology processes, Energy 28 (2003) 55–97.

[24] (a) See: World Crude Oil and Natural Gas Reserves, January 2004. http://www.eia.doe.gov/pub/international/iea2003/table81.xls.;
(b) World Energy Council, http://www.worldenergy.org.

[25] P. Jean-Baptiste, R. Ducroux, Energy policy and climate change, Energ. Policy 31 (2003) 155–166.

[26] Z. Ouyang, Z. Guo, D. Duan, X. Song, X. Yu, Experimental study of coal gasification coupling with natural gas autothermal re-forming for synthesis gas production, Ind. Eng. Chem. Res. 44 (2005) 279–284.

[27] See e.g.: J.C. Ganley, Ammonia Fuel Cell Systems, http://energy.iastate.edu/renewable/biomass/download/2005/Ganley_fuelcell.pdf and Innovation in Ammonia Fuel Cells, Natural Resources Canada, Energy Technology Center Ottawa, http://www.nrcan.gc.ca/etb/cetc.