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## PROCESS DESIGN AND CONTROL

# Ammonia Production via a Two-Step $\text{Al}_2\text{O}_3/\text{AlN}$ Thermochemical Cycle. 1. Thermodynamic, Environmental, and Economic Analyses

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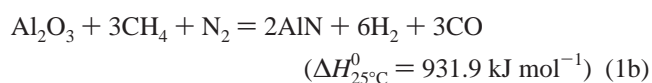
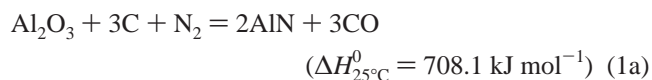
The production of ammonia via a two-step cyclic process is proposed as an alternative to its conventional production by the Haber–Bosch process. The first endothermic step is the production of AlN by carbothermal reduction of  $\text{Al}_2\text{O}_3$  in a  $\text{N}_2$  atmosphere at above 1500 °C. The second exothermic step is the steam-hydrolysis of AlN to produce  $\text{NH}_3$  and reform  $\text{Al}_2\text{O}_3$ ; the latter is recycled to the first step. Both reaction steps proceed at 1 bar, without added catalysts, and bypass the energy-intensive production of hydrogen, resulting in significant fuel and cost savings. Furthermore, the endothermic reduction step could be carried out using concentrated solar energy as the source of high-temperature process heat, eliminating concomitant  $\text{CO}_2$  emissions derived from fossil-fuelled processes.

## Introduction

More than 90% of the world consumption of ammonia, the second largest synthetic chemical product, is manufactured from  $\text{N}_2$  and  $\text{H}_2$  via the catalytic Haber–Bosch process.<sup>1</sup> Although this reaction is exothermic ( $\Delta H_{25^\circ\text{C}}^0 = -46.2 \text{ kJ mol}^{-1}$ ) and should occur spontaneously, significant energy input is needed for  $\text{N}_2$  to achieve the activated state because of its high dissociation energy ( $941 \text{ kJ mol}^{-1}$ ). The use of catalysts lowers the activation energy and effects the reaction in the range of 250–400 °C, but even with added catalysts, the yield is low because of the unfavorable thermodynamic equilibrium. At 30 MPa, the yield after one pass usually does not surpass 25%, requiring separation by condensation and recycling of the unreacted  $\text{H}_2$ – $\text{N}_2$  mixture, about 4–6 kg per kg of  $\text{NH}_3$  synthesized.<sup>2</sup> Furthermore, the overall process is characterized by the high-energy consumption associated with the production of the reactants. Usually,  $\text{H}_2$  is obtained by steam-reforming of natural gas, while  $\text{N}_2$  is obtained by cryogenic separation from air. Both of these processes require a major input of energy, either in the form of high-temperature process heat or in the form of electricity, and consequently cause a significant concomitant pollution derived from the combustion of fossil fuels for heat and electricity generation. In modern plants, the total energy requirement is estimated to be  $28 \text{ GJ ton}^{-1}$ .<sup>2,3</sup>

In the present work, a novel cyclic process is proposed for the production of  $\text{NH}_3$  that involves two thermochemical noncatalytic steps. The first, high-temperature, endothermic step is the production of AlN and CO by carbothermal reduction of  $\text{Al}_2\text{O}_3$  in a  $\text{N}_2$  atmosphere. Either C (e.g., charcoal, petcoke, etc.) as in reaction 1a or  $\text{CH}_4$  (e.g., natural gas) as in reaction

1b can be used as reducing agents. The second exothermic step is the hydrolysis of AlN to produce  $\text{NH}_3$  and reform  $\text{Al}_2\text{O}_3$ ; the latter is recycled to the first step. The overall reaction steps can be represented by (first endothermic step)



and (second exothermic step)

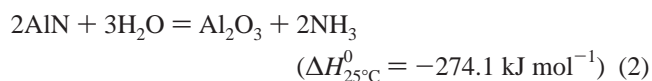


Figure 1 illustrates the proposed cycle. The CO produced in the first step when employing a source of fixed carbon as the reducing agent, reaction 1a, may be water-gas shifted to syngas and further used as a fuel or as an intermediate to methanol or Fischer–Tropsch products. Syngas with a  $\text{H}_2/\text{CO}$  molar ratio of 2 suitable for  $\text{CH}_3\text{OH}$  synthesis would be directly produced by employing  $\text{CH}_4$  as the reducing agent (reaction 1b). Relative to the conventional production of  $\text{NH}_3$  via the Haber–Bosch process, the proposed two-step process offers the following 3-fold advantages: (1) it eliminates the need for high pressure, minimizing costs and safety concerns; (2) it eliminates the need for catalysts; minimizing costs associated with their production and recycling; and (3) it eliminates the need for hydrogen as feedstock, reducing energy consumption and associated  $\text{CO}_2$  emissions. It does not, however, eliminate the need for nitrogen.

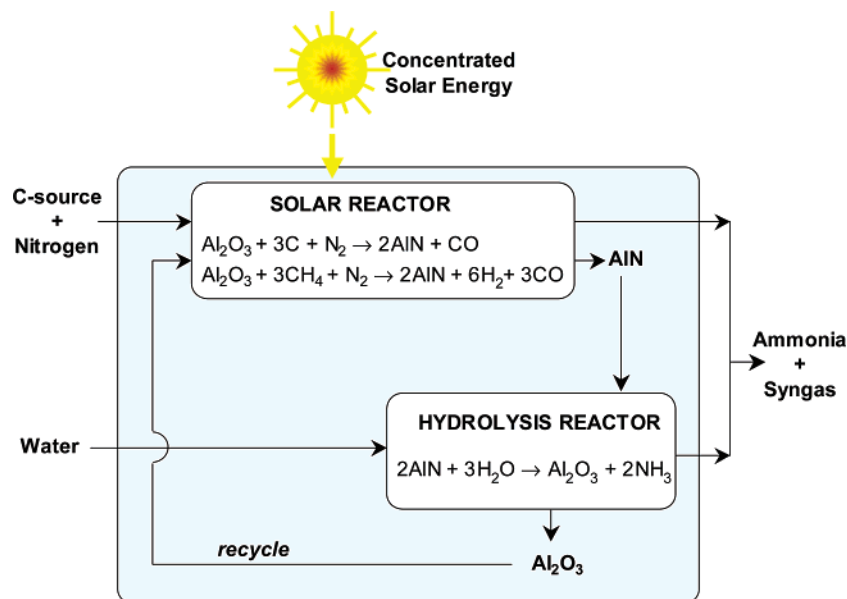
Furthermore, the endothermic reduction of  $\text{Al}_2\text{O}_3$ , either by reaction 1a or by reaction 1b, is an attractive candidate for the use of concentrated solar energy as the source of high-temperature process heat, avoiding the discharge of greenhouse gases and other pollutants derived from the combustion of fossil

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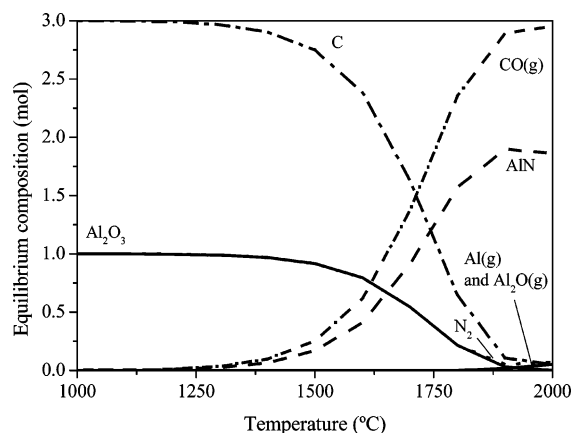
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**Figure 1.** Scheme of the two-step cyclic solar thermochemical cyclic process for ammonia production. The first endothermic step is the solar production of AlN by carbothermic reduction of  $\text{Al}_2\text{O}_3$  in a  $\text{N}_2$  atmosphere. The second exothermic step is the steam-hydrolysis of AlN to produce  $\text{NH}_3$  and to reform  $\text{Al}_2\text{O}_3$ ; the latter is recycled to the first step.

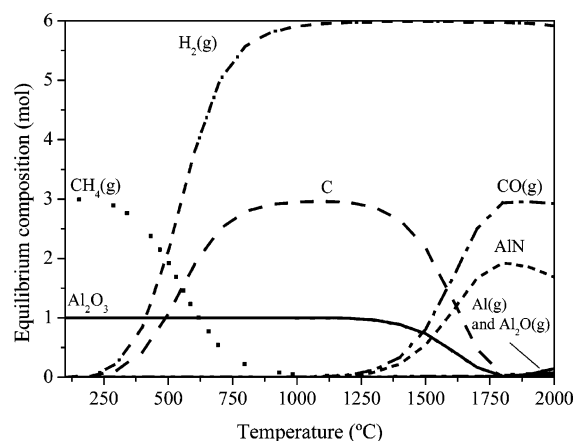


**Figure 2.** Equilibrium composition of the system  $\text{Al}_2\text{O}_3 + 3\text{C} + \text{N}_2$  (reaction 1a) as a function of temperature at 1 bar.

fuels. Previous relevant thermochemical processes effected in solar furnaces include the carbothermal reductions of  $\text{Fe}_3\text{O}_4$ ,  $\text{MgO}$ , and  $\text{ZnO}$  with  $\text{C}(\text{gr})$  and  $\text{CH}_4$  to produce  $\text{Fe}$ ,  $\text{Mg}$ , and  $\text{Zn}$ , respectively;<sup>4–9</sup> the carbothermal reductions of  $\text{Al}_2\text{O}_3$ ,  $\text{CaO}$ ,  $\text{SiO}_2$ , and  $\text{TiO}_2$  with  $\text{C}(\text{gr})$  in an inert atmosphere to produce  $\text{Al}_3\text{C}_4$ ,  $\text{CaC}_2$ ,  $\text{SiC}$ , and  $\text{TiC}$ , respectively; and the carbothermal reductions of  $\text{Al}_2\text{O}_3$ ,  $\text{SiO}_2$ ,  $\text{TiO}_2$ , and  $\text{ZrO}_2$  with  $\text{C}(\text{g})$  in a  $\text{N}_2$  atmosphere to produce AlN,  $\text{Si}_3\text{N}_4$ , TiN, and ZrN, respectively.<sup>10–12</sup> Specifically, experimental studies on the carbothermal reduction of  $\text{Al}_2\text{O}_3$  in the presence of  $\text{N}_2$  have been carried out at above 1500 °C using a graphite crucible reactor, directly exposed to high-flux solar irradiation.<sup>11,12</sup> A review of the solar chemical process technology is found in ref 13. The chemical kinetics of the pertinent reactions has been investigated in the accompanying article.<sup>14</sup>

### Thermodynamic Analysis

Thermochemical equilibrium calculations were performed using the FactSage,<sup>15</sup> CET85,<sup>16</sup> and HSC Outokumpu<sup>17</sup> program codes. Product species with mol fractions less than  $10^{-5}$  have been omitted. Figure 2 shows the equilibrium composition of the system  $\text{Al}_2\text{O}_3 + 3\text{C} + \text{N}_2$  (reaction 1a) at 1 bar and as a function of temperature in the range of 1000–2000 °C. The



**Figure 3.** Equilibrium composition of the system  $\text{Al}_2\text{O}_3 + 3\text{CH}_4 + \text{N}_2$  (reaction 1b) as a function of temperature at 1 bar.

conversion of  $\text{Al}_2\text{O}_3$  begins at about 1300 °C, is notably accelerated at 1500 °C, and reaches completion at 2000 °C. At this temperature, the gas phase consists of 94.9%  $\text{CO}$ , 2.2%  $\text{N}_2$ , 1.3%  $\text{Al}(\text{g})$ , and 1.6%  $\text{Al}_2\text{O}(\text{g})$ , while the solid phase consists of 97.4% AlN and 2.6%  $\text{C}$ . Figure 3 shows the equilibrium composition of the system  $\text{Al}_2\text{O}_3 + 3\text{CH}_4 + \text{N}_2$  (reaction 1b) at 1 bar and as a function of temperature in the range of 1000–2000 °C. Methane cracking occurs at relatively low temperatures and is completed at 600 °C, leading to the formation of  $\text{C}(\text{s})$ , which in turn reacts with  $\text{Al}_2\text{O}_3$  at higher temperatures.  $\text{Al}_2\text{O}_3$  conversion reaches completion at 1900 °C. At 2000 °C, the gas phase consists of 31.3%  $\text{CO}$ , 63.4%  $\text{H}_2$ , 1.5%  $\text{N}_2$ , small amounts of  $\text{Al}(\text{g})$ ,  $\text{Al}_2\text{O}(\text{g})$ ,  $\text{H}(\text{g})$ ,  $\text{C}_2\text{H}_2(\text{g})$ ,  $\text{AlH}(\text{g})$ , and  $\text{HCN}(\text{g})$ , while the solid phase consists of 100% AlN. By applying either  $\text{C}$  or  $\text{CH}_4$  as reducing agents in a  $\text{N}_2$  atmosphere, no formation of  $\text{Al}_4\text{C}_3$  or oxycarbides (e.g.,  $\text{Al}_2\text{O}_2\text{C}$ ,  $\text{Al}_4\text{O}_2\text{C}$ ) is foreseen by the thermodynamic calculations in this temperature range.

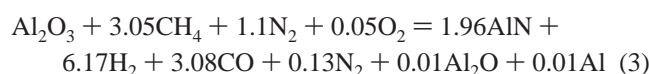
Since the presence of unreacted solids  $\text{C}$  or  $\text{Al}_2\text{O}_3$  within the AlN produced is undesirable, the effect of adding  $\text{O}_2$  was evaluated in an effort to select the optimal conditions that minimize the inclusion of these residues in the final product. Results of thermodynamic equilibrium computations at 1800

**Table 1.** Thermochemical Equilibrium Composition at 1800 °C and 1 Bar, for an Initial Mixture of 1 mol of Al<sub>2</sub>O<sub>3</sub> + 1.1 mol of N<sub>2</sub> + 3.05 mol of Either C or CH<sub>4</sub> as Reducing Agents in the Presence of Varying Amounts of O<sub>2</sub><sup>a</sup>

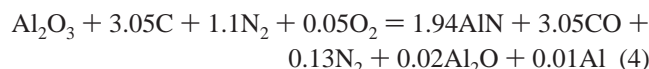
Initial		Equilibrium Mole Fraction					H <sub>2</sub> /CO molar ratio	yield of AlN(s) (%)
reducing agent	O <sub>2</sub> (mol)	AlN (s)	Al <sub>2</sub> O <sub>3</sub>	C (g)	H <sub>2</sub>	CO		
C	0	0.362	0.0128	0.048		0.544		99.8
C	0.05	0.360	0.0138	0.032		0.560		99.8
CH <sub>4</sub>	0	0.176	0	0.0018	0.540	0.267	2.03	98.7
CH <sub>4</sub>	0.02	0.175	0	0	0.540	0.269	2.01	98.3
CH <sub>4</sub>	0.05	0.171	0.0016	0	0.540	0.270	2.00	97.9

<sup>a</sup> Products are expressed in mol fractions. A mole fraction value of “0” means <10<sup>-5</sup>. Yield is defined as the number of moles of AlN in equilibrium, relative to the initial number of moles of Al<sub>2</sub>O<sub>3</sub>.

°C and 1 bar are presented in Table 1. Using either C or CH<sub>4</sub> as reducing agents in the absence of added O<sub>2</sub>, the products of both reaction 1a and reaction 1b would contain unreacted Al<sub>2</sub>O<sub>3</sub>. Adding 0.05 mol of O<sub>2</sub> to the mixture of reaction 1b eliminates both Al<sub>2</sub>O<sub>3</sub> and C. The equilibrium mixture would contain only some traces of the gaseous products Al<sub>2</sub>O and Al. Under these conditions, the reaction at 1800 °C can be represented as



In the case of reaction 1a in the presence of 0.05 mol of O<sub>2</sub>, the total absence of unreacted C and Al<sub>2</sub>O<sub>3</sub> is predicted at above 1900 °C, according to



The operation of the cyclic process based on reaction 3 could involve periodic switching between a gas stream of N<sub>2</sub>, CH<sub>4</sub>, and a small amount of air at a higher temperature, about 1800–1900 °C, and between a gas stream of H<sub>2</sub>O at a lower temperature, while the Al<sub>2</sub>O<sub>3</sub> and AlN solids would remain as a stationary bed. A cyclic process based on reaction 4 would presumably require a more complicated recharging of solids to make up for the consumed carbon.

The first step of the cycle proceeds endothermically. The enthalpy change of reactions 1a and 1b is defined for reactants fed at ambient temperature (25 °C) and products obtained at the reaction temperature *T* and having an equilibrium composition given in Figures 2 and 3, respectively

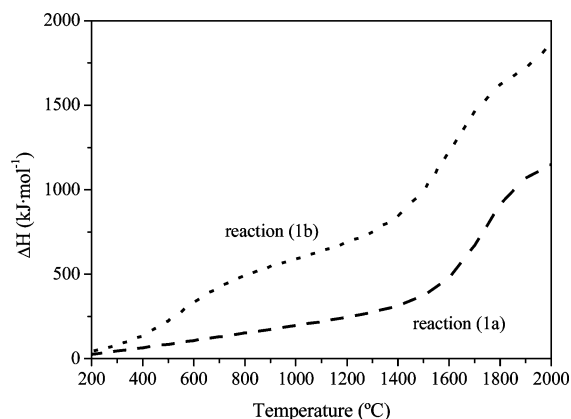
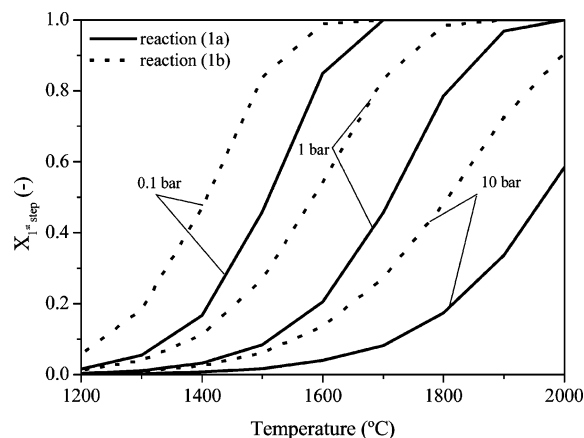
$$\Delta H = H_{\text{T}}^{\text{products in equilibrium}} - H_{25^\circ\text{C}}^{\text{reactants}} \quad (5)$$

Figure 4 shows  $\Delta H$  of reactions 1a and 1b as a function of temperature. For reaction 1a,  $\Delta H = 1147.5 \text{ kJ mol}^{-1}$  at 2000 °C. The change in the slope of the curve is due to the sensible heat needed to heat the reactants from ambient to the reaction temperature and to the process heat for the chemical transformation at above 1300 °C. For reaction 1b,  $\Delta H = 1859.2 \text{ kJ mol}^{-1}$  at 2000 °C. The changes in the slope of the curve are mainly due to methane cracking in the range of 400–700 °C and to the Al<sub>2</sub>O<sub>3</sub> reduction at above 1300 °C.

The reaction extent for the first step of the cycle,  $X_{\text{firststep}}$ , is defined as

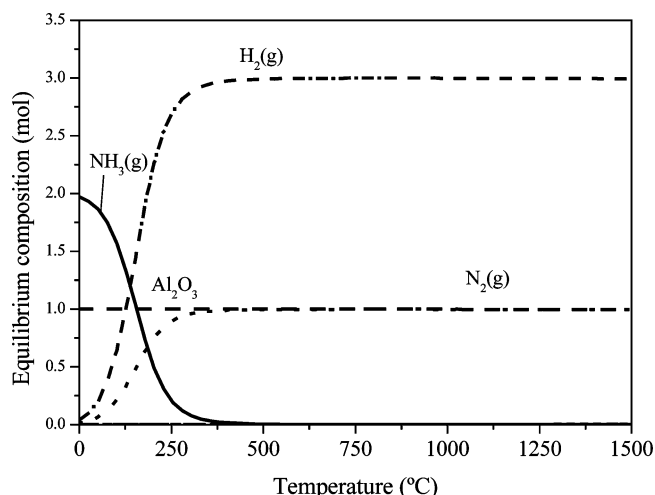
$$X_{\text{firststep}} = 1 - \frac{n_{\text{Al}_2\text{O}_3}^{\text{T}}}{n_{\text{Al}_2\text{O}_3}^0} \quad (6)$$

where  $n_{\text{Al}_2\text{O}_3}^0$  and  $n_{\text{Al}_2\text{O}_3}^{\text{T}}$  denote the initial number of moles and the equilibrium number of moles at temperature *T*. Figure 5 shows the reaction extent for reactions 1a and 1b as a function of temperature at 0.1, 1, and 10 bar. At higher pressures, as

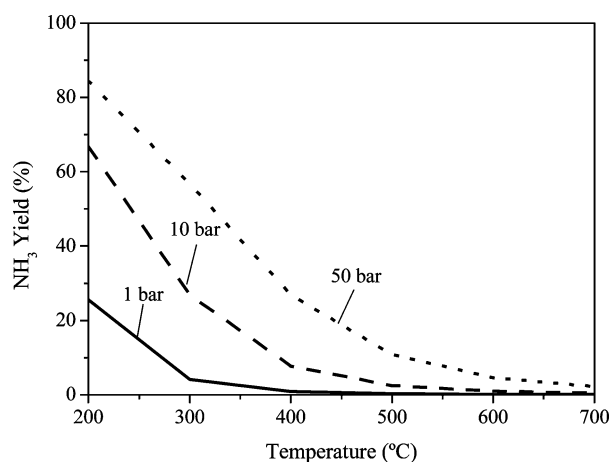
**Figure 4.** Enthalpy change of reactions 1a and 1b as a function of temperature.**Figure 5.** Extent of reactions 1a and 1b as a function of temperature at 0.1, 1, and 10 bar.

preferred in industrial applications, the thermodynamic equilibrium is shifted to the left in such a way so as to relieve the pressure in accordance with Le Chatelier's principle. For example, at 2000 °C,  $X_{\text{firststep}}$  for reaction 1a decreases from 100 to 58.5% when the pressure is increased from 1 to 10 bar. In contrast, reaction 1b is less affected:  $X_{\text{firststep}} = 90.7\%$  at 2000 °C and 10 bar. Both reaction 1a and reaction 1b reach completion already at 1700 °C when operating at 0.1 bar, while their extent reaches only 8 and 28%, respectively, when operating at 10 bar.

The equilibrium composition for reaction 2 is shown in Figure 6 in the range of 0–1500 °C. Thermodynamically, NH<sub>3</sub> is only partly stable until 375 °C, while AlN can be fully converted to Al<sub>2</sub>O<sub>3</sub> at any temperature. However, the presence of metastable NH<sub>3</sub> is possible in the absence of catalysts. As it was shown experimentally in a dynamic thermogravimeter run under a 80% H<sub>2</sub>O–Ar gas stream (nonequilibrium open system),<sup>14</sup> almost complete hydrolysis of AlN to Al<sub>2</sub>O<sub>3</sub> (93% reaction extent) was achieved within 100 min at 1000 °C and 1 bar, with a NH<sub>3</sub>



**Figure 6.** Equilibrium composition of the system  $2\text{AlN} + 3\text{H}_2\text{O}$  (reaction 2), as a function of temperature at 1 bar.



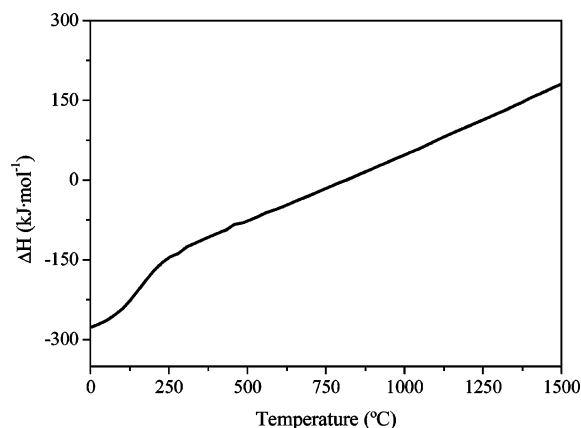
**Figure 7.** Ammonia yield as a function of temperature at 1, 10, and 50 bar.

yield of 88%. Higher pressures favor the thermodynamic stability of  $\text{NH}_3$ . Figure 7 shows the  $\text{NH}_3$  yield as a function of temperature for 1, 10, and 50 bar. For example, increasing the pressure from 1 to 50 bar results in an increase of the  $\text{NH}_3$  yield from 26 to 84% at 200 °C.

The enthalpy change for reaction 2, as defined in eq 5, is shown in Figure 8. The slope change in the range of 0–375 °C is due to the different composition of the gaseous products, with decreasing  $\text{NH}_3$  content. Above 375 °C, the enthalpy change increases monotonically due to the constant composition of the products, becoming positive (endothermic) at above 800 °C.

### Economic Estimate, Fuel Saving, and $\text{CO}_2$ Emission Avoidance

A preliminary economic analysis is presented in Table 2 for the proposed thermochemical cycle that coproduces ammonia and methanol. It has been carried out for one complete cycle, assuming the formation of  $\text{AlN}$  according to the thermochemical equilibrium reaction at 1900 °C and 1 bar described in reaction 4, followed by  $\text{CO}$  conversion by water-gas shift (WGS) to a syngas mixture with a  $\text{H}_2/\text{CO}$  molar ratio of 2, which then undergoes methanol synthesis. In a subsequent hydrolysis step,  $\text{AlN}$  is reformed to  $\text{Al}_2\text{O}_3$ , releasing  $\text{NH}_3$ . The reference plant is designed for an initial capacity load of 10 kmol (or 1.02 ton) of  $\text{Al}_2\text{O}_3$  per cycle. The assumed loss of  $\text{Al}_2\text{O}_3$  per cycle is 5%, which accounts for the possible formation of volatile  $\text{Al}_2\text{O}_3$ .



**Figure 8.** Enthalpy change of reaction 2 as a function of temperature.

**Table 2. Preliminary Economic Analysis for the Combined Production of  $\text{CH}_3\text{OH}$  and  $\text{NH}_3$  via One Complete Cycle with 10 kmol of  $\text{Al}_2\text{O}_3$ <sup>a</sup>**

Design Parameters	
Design $\text{Al}_2\text{O}_3$ load (kmol)	10
Design $\text{Al}_2\text{O}_3$ load (ton)	1.02
Makeup $\text{Al}_2\text{O}_3$ (ton/cycle)	0.051
Carbon feed (kmol/cycle)	30.5
Carbon feed (GJ/cycle) <sup>b</sup>	11.97
Carbon feed (ton/cycle)	0.366
$\text{N}_2$ feed (kmol/cycle)	11
Methanol production (kmol/cycle) <sup>c</sup>	9.0
Methanol production (ton/cycle)	0.288
$\text{NH}_3$ production (kmol/cycle) <sup>d</sup>	17.7
$\text{NH}_3$ production (ton/cycle)	0.301
$\text{CO}_2$ release (kmol/cycle)	20
$\text{CO}_2$ release (ton/cycle)	0.88
Cost per Cycle (USD)	
$\text{CH}_3\text{OH}$ production (30 USD/ton) <sup>e</sup>	8.6
$\text{NH}_3$ production (33 USD/ton) <sup>f</sup>	10.0
Coke cost (99 USD/ton) <sup>g</sup>	36.2
$\text{Al}_2\text{O}_3$ makeup (257 USD/ton) <sup>h</sup>	13.1
Total	67.9
Sales per Cycle (USD)	
$\text{CH}_3\text{OH}$ (323 USD/ton) <sup>i</sup>	98.8
$\text{NH}_3$ (280 USD/ton) <sup>j</sup>	84.3
Total	183.1

<sup>a</sup> Assumed are the formation of  $\text{AlN}$  according to eq 4, followed by 2/3 WGS conversion of  $\text{CO}$  to a syngas mixture for  $\text{CH}_3\text{OH}$  synthesis. In the subsequent hydrolysis step, eq 2,  $\text{AlN}$  is reformed to  $\text{Al}_2\text{O}_3$ , releasing  $\text{NH}_3$ . Ton = metric ton. <sup>b</sup> Taken as the HHV of carbon the value for graphite, 0.3935 GJ/kmol. <sup>c</sup> Assume 90% yield of methanol from syngas. <sup>d</sup> Assume 90% yield of  $\text{NH}_3$  per cycle. <sup>e</sup> Estimated cost of conversion of syngas to methanol. <sup>f</sup> See [www.potashcorp.com/npk\\_markets/industry\\_overview/nitrogen](http://www.potashcorp.com/npk_markets/industry_overview/nitrogen). <sup>g</sup> May 2006. See [www.eia.doe.gov/cneaf](http://www.eia.doe.gov/cneaf). <sup>h</sup>  $\text{Al}_2\text{O}_3$  price usually linked 11–13% to the London Metal Exchange aluminum price. August 2006 aluminum price 2140 USD/ton. See [www.lme.com](http://www.lme.com). <sup>i</sup> August 2006. See [www.methanex.com](http://www.methanex.com).

The cost of producing the  $\text{N}_2$  gas feed has not been considered but may be compensated by the lower cost of coke or petcoke relative to natural gas. The combined production per cycle of 0.288 ton of  $\text{CH}_3\text{OH}$  and of 0.301 ton of  $\text{NH}_3$  would require 11.97 GJ of carbon. By the conventional separate productions of  $\text{CH}_3\text{OH}$  and  $\text{NH}_3$  via coal gasification to syngas, the corresponding specific fuel consumptions are 44.5 GJ/ton of  $\text{CH}_3\text{OH}$ <sup>1</sup> and 165.9 GJ/ton of  $\text{NH}_3$ ,<sup>2</sup> and the corresponding specific  $\text{CO}_2$  emissions are 2.088 ton of  $\text{CO}_2$ /ton of  $\text{CH}_3\text{OH}$  and 16.7 ton of  $\text{CO}_2$ /ton of  $\text{NH}_3$ .<sup>18,19</sup> Thus, the production of 0.288 ton of  $\text{CH}_3\text{OH}$  and 0.301 ton of  $\text{NH}_3$  by coal gasification would require an input of energy of 12.8 and 49.9 GJ, respectively, or a total of 62.7 GJ, and would discharge 5.03 and 0.60 ton of  $\text{CO}_2$ , respectively, or a total of 5.63 ton of  $\text{CO}_2$ .



**Table 3. Preliminary Economic Analysis for the Combined Production of CH<sub>3</sub>OH and NH<sub>3</sub> via One Complete Cycle with 10 kmol of Al<sub>2</sub>O<sub>3</sub><sup>a</sup>**

Design Parameters	
Design Al <sub>2</sub> O <sub>3</sub> load (kmol)	10
Design Al <sub>2</sub> O <sub>3</sub> load (ton)	1.02
Makeup Al <sub>2</sub> O <sub>3</sub> (ton/cycle)	0.051
NG feed (kmol/cycle)	30.5
NG feed (GJ/cycle)	27.17
NG feed (mmBtu/cycle)	25.74
N <sub>2</sub> feed (kmol/cycle)	11
CH <sub>3</sub> OH production (kmol/cycle) <sup>b</sup>	27.27
CH <sub>3</sub> OH production (ton/cycle)	0.87
NH <sub>3</sub> production (kmol/cycle) <sup>c</sup>	17.7
NH <sub>3</sub> production (ton/cycle)	0.301
Cost per Cycle (USD)	
CH <sub>3</sub> OH production (30 USD/ton) <sup>d</sup>	26.1
NH <sub>3</sub> production (33 USD/ton) <sup>e</sup>	10.0
NG cost (6.927 USD/mm Btu) <sup>f</sup>	178.3
Al <sub>2</sub> O <sub>3</sub> makeup (306 USD/ton) <sup>g</sup>	15.6
Total	230.0
Sales per Cycle (USD)	
CH <sub>3</sub> OH (365 USD/ton) <sup>h</sup>	294.9
NH <sub>3</sub> (280 USD/ton) <sup>e</sup>	84.3
Total	379.2

<sup>a</sup> Assumed are the formation of AlN according to eq 3, followed by syngas conversion to CH<sub>3</sub>OH. In the subsequent hydrolysis step, eq 2, AlN is reformed to Al<sub>2</sub>O<sub>3</sub>, releasing NH<sub>3</sub>. NG = natural gas and ton = metric ton. <sup>b</sup> Assume 90% yield of methanol from syngas. <sup>c</sup> Assume 90% yield of NH<sub>3</sub> per cycle. <sup>d</sup> Estimated cost of conversion of syngas to methanol. <sup>e</sup> See www.potashcorp.com/npk\_markets/industry\_overview/nitrogen. <sup>f</sup> April 6, 2006. See www.nymex.com. <sup>g</sup> Al<sub>2</sub>O<sub>3</sub> price usually linked 11–13% to the London Metal Exchange aluminum price. April 2006 aluminum price 2551 USD/ton. See www.lme.com. <sup>h</sup> April 2006. See www.methanex.com.

The predicted fuel saving by the proposed combined production of CH<sub>3</sub>OH and NH<sub>3</sub> via the cyclic process relative to the conventional separate processes would be 81%, and the CO<sub>2</sub> emission avoidance would be 84%. No correction has been applied for the economic cost, fuel consumption, and CO<sub>2</sub> emissions per cycle associated with the construction and maintenance of the solar concentrating plant. In a previous life cycle assessment of the solar coproduction of syngas and zinc metal from ZnO and CH<sub>4</sub>, the equivalent CO<sub>2</sub> emissions derived from the solar heliostat field were reported to be negligible.<sup>18</sup> Table 3 shows the preliminary economic estimate for the cycle using NG (natural gas) as reducing agent (reaction 1b) at 1800 °C and 1 bar. In this case, the combined production per cycle of 0.87 ton of CH<sub>3</sub>OH and of 0.272 ton of NH<sub>3</sub> would require an input of energy of 27.17 GJ, resulting in fuel savings of 18% relative to the conventional separate processes. There would not be any CO<sub>2</sub> emission discharged directly from the chemical process.

## Conclusion

In the proposed cyclic process, the carbothermal reduction of Al<sub>2</sub>O<sub>3</sub> by C or CH<sub>4</sub> in N<sub>2</sub> to AlN and syngas (which may be converted to methanol) is followed by steam-hydrolysis of AlN back to Al<sub>2</sub>O<sub>3</sub>, with simultaneous formation of NH<sub>3</sub>. In contrast to the Haber–Bosch process, both reaction steps proceed at 1 bar, without added catalysts, and bypass the energy-intensive production of hydrogen. Preliminary environmental and economic analyses indicate favorable fuel economy and hence cost. The predicted fuel saving by the combined production of CH<sub>3</sub>-

OH and NH<sub>3</sub> via the proposed cyclic process relative to the coal-gasification-based separate processes would be 81%, by employing carbon as reducing agent. Furthermore, the use concentrated solar energy as the source of process heat for the endothermic carbothermal reduction reduces significantly or completely eliminates concomitant CO<sub>2</sub> emissions, as demonstrated experimentally in a high-flux solar furnace. A major drawback, however, remains the energy-intensive separation of N<sub>2</sub> from air. It would also be necessary to determine if inexpensive carbonaceous reducing agents (petcoke or low grade coals) could be used as reducing agents.

## Literature Cited

- (1) Ullmann's *Encyclopedia of Industrial Chemistry*, 6th ed; John Wiley and Sons: New York, 2002.
- (2) Kirova-Yordanova, K. Exergy analysis of industrial ammonia synthesis. *Energy* **2004**, *29*, 2373–2384.
- (3) Rafiqul, I.; Weber, C.; Lehman, B.; Voss, A. Energy efficiency improvements in ammonia production perspectives and uncertainties. *Energy* **2005**, *30*, 2487–2504.
- (4) Steinfeld, A.; Fletcher, E. A. Theoretical and experimental investigation of the carbothermal reduction of Fe<sub>2</sub>O<sub>3</sub>, using solar energy. *Energy* **1991**, *16*, 1011–1019.
- (5) Steinfeld, A.; Kuhn, P.; Karni, J. High-temperature solar thermochemistry: Production of iron and synthesis gas by Fe<sub>3</sub>O<sub>4</sub> reduction with methane. *Energy* **1993**, *18*, 239–249.
- (6) Steinfeld, A.; Frei, A.; Kuhn, P. Thermoanalysis of the combined Fe<sub>3</sub>O<sub>4</sub>-reduction and CH<sub>4</sub>-reforming processes. *Metall. Mater. Trans. B* **1995**, *26*, 509–515.
- (7) Steinfeld, A.; Brack, M.; Meier, A.; Weidenkaff, A.; Wüillemin, D. A solar chemical reactor for the co-production of zinc and synthesis gas. *Energy* **1998**, *23*, 803–814.
- (8) Kräupl, S.; Steinfeld, A. Operational performance of a 5 kW solar chemical reactor for the co-production of zinc and syngas. *J. Solar Energy Eng.* **2003**, *125*, 124–126.
- (9) Osinga, T.; Olalde, G.; Steinfeld, A. Solar carbothermal reduction of ZnO: Shrinking packed-bed reactor modelling and experimental validation. *Ind. Eng. Chem. Res.* **2004**, *43*, 7981–7988.
- (10) Duncan, D. A.; Dirksen, H. A. Calcium carbide production in a solar furnace; Technical Report No. SERI/TR-98326-1: Golden, CO, 1980.
- (11) Murray, J. P.; Steinfeld, A.; Fletcher, E. Metals, nitrides, and carbides via solar carbothermal reduction of metal oxides. *Energy* **1995**, *20*, 695–704.
- (12) Murray, J. P. Solar production of aluminum by direct reduction of ore to Al–Si alloy: Preliminary results for two processes. *J. Solar Energy Eng.* **2001**, *123*, 125–132.
- (13) Steinfeld, A.; Palumbo, R. Solar thermochemical process technology. *Encycl. Phys. Sci. Technol.* **2001**, *15*, 237–256.
- (14) Gálvez, M. E.; Frei, A.; Halmann, M.; Steinfeld, A. Ammonia production via a two-step Al<sub>2</sub>O<sub>3</sub>/AlN thermochemical cycle. 2. Kinetic analysis. *Ind. Eng. Chem. Res.* **2007**, *46*, 2047–2053.
- (15) Thermochemical Software and Database Package FactSage, Centre for Research in Computational Thermochemistry, Ecole Polytechnique de Montreal, Canada; www.crct.polymtl.ca.
- (16) Gordon, S.; McBride, J. B. *NASA SP-273*; NASA Lewis Research: Cleveland, OH, 1976. (A PC version was prepared by Kappauf, T.; Piphio, M.; Whitby, E. for Fletcher, E. E. at the University of Minnesota.)
- (17) Roine, A. *Outokumpu HSC chemistry for Windows*; Outokumpu Research: Pori, Finland, 1997.
- (18) [http://www.potashcorp.com/npk\\_markets/industry\\_overview/nitrogen](http://www.potashcorp.com/npk_markets/industry_overview/nitrogen).
- (19) Werder, M.; Steinfeld, A. Life cycle assessment of the conventional and solar thermal production of zinc and synthesis gas. *Energy* **2000**, *25*, 395–409.

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