Processes for Production of Ammonia and Coproducts with Reduced CO_2 Emissions

By

Meyer Steinberg
HCE, LLC
Melville, NY
www.hceco.com
steinberg@hceco.com

April 2006

Polycarbonsuboxide Ammonia / Fertilizer Process is Patent Pending

Global Greenhouse Effect

Carbon Dioxide – Major Greenhouse Gas

Contributes 60% of Warming Effect

Expected to Double in Concentration within the Next Century

Effect – Oceans will Rise
Islands will Disappear
Hurricanes will Increase
Disease will Increase

Efforts: Reduce CO_2 Emissions from Use of Fossil Fuels

Contributing: Ammonia Industry is a Contributor to Greenhouse Effect

Polycarbonsuboxide Ammonia / Fertilizer Process is Patent Pending

Table 1 Global Energy Consumption by Energy Source and Equivalent CO_2 Emissions (1995)			
Source	**EJ/year**	**%**	**GT(C)/yr**
Coal	91	23.7	2.5
Oil	128	33.2	2.6
Gas	71	18.4	1.0
Nuclear	19	4.9	
Hydro	21	5.5	
Biomass	55	14.3	
Total	385	100.0	6.1 (22.4 GT CO_2) / yr

EJ = 10^{18} Joules + 0.95 x 10^{15} BTU = 0.95 Quads
GT(C) / yr = 10^9 tons of C as CO_2 per year

Table 2 Distribution of World CO_2 Emissions	
Energy-Consuming Sector	**% of World CO_2 Emissions**
Power and Heat Generation from Industry	47
Transportation	22
Commercial and Residential	31
Total	100
Total CO_2 Emission	6.1 GT(C)/yr

Table 3 U.S. Distribution of CO_2 Emissions (1995)				
Energy Sector	**Major Fuel**	**Quad**	**GT(CO_2)/yr**	**%**
Electric Power	Coal	20	2.15	35
Automotive Transport	Oil	35	2.00	45
Heating Systems	Gas	21	1.21	20
U.S. Total		76	6.16	100

Quad = 10^{15} BTU
U.S. Contribution to World = 27%

Table 4 Ammonia Production and CO_2 Emission from Ammonia Plants Units in Millions Of Tons		
Year	**2001**	**2005**
Worldwide Production, NH_3	173	180
Worldwide Emission CO_2	288	302
U.S. Production, NH_3	18	14
U.S. Emission CO_2	30	23
Total World CO_2 Emission	23,000	24,000
Contribution by Worldwide NH_3 Production - %	1.25	1.26
Contribution by U.S. NH_3 Production - %	0.13	0.10

*CO_2 Emission calculated based mainly on natural gas feedstock, generating 1.66 Tons CO_2 / ton NH_3

Ammonia Production Based on Hydrogen Production

Conventional Processes from Fossil Fuels

- Natural Gas Reforming
- Steam-Oxygen Coal Gasification

Alternative Energy Sources with Electrolysis of Water to Produce Hydrogen with Zero CO_2 Emission

- Nuclear Power
- Solar Power
- Wind Power
- Geothermal Power
- Renewable Biomass Power & Gasification

Table 5
Conventional Ammonia Process Steam Reforming of Natural Gas Feedstock
Unit Operations and Process Chemistry

(1) Steam Reforming of Natural Gas

$$CH_4 + H_2O = CO + 3 H_2$$
$$\Delta H = +60 \text{ Kcal / g-mol } CH_4$$

This is an endothermic reaction, heat must be generated in the reformer furnace by combustion of natural gas.

$$CH_4 + 2 O_2 = CO_2 + 2 H_2O$$
$$\Delta H = -212 \text{ Kcal / mol } CH_4$$

Amount of methane needed to supply energy at 80% furnace efficiency

$$= [60 / 212] \times 0.8 = 0.35 \text{ moles } CH_4$$

(2) the CO from the reformer is then water gas shifted to produce more hydrogen with the emissions of CO_2

$$CO + H_2 = CO_2 + H_2$$
$$\Delta H = 0$$

Thermally neutral based on higher heating value of H_2

(3) The CO_2 is removed from the shifter gases by absorption-stripping or pressure swing adsorption (PSA).

The nitrogen can either be obtained from the methane combustion gases or from air separation plant. Using the latter it takes about 300 Kwh(e) / ton O_2 to separate. Based on the NH_3 produced (shown below 2.67 moles NH_3 per mol CH_4, it takes about 0.05 g-mol methane to generate the electricity for the air separation plant.

Polycarbonsuboxide Ammonia / Fertilizer Process is Patent Pending

Table 5 (Con't)
Conventional Ammonia Process Steam Reforming of Natural Gas Feedstock
Unit Operations and Process Chemistry

(5) The hydrogen is mixed with the separated nitrogen in the molar ratio of 3 to 1 and compressed typically to 300 atm pressure and sent tot the catalytic ammonia converter. It is estimated that the CH_4 required to run the compressors is about 0.10 mol CH_4 / mole CH_4 to reformer.

(6) Ammonia synthesis takes place on doubly promoted iron catalyst in an exothermic process at 300 atm and 500°C. Gas recycle and heat exchange is provided. Since 1 mol CH_4 produces 4 mol H_2, the process stoichiometry is:

$$4H_2 + 4/3\ N_2 = 8/3\ NH_3 = 2.63 \text{ mol } NH_3$$

The reaction is exothermic, $\Delta H = -11.0$ Kcal / mol NH_3

(7) The net methane feedstock required for each operation:

= Reformer + Furnace + Air Liquefaction + Compression

CH_4 = 1.00 + 0.35 + 0.05 + 0.10 = 1.50

(8) Methane yield molar CH_4 / NH_3 = 1.5 / 2.67 = 0.56 mol CH_4 / mol NH_3

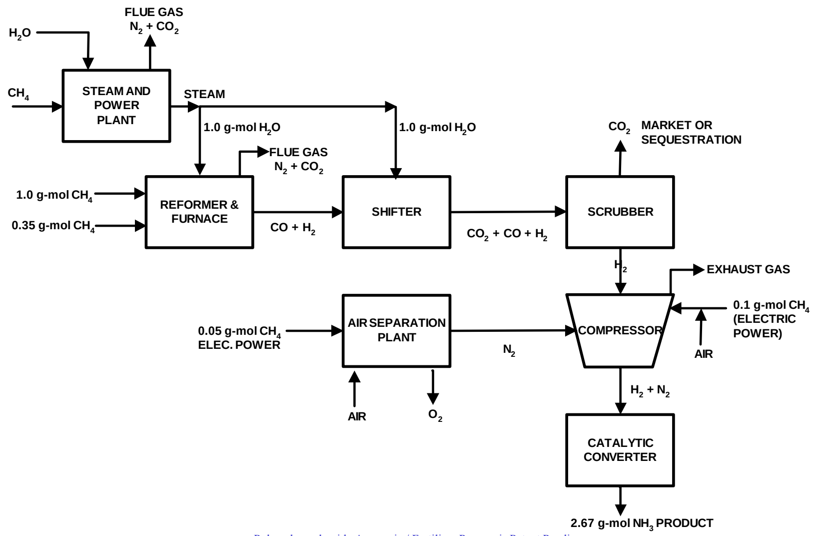
MMBTU / ton NH_3 = (0.56 / 17)(380 x 2000 / 1000) = 25.0 MMBTU / ton

(9) CO_2 Emissions = (1.5 / 2.67)(44/17) = 1.45 Tons CO_2 / Ton NH_3

Older plants generate as much as 1.66 Tons CO_2 / ton NH_3

Polycarbonsuboxide Ammonia / Fertilizer Process is Patent Pending

Figure 1 - Conventional Ammonia Process
Natural Gas Feed - Steam Reforming
Basis 1 g-mol CH_4



Polycarbonsuboxide Ammonia / Fertilizer Process is Patent Pending

Carbon as a Coproduct of Ammonia Production

Carbon Produced by Thermal Decomposition of Methane
Energy Requirement is Low by Plasma or Thermally
Carbon Use – Vulcanization of Tire Rubber
Strengthen Plastics
Printing Inks
Clean Carbon – As Clean Fuel for Combustion Turbines in Combined cycle Power Production
Benefits - Building Materials Carbon Bricks
As a soil Conditioner
Ammonia Production with Zero CO_2 Emission
Carbon easier to Sequester than CO_2
As Landfill or Placed into Depleted Mines

Polycarbonsuboxide Ammonia / Fertilizer Process is Patent Pending

Table 6
New Ammonia Process – Natural Gas Cracking
Unit Operations and Process Chemistry

(1) The thermal decomposition of methane is conducted by a hydrogen gas fired tubular reactor. Practically complete decomposition to C and H_2 takes place at temperatures of about 900°C and pressures of less than 5 atm.

$$CH_4 = C + 2\,H_2$$
$$\Delta H = +18 \text{ Kcal / mol } CH_4 \text{ endothermic}$$

(2) The energy is provided by the combustion of hydrogen with air

$$H_2 + \tfrac{1}{2}\,O_2 = H_2O$$
$$\Delta H = -68 \text{ Kcal / mol } H_2 \text{ (HHV)}$$

The amount of H_2 required to decompose 1 mol of CH_4 at 80% thermal efficiency

$$= (18 / 68)(0.8) = 0.33 \text{ g-mol } H_2$$

(3) The nitrogen for the NH_3 synthesis is obtained from the flue gas combustion of hydrogen

$$H_2 + 0.5\,O_2 + 1.88\,N_2 = H_2O + 1.88\,H_2$$

For 0.33 mol H_2, 0.33 x 1.88 = 0.62 mol N_2 is produced.

(4) An additional 0.17 mol H_2 is required to drive the gas combustion compressor to compress the gases to 300 atm and 300°C.

Polycarbonsuboxide Ammonia / Fertilizer Process is Patent Pending

Table 6 (Con't)
New Ammonia Process – Natural Gas Cracking
Unit Operations and Process Chemistry

(5) Net hydrogen to ammonia converter per g-mol CH_4 to decompose
Hydrogen = Decomposer - Furnace - Compressor
1.50 = 2.00 - 0.33 - 0.17

(6) NH_3 synthesis

$$1.5\ H_2 + 0.5\ N_2 = 1.0\ NH_3$$

The reaction is exothermic $\Delta H = -11$ Kcal / mol NH_3

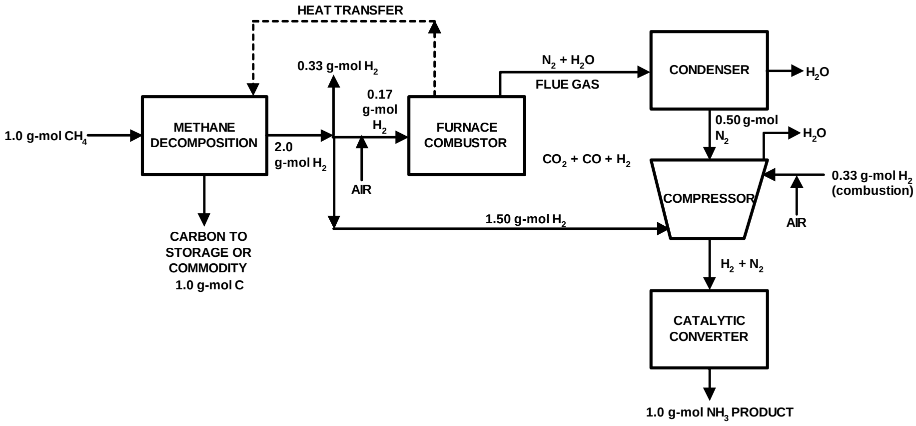
(7) Yield g-mol CH_4 / g-mol NH_3 = 1.0 / 1.0 = 1.0, same as lb-mol CH_4 / lb-mol NH_3
MMBTU / ton = (1.0 / 17)(380 x 2000 / 1000) = 44.8 MMBTU / ton

(8) Yield, tons carbon / tons NH_3 = 1.0 x 12 / 17 = 0.70

(9) CO_2 emission = 0.0
Sequestering carbon, using H_2 combustion for methane decomposer, results in zero CO_2 emissions.

Polycarbonsuboxide Ammonia / Fertilizer Process is Patent Pending

Figure 2 - New Ammonia Process
Natural Gas Feed - Cracking
Basis 1 g-mol CH_4



Polycarbonsuboxide Ammonia / Fertilizer Process is Patent Pending

Table 7

Basic Data for Coal and Biomass Feedstocks Used in the Study
Composition and Thermodynamic Data*

Feedstock	Biomass Wood	Bituminous Kentucky Coal	Lignite N. Dakota Coal	Sub-bituminous Wyodak Coal	Alaskan Beluga Coal	Sewage Sludge
Composition (wt%)						
C	45.86	67.02	43.37	49.95	49.33	28.55
H	5.27	4.54	2.78	3.51	4.00	4.09
O	36.07	7.22	13.97	12.58	15.56	6.03
H_2O	11.67	8.60	30.10	26.40	21.78	9.82
Ash	0.66	8.34	8.30	6.03	8.67	36.53
S	0.04	2.85	0.81	0.60	0.12	1.36
N	0.43	1.43	0.67	0.93	0.54	3.62
Molar Composition (MAF)	$CH_{1.33}O_{0.59}$	$CH_{0.81}O_{0.08}$	$CH_{0.77}O_{0.24}$	$CH_{0.84}O_{0.19}$	$CH_{0.97}O_{0..24}$	$CH_{1.72}O_{0.42}$
MW	22.82	14.09	16.61	15.88	16.81	20.44

Table 7 (Con't)

Basic Data for Coal and Biomass Feedstocks Used in the Study
Composition and Thermodynamic Data*

Feedstock	Biomass Wood	Bituminous Kentucky Coal	Lignite N. Dakota Coal	Sub-bituminous Wyodak Coal	Alaskan Beluga Coal	Sewage Sludge
Heating Value (HHV)						
BTU/lb MF	-8800.0	-13650	-10254	-11730	-11082	-5510
kcal /kg MF	-4888.9	-7583.3	-5696.7	-6516.7	-6156.7	-3061.1
kcal / g-mol MAF	-112.8	-119.0	-110.3	-115.3	-117.5	-115.9
Heat of Formation (MAF)						
kcal/kg	-1214.4	-183.0	-593.0	-461.7	-584.9	-1769.7
$?H_F$ kcal/g-mol	-27.7	-2.6	-9.8	-7.3	-9.8	-36.2
Heat Capacity						
(kcal/Kg MF / °C)	0.570	0.315	0.315	0.315	0.315	0.250
kcal/kg mol MF/ °C	13.00	4.44	5.23	5.00	5.30	5.11
Moisture						
Mol H_2O / mol C	0.170	0.086	0.462	0.353	0.294	0.230

MAF Moisture Ash Free
MF Moisture Free
HHV Higher Heating Value
MW Molecular Weight

*From various sources, thermodynamic tables and calculated values

Polycarbonsuboxide Ammonia / Fertilizer Process is Patent Pending

Table 8
Conventional Steam-Oxygen Gasification of Coal
For Ammonia Production
Unit Operation and Process Chemistry
Coal Feedstock – Lignite – Basis – 1 g-mol (MAF)

---

(1) Steam-oxygen gasification

$CH_{0.8}O_{0.2} + 0.8\ H_2O = 1.2\ H_2 + CO$

$\Delta H = +38.2$ Kcal / g-mol endothermic

Energy is provided by lignite combustion with oxygen in gasifier

$CH_{0.8}O_{0.2} + 1.1\ O_2 = 0.4\ H_2O + CO_2$

$\Delta H = -110$ Kcal / mol exothermic

Due to equilibrium heat loss and inefficiency of gasifier,
the thermal efficiency = 50% of endothermic energy
Lignite required = 38.2 / 110.3 x 0.50 = 0.70 g-mol

(2) Air separation plant for 0.77 g-mol oxygen (1.1 x 0.70) production powered by electricity from a power plant fired by lignite at 38% efficiency requires 300 Kwh(t) / ton equivalent to 25.4 Kcal / g-mol lignite = 25.4/110.3 = 0.23 g-mol lignite

(3) Hot gas cleanup removes N, S and particulates

(4) Water gas shift for H_2 production

$CO + H_2O = CO_2 + H_2$

$\Delta H = 0.0$ Kcal / g-mol CO

Polycarbonsuboxide Ammonia / Fertilizer Process is Patent Pending

Table 8 (Con't)
Conventional Steam-Oxygen Gasification of Coal
For Ammonia Production
Unit Operation and Process Chemistry
Coal Feedstock – Lignite – Basis – 1 g-mol (MAF)

---

(5) CO_2 gas separation – Pressure Swing Adsorption (PSA) or cryogenic

(6) Overall H_2 production = 2.2 g-mol H_2 / g-mol lignite

$CH_{0.8}O_{0.2} + 1.8\ H_2O = 2.2\ H_2 + CO_2$

(7) For ammonia production, N_2 supplied from air separation plant

$2.2\ H_2 + 0.735\ N_2 = 1.47\ NH_3$

(8) Gas compressor compresses gas from 70 atm to 300 atm
Requires 10 Kcal lignite (0.1 g-mol) producing electricity at 30% efficiency

(9) Total amount of lignite consumed = 1.00 + 0.70 + 0.23 + 0.10 = 2.03

(10) Yield g-mol NH_3 / g-mol lignite = 1.47 / 2.03 = 0.724
Tons MAF lignite / ton NH_3 = 16.6 / 0.724 x 17 = 1.35
Energy = 22.3 MMBTU x 1.35 = 30.1 MMBTU / ton NH_3

(11) CO_2 emission = (2.03 / 1.47)(44 / 17) = 3.57 Tons CO_2 / ton NH_3

Polycarbonsuboxide Ammonia / Fertilizer Process is Patent Pending

FIGURE 3 - STEAM-OXYGEN COAL GASIFICATION FOR AMMONIA PRODUCTION

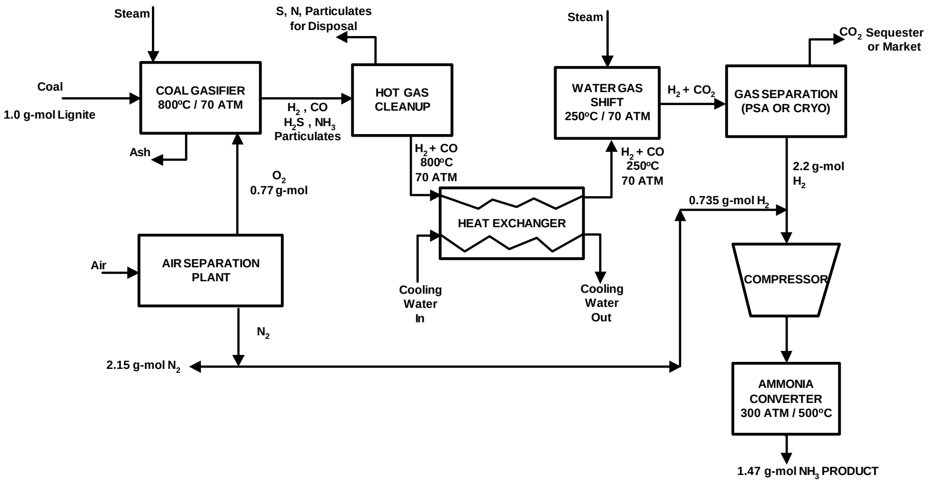


Table 9
Coal Hydrogasification with Steam Reforming of Methane
For Ammonia Production
Unit Operation and Process Chemistry
Coal Feedstock – Lignite – Basis: 1 g-mol (MAF)

(1) Hydrogasification of lignite

$$CH_{0.8}O_{0.2} + 1.2\ H_2 = 0.8\ CH_4 + 0.2\ CO$$

$$\Delta H = -9.8 \text{ Kcal / g-mol lignite - exothermic}$$

(2) Hot gas cleanup, removes N, S and particulates

(3) Steam reforming of methane

$$0.8\ CH_4 + 0.8\ H_2O = 2.4\ H_2 + 0.8\ CO$$

$$\Delta H = +48 \text{ Kcal / g-mol - endothermic}$$

Hydrogen Combustion provides energy at 80% efficiency

H_2 required = 48 / 68 x 0.8 = 0.88 g-mol H_2

(4) Water gas shift of all the CO; and, CO_2 separation by PSA

$$1.0\ CO + 1.0\ H_2O = 1.0\ CO_2 + 1.0\ H_2$$

$$\Delta H = 0$$

Table 9 (Con't)
Coal Hydrogasification with Steam Reforming of Methane
For Ammonia Production
Unit Operation and Process Chemistry
Coal Feedstock – Lignite – Basis: 1 g-mol (MAF)

(5) Overall H_2 production reaction from lignite

$$CH_{0.8}O_{0.2} + 1.8\ H_2O = 2.2\ H_2 + 1.0\ CO_2$$

Net H_2 production = 2.2 - 0.88 = 1.32 g-mol H_2 / g-mol lignite

(6) The compressor takes the equivalent energy of 0.1 g-mol lignite in the form of the electrical power generated at 35% efficiency.

(7) For ammonia production – N_2 from flue gas – 0.44 g-mol

$$1.32\ H_2 + 0.44\ N_2 = 0.88\ NH_3$$

(8) Total lignite required = 1.0 + 0.10 + 0.05 = 1.15 g-mol

(9) Yields g-mol NH_3 / g-mol lignite = 0.88 / 1.15 = 0.76

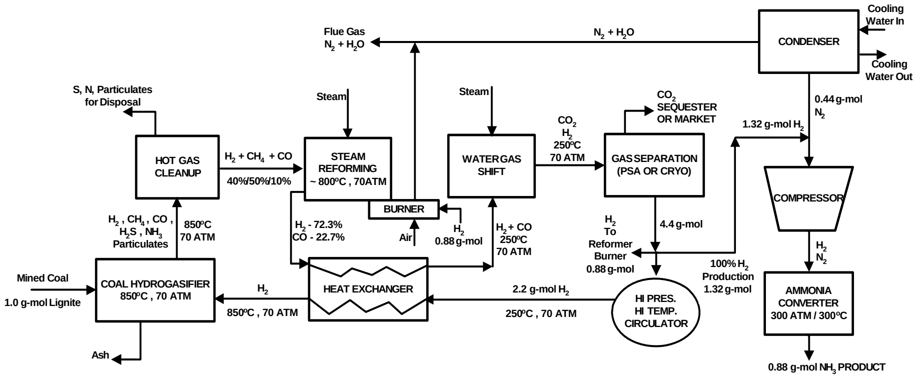
Tons MAF lignite / ton NH_3 = 16.6 / 0.76 x 17 = 1.28

Energy MMBTU / ton NH_3 = 22.3 MMBTU / ton x 1.28 + 28.5

(10) CO_2 emission = (44 / 0.76)(17) = 3.40 tons CO_2 / ton NH_3

Polycarbonsuboxide Ammonia / Fertilizer Process is Patent Pending

FIGURE 4 - COAL HYDROGASIFICATION
WITH STEAM REFORMING OF METHANE FOR AMMONIA PRODUCTION
Coal Feedstock - Basis: 1 mol lignite (MAF)



Polycarbonsuboxide Ammonia / Fertilizer Process is Patent Pending

Table 10
Coal Hydrogasification with Methane Decomposition
For Ammonia and Carbon Production
Unit Operation and Process Chemistry
Coal Feedstock Lignite – 1 g-mol (MAF)

(1) Hydrogasification of lignite

$CH_{0.8}O_{0.2}$ + 1.2 H_2 = 0.8 CH_4 + 0.2 CO

ΔH = -9.8 Kcal / mol lignite exothermic

(2) Methane decomposition

0.8 CH_4 = 0.8 C + 1.6 H_2

ΔH = +14.4 Kcal / mol CH_4 endothermic

Net energy required = 14.4 - 9.8 = 4.6 Kcal / mole CH_4

Supplied by combustion of H_2 at 80% efficiency = 4.6 / 68 x 0.8 = 0.09

(3) Water Gas Shift of CO and CO_2 separation (PSA)

0.2 CO + 0.2 H_2O = 0.2 CO_2 + 0.2 H_2

ΔH = 0

(4) Overall reaction for H_2 production

$CH_{0.8}O_{0.2}$ + 0.2 H_2O = 0.8 C + 0.2 CO_2 + 0.6 H_2

Polycarbonsuboxide Ammonia / Fertilizer Process is Patent Pending

Table 10 (Con't)
Coal Hydrogasification with Methane Decomposition
For Ammonia and Carbon Production
Unit Operation and Process Chemistry
Coal Feedstock Lignite – 1 g-mol (MAF)

(5) Net hydrogen production

0.60 - 0.09 = 0.51 H_2

N_2 Required = 0.51 / 3 = 0.17

0.51 H_2 + 0.17 N_2 = 0.34 NH_3

The nitrogen is provided from the flue gas of the decomposer

(6) Electrical energy to power compressor and circulator requires combustion of lignite of 0.15 g-mol in a power plant at 35% efficiency

(7) Total lignite required = 1.0 + 0.15 = 1.15 g-mol

(8) Yield, g-mol NH_3 / g-mol lignite = 0.34 / 1.15 = 0.30

Tons MAF lignite / ton NH_3 = 16.6 / 0.30 x 17 = 3.25

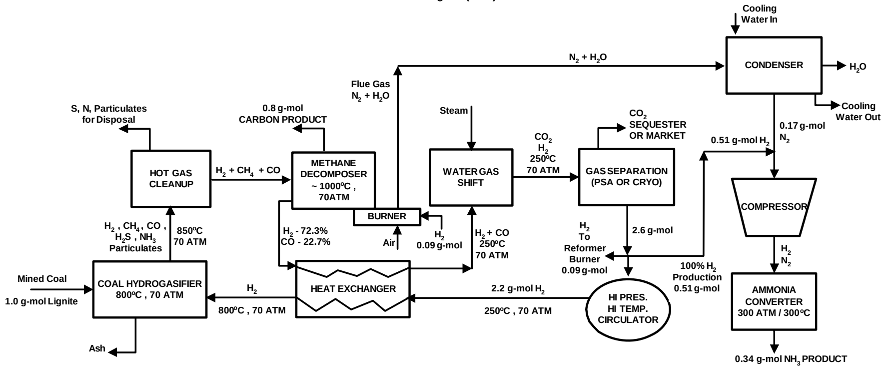
Energy MMBTU / ton NH_3 = 22.3 MMBTU / ton x 3.25 = 72.5

(9) Yield, tons carbon / ton NH_3 = (0.8 / 0.34)(12 / 17) = 1.66 ton C / ton NH_3

(10) CO_2 emission = (0.2 / 0.34)(44 / 17) = 1.52 tons CO_2 / ton NH_3

Polycarbonsuboxide Ammonia / Fertilizer Process is Patent Pending

FIGURE 5 - COAL HYDROGASIFICATION
WITH METHANE DECOMPOSITION FOR AMMONIA AND CARBON PRODUCTION
Coal Feedstock - Basis: 1 mol lignite (MAF)



Polycarbonsuboxide Ammonia / Fertilizer Process is Patent Pending

PolyCarbonSuboxide as a Coproduct of Ammonia Production

Carbon Suboxide is an Anhydride of Malonic Acid

$$CH_2(COOH)_2 \xrightarrow[P_2O_5]{} C_3O_2 + 2H_2O$$

C_3O_2 is a Stable Gas at –78ºC

Polymerizes at 25ºC to Polycarbonsuboxide

$(C_3O_2)_n$ is a Colored, Yellow, Brown, Red Solid Polymer

Has the Structure of Humic Acid Found in Soils

Acts as a Soil Conditioner and Fertilizer

Can Be Produced By Partial Oxidation of Natural Gas and Coal

$$CH_4 + 1/3\ O_2 = 1/3\ C_3O_2 + 2\ H_2 \quad \Delta H = -8.3\ \text{Kcal}$$

$$C + 1/3\ O_2 = 1/3\ C_3O_2 \quad \Delta H = -26.8\ \text{Kcal}$$

Using Air and Steam with Coal in a Non-Equilibrium Cold Plasma

H_2 and N_2 Gas is Co-produced with a Polycarbonsuboxide

Benefit = Produce a Valuable Co-product with Ammonia

And Eliminating CO_2 Emission

Polycarbonsuboxide Ammonia / Fertilizer Process is Patent Pending

Table 11
Coal to Coproduct Polycarbonsuboxide (PCS) and Ammonia Fertilizers
Unit Operation and Process Chemistry

(1) PCS Synthesis in a Plasma Reactor – Lignite Feed

$$2.31\ CH_{0.8}O_{0.2} + (0.15O_2 + 0.57\ N_2) + 0.79\ H_2O$$

Lignite + Air + Steam

$$= 0.78\ (C_3O_2) + 1.73\ H_2 + 0.57\ N_2$$

= PCS + Hydrogen + Nitrogen

The enthalpy for this reaction = 5.9 Kcal / 2.31 = 2.6 Kcal / g-mol lignite

(2) The lignite-fired power plant required for providing electric power to plasma reactor assuming 30% plasma efficiency and 35% power efficiency.

= 2.6 / 0.3 x 0.35 = 25 Kcal / g-mol lignite feed

+ 25 / 110.3 = 0.23 g-mol lignite

(3) Lignite fuel consumed to produce electrical power for compressor = 0.07 g-mol

Total lignite = 1.0 + 0.23 + 0.07 = 1.30

Polycarbonsuboxide Ammonia / Fertilizer Process is Patent Pending

Table 11 (Con't)
Coal to Coproduct Polycarbonsuboxide (PCS) and Ammonia Fertilizers
Unit Operation and Process Chemistry

(4) Ammonia formation at 300 atm and 500^oC

$$1.73\ H_2 + 0.57\ N_2 = 1.14\ NH_3$$

(5) Ammonia Yield g-mol NH_3 / g-mol lignite = 1.14 / 2.31 = 0.49

Net yield = 0.49 / 1.30 = 0.38 g-mol NH_3 / g-mol lignite

Tons lignite / ton NH_3 = (16.6 / 0.38)(17) = 2.56

Tons lignite / ton NH_3 = 22.3 x 2.56 = 57.0 MMBTU / ton NH_3

CO_2 Emission = 0.0 from process

Tons PCS / ton NH_3 = (0.78 / 1.14)(68 / 17) = 2.74

CO_2 from electrical production = (0.3 / 1.14)(44 / 17) = 0.64 tons CO_2 / ton NH_3

Polycarbonsuboxide Ammonia / Fertilizer Process is Patent Pending

FIGURE 6 - COAL HYDROGASIFICATION
COAL TO COPRODUCT POLYCARBONSUBOXIDE AND AMMONIA
Coal Feedstock - Basis: 1 mol lignite (MAF)

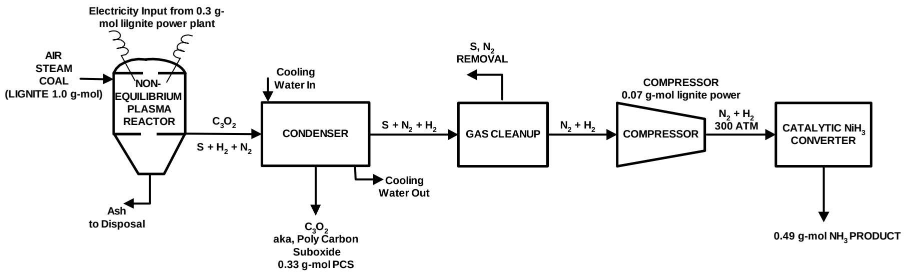


Table 12 - Summary of Conventional and Alternative Ammonia Processes

Process	Conventional Nat. Gas Reforming	Nat. Gas Cracking to Carbon	Coal Steam-oxygen gasification	Coal Hydrogasification with Gas Reforming	Coal Hydrogasification with Gas Cracking	Coal to Coproduct Polycarbonsub-oxide (PCS)
Feedstock	**Nat. Gas**	**Nat. Gas**	**Lignite**	**Lignite**	**Lignite**	**Lignite**
Energy Consumption MMBTU/ton NH_3	25.0	44.8	30.1	28.5	72.5	57.0
Coproduct Carbon Tons C / ton NH_3	0.00	0.70	0.00	0.00	1.66	2.74*PCS
CO_2 emission Tons CO_2 / ton NH_3	1.45	0.00	3.57	3.40	1.52	0.64
Major Capital Equipment Units	Steam Plant Reformer Furnace Water Gas Shift CO_2 Separator Air Separator Compressor NH_3 Converter	Methane Decomp. Flue Gas Condenser Compressor NH_3 Converter	Coal Gasifier Air Separator Water Gas Shift CO_2 Separator Compressor NH_3 Converter Heat Exchanger	Hydrogasifier Steam Reformer Water Gas Shift CO_2 Separator Compressor NH_3 Converter Heat Exchanger	Hydrogasifier Methane Decomp. Water Gas Shift CO_2 Separator Compressor NH_3 Converter Heat Exchanger	Plasma Reactor Condenser Compressor NH_3 Converter
Number of Capital Cost Units	7	4	7	7	7	4
Operating Cost **Energy Cost Units** **Capital Cost Units**	 80 20	 143 11	 10 20	 9 20	 23 20	 18 12
Production Cost **CO_2 Sequestration Cost Units**	100 20	154 0	30 18	29 17	43 8	30 4
Total Production Cost Units	120	154	48	46	51	34
Production Cost $/ton NH_3*	360	463	144	134	153	102
Credit for Coproduct Carbon at $2 / MMBTU	-----	-60	-----	-----	-93	-65
Net Production Cost $ / ton NH_3	360	403	144	138	60	37

*Based on natural gas cost = $10 / MMBTU and coal cost = $1 / MMBTU

Polycarbonsuboxide Ammonia / Fertilizer Process is Patent Pending

Utilization of CO_2

Two other fertilizer products, which can utilize CO_2 and reduce CO_2 from ammonia plants are urea and ammonium carbonate. These are exothermic reactions, which do not require energy input, which would generate additional CO_2

For ammonium carbonate

$$2\,NH_3 + CO_2 + H_2O = (NH_4)_2CO_3$$

$$CO_2 \text{ utilization} = 44 / 2 \times 17 = 1.3 \text{ tons } CO_2 / \text{ton } NH_3$$

For urea

$$2\,NH_3 + CO_2 + H_2O = (NH_2)_2CO + 2\,H_2O$$

$$CO_2 \text{ utilization} = 44 / 2 \times 17 = 1.3 \text{ tons } CO_2 / \text{ton } NH_3$$

From summary table 7 shown below, it is noted that the conventional natural gas reforming process can utilize almost all (90%) of the CO_2 emitted in the conversion to urea or ammonium carbonate. The gasification process can utilize only 37% of the CO_2 emitted, while the hydrogasification and gas-cracking process can also utilize almost all (86%) of the CO_2 generated.

Conclusions

1. The conventional natural gas steam reforming process has the lowest per ton ammonia energy consumption.
2. Coal hydrogasification with steam-reforming of the methane is only slightly more (10%) energy consuming than conventional natural gas.
3. At current world prices for natural gas ($10/MMBTU), the cost of ammonia is more than twice as high as the coal feedstock processes since the current cost of coal energy ($1/MMBTU) is 10 times less than natural gas.

Conclusions (con't)

4. Production co-product carbon with high price natural gas feedstock would require a high value market for the carbon in order to substantially reduce the current cost of ammonia. The CO_2 emission, however, is eliminated.
5. The possible co-production of polycarbonsuboxide as a soil conditioner and fertilizer appears economically attractive, with substantially reduced CO_2 emission.
6. It is recommended that further studies be performed using coal as a feedstock with hydrogasification and with co-production of polycarbonsuboxides.

Polycarbonsuboxide Ammonia / Fertilizer Process is Patent Pending