APPENDIX A

COST ESTIMATION PROCEDURE FOR CARBON MONOXIDE

The price of carbon monoxide was estimated based on the fuel value of carbon monoxide, and the cost and heat of combustion of methane since the price for carbon monoxide was not available from the Chemical Market Reporter. The price ($/kg), and heats of combustion of methane (kcal/kg) and carbon monoxide are given in Table 4.24. The heats of combustion values for both the gases were taken from Perry's Chemical Engineers' Handbook. Using this information, the price of carbon monoxide was estimated in $/kg of CO. The procedure for estimating the price of CO is given below.

Table A.1. Heats of Combustion of Methane and Carbon Monoxide, and Price of Methane.

Property	**Methane**	**Carbon Monoxide**	**Source**
Heat of Combustion (kcal/kg)	13,265.1	2414.7	Perry's Chemical Engineers' Handbook
Selling Price ($/kg)	$0.172/kg, or $3.5/MBTU		http://www.repartners.org/renewables/recosts.htm

Price of methane = $0.172 /kg or $3.5 /MBTU

Heat of combustion of methane = 13265.1 kcal/kg-methane

$$\text{Price of methane in terms of \$/kcal} = \frac{\$\ 0.172\ /\text{kg}}{13265.1\ \text{kcal/kg-methane}}$$

$$= \$\ 1.2966 \times 10^{-5}\ /\text{kcal}$$

Heat of combustion of carbon monoxide = 2414.7 kcal/kg-CO

$$\text{Price of CO in terms of \$/kg-CO} = (\$\ 1.2966 \times 10^{-5}\ /\text{kcal})\ (2414.7\ \text{kcal/kg-CO})$$

$$= \$\ 0.031\ /\text{kg-CO}$$

Thus, the price of CO was estimated to be $ 0.031 /kg-CO.

APPENDIX B

COST ESTIMATION PROCEDURE FOR HYDROGEN

The price of hydrogen depends on the price of natural gas. Using the price of natural gas as \$3.5 per thousand cubic feet or million BTUs, the formula given by Kuehler, 2003 to compute the hydrogen price is:

$$\text{Hydrogen price (\$/Thousand SCF)} = \frac{[0.9(\text{natural gas price in \$/MBTU})]}{2} + 0.45$$

where, SCF is standard cubic feet

$$= 0.45(\text{natural gas price in \$/MBTU}) + 0.45$$

$$= (0.45 \times 3.5 + 0.45)\ \$/1000\ ft^3$$

$$= 0.0715\ \$/m^3$$

Thus, 1 m^3 of hydrogen costs \$ 0.0715

Kuehler, 2003, reported that the energy content (heat of combustion) of natural gas was 310 BTU/SCF. The density of hydrogen at standard state taken from Perry's Chemical Engineers' Handbook is 0.0898 kg/m^3. Using the density of hydrogen, the price of hydrogen can be represented in terms of \$/kg of H_2.

$$\text{Thus, the price of hydrogen} = \$\ \frac{0.0175}{0.0898}\ /\text{kg } H_2 = \$\ 0.796/\ \text{kg } H_2$$

APPENDIX C

PROCEDURE FOR VALUE ADDED ECONOMIC ANALYSIS FOR A PROCESS

The procedure for evaluating a value added economic analysis for a process is discussed below with an example. The procedure is shown for the potentially new process for the production of acetic acid described by Taniguchi, et al., 1998. The calculations involve the raw material costs, product sales, and the energy costs. All the heat energy involved in the potentially new processes was assumed to be in the form of high-pressure (HP) steam. The conditions for HP steam are 47 bar, 260 ºC, and with a specific heat of 1.067 kcal/kg ºC.

The profit is calculated as the difference between the total product sales, raw material costs, and utility costs. The general equation for the calculation of value added economic profit is:

$$\text{Profit} = \Sigma \text{ Product Sales} - \Sigma \text{ Ram Material Costs} - \Sigma \text{ Utility Costs} \qquad (4.1)$$

Utilities include the cost of process steam, cooling water and electricity. In the value added economic analysis, the cost of steam and cooling water are included, but electricity is not included. Evaluating electricity requires a detailed process flow diagram with all pumps and compressors sized. Then the electrical requirements for the prime movers are summed.

The acetic acid process by Taniguchi, et al., 1998, described in Chapter Three is used to illustrate the evaluation. From the HYSYS simulation, the energy supplied to the process was 1,273 x 10^3 kJ/hr, and the process produced 933 kg/hr of acetic acid (Figure 4.12 and Table 4.13). Energy is supplied from the enthalpy of vaporization (ΔH_{vap}) of high-pressure (HP) steam, and the amount of HP steam required for this process is calculated as follows. The enthalpy of evaporation of HP steam at 260ºC is 1661.5 kJ/kg (Smith, et al., 1996).

HP steam required for this process = Energy from HYSYS/ ΔH_{vap} (kJ/hr)(kg/kJ)

$= 1{,}273 \times 10^3 / 1661.5$ kg/hr

= 766 kg/hr

From HYSYS flow sheet, Figure 4.12, the total energy liberated from this process was calculated to be $1{,}148 \times 10^3$ kJ/hr. Cooling water was heated from 30ºC and 50ºC (Turton, et al., 1998). The amount of cooling water required is given by the following equation.

$$q = mc_p\Delta T \quad (4.2)$$

Where, q = Energy absorbed, kcal/hr

m = Mass flow rate of cooling water, kg/hr

c_p = Specific heat of water, kJ/kg-ºC

ΔT = Change in temperature, ºC

The specific heat of water is 1 kcal/kgºC, and the difference in temperature is 20ºC since the water is entering at 30ºC and leaving at 50ºC. The value of q is the energy absorbed by the cooling water, and for acetic acid plant it was $1{,}148 \times 10^3$ kJ/hr. Substituting the values in Equation 4.2, the amount of cooling water required for this process was calculated to be 13,730 kg/hr.

The economic data used for this process is shown in Table 4.13, and it is repeated here for convenience.

Table 4.13. Economic Results for the HYSYS Simulated Process for the Production of Acetic Acid described by Taniguchi, et al., 1998.

Product/Raw Material	**Flow Rate from HYSYS Simulation (kg/h)**	**Cost/Selling Price ($/kg)**	**Source**
Carbon Dioxide	685	0.003	Hertwig, T. A., Private Communication, 2003
Methane	249	0.172	http://www.repartners.org/renewables/recosts.htm
Acetic Acid	933	1.034	Chemical Market Reporter, February 1, 2002
High Pressure Steam	766	0.00865	Turton, et al., 1998
Cooling Water	13,730	6.7×10^{-6}	Turton, et al., 1998
Value Added Profit	$ 913 / hr	97.9 cents/kg-acetic acid	

The product sales, raw material costs, cooling water costs, and the energy costs were calculated using the information provided in Table 4.12. The value added economic profit was calculated by substituting these values in equation 4.1.

HP Steam Cost = 766 x 0.00865 (kg/hr)($/kg)

= $ 6.63 /hr

Cooling Water Cost = 13,730 x 6.7 x 10^{-6} (kg/hr)($/kg)

= $ 0.092 /hr

Methane feed cost = 249 x 0.172 (kg/hr)($/kg)

= $ 42.83 /hr

Cost for delivering CO_2 from pipeline = 685 x 0.003 (kg/hr)($/kg)

= $ 2.06 /hr

Acetic acid sales = 933 x 1.034 (kg/hr)($/kg)

= $ 964.72 /hr

Total Profit, $/h = $ (- 6.63 – 0.092 – 42.83 – 2.06 + 964.72) /hr = $ 913 /hr

Total Profit, \$/kg- acetic acid = 913 / 933 (\$/hr)/(kg-acetic acid/hr)

= 97.9 cents/kg-acetic acid

Thus, the value added economic profit for this potentially new process was 97.9 cents per kg of acetic acid. This profit was based on a selling price of \$1.03 per kg of acetic acid (Chemical Market Reporter, 2002), as shown in Table 4.13. The above economic model considered only the raw material costs, product sales, cooling water costs, and the energy costs. The other operating costs, and a return on investment were not included. Thus, the profit expected from the value added economic model decreases if all the other operating costs were included.

A list of current selling prices of products and raw material costs for various chemicals used in this research was given in Table 4.25.

Table C.1. Product Prices and Raw Material Costs.

Product/Raw Material	**Cost/Selling Price (\$/kg)**	**Source**
Methane	0.172	http://www.repartners.org/renewables/recosts.htm
Hydrogen	0.796	Appendix B
Methanol	0.300	Chemical Market Reporter, 2003
Graphite	0.882	Camford Chemical Prices, 2000
HP Steam	0.00865	Turton, et al., 1998
Cooling Water	6.7×10^{-6}	Turton, et al., 1998
Carbon Monoxide	0.031	Appendix A
Dimethyl Ether	0.946	http://www.che.cemr.wvu.edu/publications/projects/dimethyl/dme-b.pdf
Carbon Dioxide	0.003	Hertwig, T. A., Private Communication, 2003
Formic Acid	0.690	Chemical Market Reporter, April 1, 2002
Mono-Methylamine	1.606	Chemical Market Reporter, 2000
Di-Methylamine	1.606	Chemical Market Reporter, 2000
Ammonia	0.150	Chemical Market Reporter, February 4, 2002
Ethanol	0.670	Chemical Market Reporter, 2002
Acetic Acid	1.034	Chemical Market Reporter, 2002
Ethylbenzene	0.551	Chemical Market Reporter, 2002
Styrene	0.705	Chemical Market Reporter, 2002
Propane	0.163	C & EN, June 2003, p.15
Propylene	0.240	C & EN, June 2003, p.15

APPENDIX D

STREAM FLOW RATES AMONG PLANTS IN THE CHEMICAL COMPLEX

Table D.1. Stream Flow Rates Among Plants, Base Case.

Plant Name	**Entering Streams**	**Flow Rate (metric tons/year)**	**Leaving Streams**	**Flow Rate (metric tons/year)**
Contact process sulfuric acid	Sulfur	1,226,200	Sulfuric acid	3,758,700
	Air	7,847,400	Vent	6,039,200
	Boiler feed water	5,894,700	LP steam	1,952,900
	H_2O	736,600	Blowdown	424,500
			HP steam	2,929,300
			IP steam	588,000
			Others	12,300
Wet process phosphoric acid	Decant water	7,838,800	H_2SiF_6 & H_2O	26,000
	Phosphate rock	4,656,800	SiF_4 & H_2O	1,850,400
	Sulfuric acid	3,758,700	P_2O_5	2,906,100
	LP steam	2,880,400	Cooled LP steam	2,880,400
	H_2O	537,100	H_2O	4,233,600
			Others	1,997,000
GTSP	Phosphate rock	331,000	GTSP	822,300
	P_2O_5	552,200	HF	10,700
			Vapor	30,500
			Others	19,700
MAP & DAP	P_2O_5	2,324,900	MAP	321,900
	NH_3	494,500	DAP	2,062,100
	Urea	28,100	H_2O	128,500
			Others	335,000
Power generation	HP steam	2,929,300	LP steam	3,899,400
	IP steam	588,000	H_2O	848,600
	Fuel (methane)	51,300	CO_2	140,600
	Boiler feed water	1,230,700	Electricity	1,821 (TJ)
Ammonia	Air	720,000	NH_3	658,100
	Natural gas	274,400	CO_2	752,900
	Steam	522,500	H_2O	93,800
			Purge	12,100
Nitric acid	Air	923,100	HNO_3	330,600
	NH_3	48,400	Vent	741,700
	H_2O	100,900		
Methanol	CO_2	62,900	Methanol	181,400
	H_2O	51,100	Vent	800
	Natural gas	68,200		

Table D.1. (Continued)

Ammonium nitrate	HNO_3 NH_3	330,600 48,300	NH_4NO_3 H_2O	246,300 132,600
UAN	NH_4NO_3 Urea	27,900 32,600	UAN	60,500
Urea	NH_3 CO_2 LP steam	56,700 73,200 37,400	Urea H_2O Cooling water NH_3 CO_2	99,800 29,900 37,400 100 100
Acetic acid	CO_2 Methanol CH_4	4,500 4,400 500	Acetic acid H_2O	8,200 1,200
Ethylbenzene	Benzene Ethylene	634,000 227,800	Ethylbenzene	861,800
Styrene	Ethylbenzene	861,800	Styrene Fuel gas Toluene C Benzene	753,300 35,500 6,700 15,600 50,700

Table D.2. Stream Flow Rates Among Plants in Optimal Structure from Superstructure, Case Study One.

Plant Name	Entering Streams	Flow Rate (metric tons/year)	Leaving Streams	Flow Rate (metric tons/year)
Contact process sulfuric acid	Sulfur Air Boiler feed water H_2O	1,226,200 7,847,400 5,894,700 736,600	Sulfuric acid Vent LP steam Blowdown HP steam IP steam Others	3,758,700 6,039,200 1,952,900 424,500 2,929,300 588,000 12,300
Wet process phosphoric acid	Decant water Phosphate rock Sulfuric acid LP steam H_2O	7,838,800 4,656,800 3,758,700 2,880,400 537,100	H_2SiF_6 & H_2O SiF_4 & H_2O P_2O_5 Cooled LP steam H_2O Others	26,000 1,850,400 2,906,100 2,880,400 4,233,600 1,997,000
GTSP	Phosphate rock P_2O_5	331,000 552,200	GTSP HF Vapor Others	822,300 10,700 30,500 19,700
MAP & DAP	P_2O_5 NH_3 Urea	2,324,900 494,500 28,100	MAP DAP H_2O Others	321,900 2,062,100 128,500 335,000
Power generation	HP steam IP steam Fuel (methane) Boiler feed water	2,929,300 588,000 89,200 2,139,900	LP steam H_2O CO_2 Electricity	4,701,200 956,000 244,500 2,149 (TJ)
Ammonia	Air Natural gas Steam	720,000 274,400 522,500	NH_3 CO_2 H_2O Purge	658,100 752,900 93,800 12,100
Nitric acid	Air NH_3 H_2O	923,100 48,400 100,900	HNO_3 Vent	330,600 741,700
Ammonium nitrate	HNO_3 NH_3	330,600 48,300	NH_4NO_3 H_2O	246,300 132,600
Methanol	CO_2 H_2O Natural gas	62,900 51,100 68,200	Methanol Vent	181,400 800
UAN	NH_4NO_3 Urea	27,900 32,600	UAN	60,500

Table D.2. (Continued).

Urea	NH_3 CO_2 LP steam	41,600 53,700 27,400	Urea H_2O Cooling water NH_3 CO_2	73,200 22,000 27,400 0 100
Ethylbenzene	Benzene Ethylene	634,000 227,800	Ethylbenzene	861,800
Styrene	Ethylbenzene	861,800	Styrene Fuel gas Toluene C Benzene	753,300 35,500 6,700 15,600 50,700
New acetic acid	CO_2 CH_4	6,000 2,200	Acetic acid	8,200
Graphite	CO_2 CH_4	67,900 36,700	H_2O C Hydrogen	55,600 46,000 3,000
Synthesis gas	CO_2 CH_4	150,000 54,700	CO Hydrogen	191,000 13,800
Formic acid	CO_2 Hydrogen	74,500 3,400	Formic acid	77,900
Methylamines	CO_2 Hydrogen NH_3	104,100 13,300 25,300	CO MMA DMA H_2O	6,800 26,400 28,700 80,800

Table D.3. Stream Flow Rates Among Plants in Optimal Structure from Superstructure, Case Study Two.

Plant Name	**Entering Streams**	**Flow Rate (metric tons/year)**	**Leaving Streams**	**Flow Rate (metric tons/year)**
Contact process sulfuric acid	Sulfur	894,800	Sulfuric acid	2,742,900
	Air	5,726,700	Vent	4,407,200
	Boiler feed water	4,301,700	LP steam	1,425,100
	H_2O	537,500	Blowdown	309,800
			HP steam	2,137,700
			IP steam	429,100
			Others	8,900
Wet process phosphoric acid	Decant water	5,720,400	H_2SiF_6 & H_2O	18,900
	Phosphate rock	3,398,400	SiF_4 & H_2O	1,350,400
	Sulfuric acid	2,742,900	P_2O_5	2,906,100
	LP steam	2,102,000	Cooled LP steam	2,120,800
	H_2O	392,00		
			H_2O	3,089,500
			Others	1,457,300
GTSP	Phosphate rock	241,500	GTSP	600,100
	P_2O_5	402,900	HF	7,800
			Vapor	22,300
			Others	14,300
MAP & DAP	P_2O_5	1,696,600	MAP	234,900
	NH_3	360,900	DAP	1,504,800
	Urea	20,500	H_2O	93,800
			Others	244,500
Power generation	HP steam	2,137,700	LP steam	4,241,900
	IP steam	429,100	H_2O	806,400
	Fuel (methane)	103,400	CO_2	283,500
	Boiler feed water	2,481,500	Electricity	1,873 (TJ)
Ammonia	Air	537,500	NH_3	491,200
	Natural gas	204,900	CO_2	562,00
	Steam	390,000	H_2O	70,000
			Purge	9,000
Nitric acid	Air	461,600	HNO_3	165,300
	NH_3	24,200	Vent	370,900
	H_2O	50,400		
Ammonium nitrate	HNO_3	165,300	NH_4NO_3	133,000
	NH_3	24,100	H_2O	56,500
Methanol	CO_2	62,900	Methanol	181,400
	H_2O	51,100	Vent	800
	Natural gas	68,200		
UAN	NH_4NO_3	27,900	UAN	60,500
	Urea	32,600		

Table D.3. (Continued).

Urea	NH_3 CO_2 LP steam	56,700 73,200 37,400	Urea H_2O Cooling water NH_3 CO_2	99,800 29,900 37,400 100 100
Ethylbenzene	Benzene Ethylene	634,000 227,800	Ethylbenzene	861,800
Styrene	Ethylbenzene	861,800	Styrene Fuel gas Toluene C Benzene	753,300 35,500 6,700 15,600 50,700
New acetic acid	CO_2 CH_4	6,000 2,200	Acetic acid	8,200
Graphite	CO_2 CH_4	67,900 36,700	H_2O C Hydrogen	55,600 46,000 3,000
Synthesis gas	CO_2 CH_4	151,800 55,400	CO Hydrogen	193,200 13,900
Formic acid	CO_2 Hydrogen	74,500 3,400	Formic acid	77,900
Methylamines	CO_2 Hydrogen NH_3	104,100 13,300 25,300	CO MMA DMA H_2O	6,800 26,400 28,700 80,800
Propylene from CO_2	Propane CO_2	43,400 21,700	CO Propylene H_2O Hydrogen	13,800 41,400 8,900 1,000

Table D.4. Stream Flow Rates Among Plants in Optimal Structure from Superstructure, Case Study Three.

Plant Name	Entering Streams	Flow Rate (metric tons/year)	Leaving Streams	Flow Rate (metric tons/year)
Contact process sulfuric acid	Sulfur Air Boiler feed water H_2O	1,226,200 7,847,400 5,894,700 736,600	Sulfuric acid Vent LP steam Blowdown HP steam IP steam Others	3,758,700 6,039,200 1,952,900 424,500 2,929,300 588,000 12,300
Wet process phosphoric acid	Decant water Phosphate rock Sulfuric acid LP steam H_2O	7,838,800 4,656,800 3,758,700 2,880,400 537,100	H_2SiF_6 & H_2O SiF_4 & H_2O P_2O_5 Cooled LP steam H_2O Others	26,000 1,850,400 2,906,100 2,880,400 4,233,600 1,997,000
GTSP	Phosphate rock P_2O_5	331,000 552,200	GTSP HF Vapor Others	822,300 10,700 30,500 19,700
MAP & DAP	P_2O_5 NH_3 Urea	2,324,900 494,500 28,100	MAP DAP H_2O Others	321,900 2,062,100 128,500 335,000
Power generation	HP steam IP steam Fuel (methane) Boiler feed water	2,929,300 588,000 9,440 2,266,200	LP steam H_2O CO_2 Electricity	4,812,600 970,900 258,900 2,195 (TJ)
Ammonia	Air Natural gas Steam	720,000 274,400 522,500	NH_3 CO_2 H_2O Purge	658,100 752,900 93,800 12,100
Nitric acid	Air NH_3 H_2O	878,800 46,000 96,000	HNO_3 Vent	314,800 706,200
Ammonium nitrate	HNO_3 NH_3	314,800 46,00	NH_4NO_3 H_2O	235,500 125,300
Methanol	CO_2 H_2O Natural gas	62,900 51,100 68,200	Methanol Vent	181,400 800
UAN	NH_4NO_3 Urea	27,900 32,600	UAN	60,500

Table D.4. (Continued).

Urea	NH_3 CO_2 LP steam	55,400 71,600 36,600	Urea H_2O Cooling water NH_3 CO_2	97,600 29,300 36,600 100 100
Ethylbenzene	Benzene Ethylene	634,100 227,800	Ethylbenzene	861,800
Styrene – new method	CO_2 Ethylbenzene	153,100 369,300	CO Styrene H_2O	97,400 362,200 62,700
New acetic acid	CO_2 CH_4	6,000 2,200	Acetic acid	8,200
Graphite	CO_2 CH_4	67,900 36,700	H_2O C Hydrogen	55,600 46,000 3,000
Synthesis gas	CO_2 CH_4	151,800 55,400	CO Hydrogen	193,200 13,900
Formic acid	CO_2 Hydrogen	74,500 3,400	Formic acid	77,900
Methylamines	CO_2 Hydrogen NH_3	66,100 8,500 16,100	CO MMA DMA H_2O	4,300 16,800 18,200 51,300
Propylene from propane dehydrogenation	Propane	43,800	Propylene Hydrogen	41,800 2,000
Propylene from CO_2	CO_2 Propane	21,700 43,400	CO Propylene H_2O Hydrogen	13,800 41,400 8,900 1,000
DME	CO_2 Hydrogen	77,400 8,000	CO DME Methanol H_2O	18,200 22,700 3,900 40,600