“Energy-Mix” for Sustainable Environment in View of Fertilizer/Agriculture/Utility Industries – Revisited

By
P.K. Bhattacharjee, Consultant
Lakeland, FL

To be presented at the annual AlChE (Central Florida) Clearwater Convention
at Sand Key, Clearwater, Florida
June 12 – 13, 2009

Table of Contents **Page No.**

Abstract

The world's energy demand has nearly doubled during the past thirty years (1970-2000) and it is expected to increase 50% more in the next thirty years (2000-2030) along with a population increase from 6 billion to 8 billion.

According to EIA, as the population of the United States increases, our energy consumption is projected to increase to approximately 131 quadrillion Btu in 2030, an increase from 106.5 quadrillion in 2007. The major increases in delivered energy consumptions are in the transportation sector (about 50%) and the commercial sector (37.5%), followed by the residential (20%) and industrial (11%) sectors.

The primary energy use grows more slowly in the industrial sector due to expected efficiency gains, higher real energy prices and economic slowdown. Even so, fossil fuels account for 87% of total primary energy use and will cause a future increase of 50% more carbon emissions from 440 million tons per year in 2000.

However, if non-renewable fuel prices increase and/or become less available; a future could be envisioned using hydrogen economy from recycling and renewables in order to meet the ever increasing energy demand as well as reducing carbon emissions.

This paper revisits 'energy-mix' for a sustainable environment from life cycle analysis (LCA). It discusses advances in hydrogen production technologies for bio-fuels/bio-energy based on nuclear and/or renewable energy sources (solar, wind, water, electrolysis, biomass, etc.) combined with fertilizer production and electricity generation from a silvicultural energy farm on 'marginal' (clay settling areas) and available reclaimed land.

Introduction

The human population has grown worldwide from 2.5 billion to approximately 6 billion between 1950 and 2000 and is estimated to grow between 8 billion and 11 billion by 2050 according to UN 2006 revision. The UN also predicts that 60% of the population will be urbanized, compared to about 30% in 1950.

In 1900, crops were grown in 850 million hectacres of cropland to feed a population of about 1.6 billion without the use of any synthetically manufactured fertilizer. If those same practices were to be applied now, it would perhaps require three to four times the agricultural land area used in 1900 for the current population of 6.5 billion (2009-2010). Instead, present agricultural output utilizes only 1500 million acres of land area with the use of inorganic and organic fertilizer combined with improved nutrient use efficiency (NUE) by intensification of farming.

The increase of 2 to 3 billion people in the world population by 2050 will present a number of significant challenges to the world agriculture as there are no large areas of potentially productive land awaiting exploitation, except perhaps parts of South America. The corresponding increases in demands for fertilizer, fossil- and bio-fuels and feeds etc. will bring business opportunities as well as corporate responsibilities to sustain the global environment and economy by determining the life cycle energy, carbon and greenhouse gas impacts and their costs of carbon capture and its sequestration as necessary. Sequestration could well act as a stepping stone to a renewable-based hydrogen economy.

Finally, the concept of a hydrogen economy envisions a future where all of our energy needs will be met by hydrogen from nuclear and renewable sources like biomass, wind power, solar energy and bio-energy as a low emission or emission free fuel by developing innovative technologies to come.

Energy Outlook – Present and Future

World primary energy consumption doubled in the past thirty-two years between 1970 and 2002 from 61 Peta watt hours to 121 Peta watt hours (10^{15} watt hours) as compared to current use of 140 Peta watt hours). In the U.S., energy consumption was about 31 Peta watt hours in 2008 or 105 quadrillion Btu as reported by EIA with about 300 million people. This is expected to grow by 0.7 quadrillion Btu per year between 2010 and 2030.

Table 1 (Ref: Annual Energy Outlook 2008 [EIA])

U.S. Energy Consumption (2005-2030) in Quadrillion Btu per Year

	Annual Growth, %	**2005**	**2006**	**2010**	**2015**	**2020**	**2025**	**2030**
Delivered Energy		72.82	72.32	75.08	77.99	80.18	82.61	84.86
Electricity Related Losses		27.26	27.19	28.26	29.27	30.67	31.93	33.16
Total	0.7	100.08	99.52	103.34	107.26	110.85	114.54	118.01

The key components for the projected growth are:

1. Faster projected growth in the use of non-hydroelectric renewable energy demand.
2. Higher projections for domestic oil production, particularly in the near term.
3. Slower projected growth in energy demand for natural gas, liquid fuels and coal.
4. Slower projected growth in energy imports, both natural gas and oil.
5. Slower projected growth in energy related CO_2 emissions.

Total energy supplies are met by domestic production and net imports (Imports-Exports).

Table 2

U.S. Energy Supply (2005-2030) in Quadrillion Btu Per Year
Total energy supplies are met by domestic production and net imports (Imports-Exports)

	Annual Growth, %	**2005**	**2006**	**2010**	**2015**	**2020**	**2025**	**2030**
Production	0.80	69.8	71.41	76.17	78.96	82.21	85.53	86.56
Import (Net)	(-) 0.50	30.3	29.98	27.04	28.28	28.75	29.20	31.66
Total		100.10	101.39	103.21	107.24	110.96	114.73	118.22

Of all energy production sources, biomass and other non-hydro renewables (landfill gas, biogenic municipal waste, wind, solar photovoltaic thermal sources etc.) combined are projected to grow 8.7% (4.3% biomass and 4.4% other) annually.

By comparison, U.S. coal production increases from 1,163 million short tons in 2006 to 1,455 million short tons in 2030 at an average rate of increase of 0.8% per year. Domestic production of natural gas is expected to increase from 18.6 trillion cu ft in 2006 to 20 trillion cu ft in 2022 and decrease to 19.5 trillion cu ft by 2030.

Likewise, U.S. crude oil production is expected to increase from 5.1 million barrels/day in 2008 to 6.3 million barrels/day in 2018 and later decrease to 5.6 million barrels/day by 2030. However, total domestic liquid supply is expected to grow from 8.2 million barrels/day in 2006 to 10.4 million barrels/day in 2030.

Table 3

Total Energy Supply in U.S. (2006-2030) in Quadrillion Btu Per Year and (%)

	Year 2006	**Year 2030**
Crude oil	30.28 (29.9)	33,84 (28.6)
(Dry) Natural gas	22.6 (22.3)	(19.7)
Liquid fuels + other petroleum + natural gas plant liquids	6.99 (6.9)	(3.6)
Coal	25.05 (24.7)	(28.9)
Biomass + other	4.8 (4.7)	(8.9)
Renewable energy	8.2 (8.1)	(8.1)
Nuclear	2.9 (2.8)	(2.5)
Hydro	93.83 (101.4)	(0.3)

Total electricity consumption in the U.S. is projected to grow at an average annual rate of 1.1% in comparison with the past annual rate of growth of 4.2% (1970), 2.6% (1980) and 2.3% (1990).

Table 4

Total Electricity Use (Billion kwh)

	Annual Growth, %	**2006**	**2010**	**2015**	**2020**	**2025**	**2030**
Total Electricity Use Including CHP	1.1	3,814	4,037	4,248	4,477	4,717	4,972

The share of coal consumption for electric power increases from about 50% in 2006 to 56.6% in 2030. The uses of natural gas and petroleum decrease by 5.3% and 0.4% respectively. The renewable sources on the other hand increase by 2.3%.

Energy-Related Carbon Dioxide Emissions

CO_2 emissions from the combustion of fossil fuels are proportional to fuel consumption and carbon content. Accordingly, in the U.S. the projected energy related CO_2 emissions will grow from 6,479 million short tons in 2005 to 7,536 million short tons in 2030. Based on the 2008 'energy-mix', U.S. Energy Information Administration (EIA) projects a 7% decrease from about 25% in 2000 to 18% by 2030. If the other industrialized nations (e.g. USA, UK, Germany, Netherlands, Denmark, Austria, Luxembourg, Belgium, Italy and Japan) as committed, lower their CO_2 emission levels, the developing nations are going to exceed their share of CO_2 emissions by 2025.

Table 5

CO_2 Emissions from Different Regions in the World

World Total Energy Related CO_2 Emission in million tons

Country	1996	2006
United States	5,512 (24%)	5,902 (20%)
China	2,937 (12.9%)	6,018 (20.6%)
Russia	1,617 (7.1%)	2,601 (8.9%)
Japan	1,138 (5%)	1,247 (4.3%)
India	835 (3.7%)	1,293 (4.4%)
Germany	892 (3.9%)	858 (2.9%)
Canada	522 (2.3%)	614 (2.1%)
UK	591 (2.6%)	586 (2%)
South Korea	404 (1.77%)	515 (1.8%)
Italy	424 (1.8%)	468 (1.6%)
Mexico	333 (1.46%)	436 (1.49%)
Brazil	307 (1.35%)	377 (1.29%)
World	**22,806 (100%)**	**29,195 (100%)**

Table 6

U.S. 'Energy-Mix' in Year 2006 and 2030 (Projected) - Quadrillion Btu

	2006	2030
Petroleum (Production + Import)	39.85 (39.3%)	40.67 (34.4%)
Dry Natural Gas (Production + Import)	22.60 (22.3%)	23.28 (19.7%)
Coal (Production + Export)	24.07 (23.5%)	30.49 (25.8%)
Nuclear (Production)	8.21 (8.10%)	9.57 (8.1%)
Hydroelectric (Production)	2.89 (2.85%)	3.00 (2.5%)
Biomass (Production)	2.94 (2.90%)	8.12 (6.9%)
Other Renewables (Production)	0.88 (0.87%)	2.45 (2.1%)
Other (Production)	0.50 (0.49%)	0.64 (0.5%)
Total	**101.94 (100%)**	**118.22 (100%)**

The combined share of carbon-neutral renewables and nuclear energy sector will grow from about 15% to 20% in the U.S. by 2030 even after an increase of 15 quadrillion Btu of energy consumption as projected between 2006 and 2030.

Global Carbon Cycle and Climate Change Issues

The carbon cycle is a complex series of processes whereby CO_2 is exchanged between the living and non-living portions of the biosphere, driven in part by biological processes and resulting in a constant supply of carbon in life.

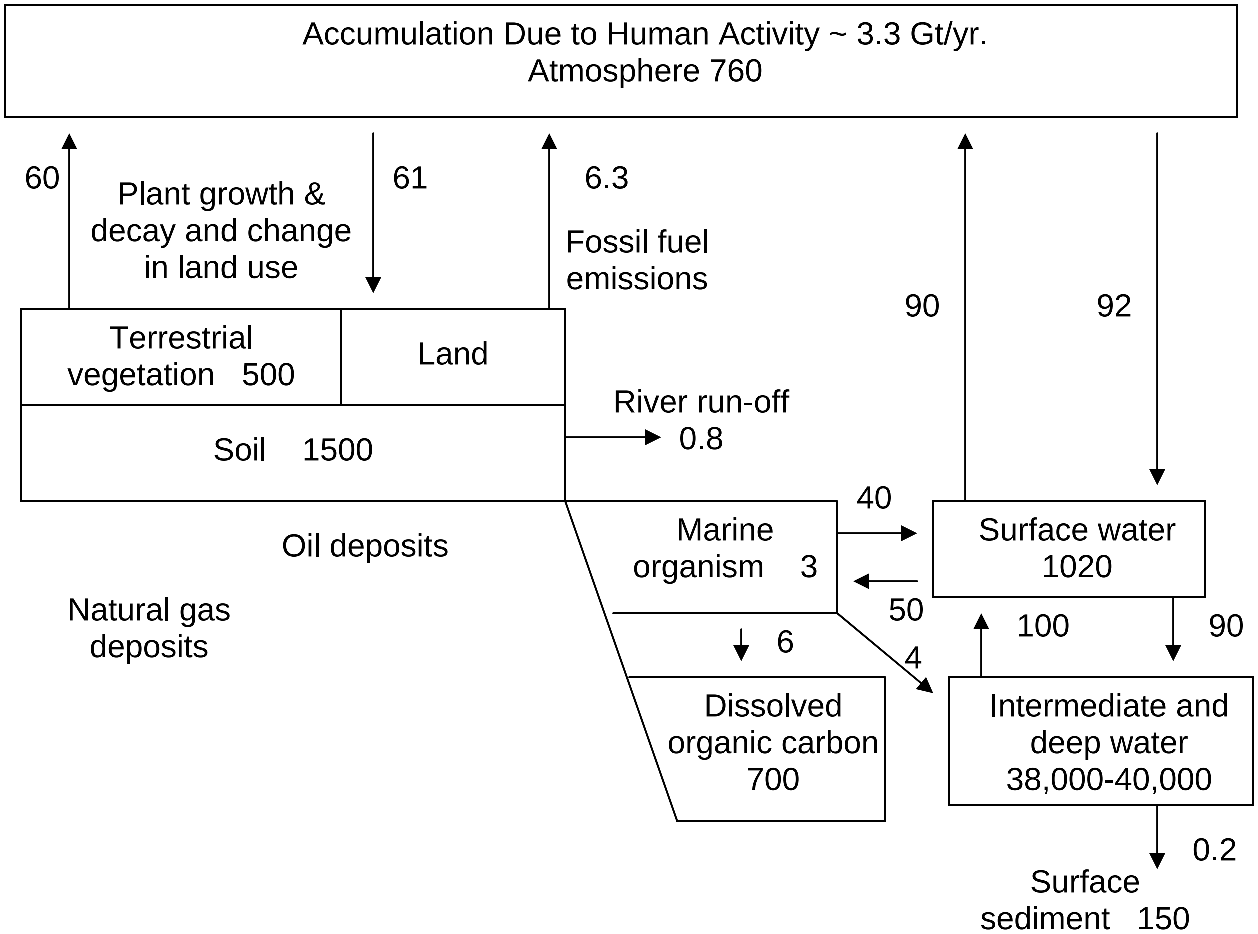


Figure – 1

(Based on Data from IPCC)

Carbon fluxes are shown in arrows expressed as gigatons of C (Gt C) per year and reservoirs in Gt of carbon (Gt C)

The current ambient CO_2 concentration has exceeded 370 ppmv and is expected to reach 550 ppmv by 2050 (Raven and Karley, 2006) causing maximum and minimum temperature increases and precipitation. This, in effect, will influence agriculture or 'agro-ecosystems' on the whole. Elevated CO_2 is also expected to reduce transpiration of most plants. When climate change variables alter soil factors to the extent that roots cannot explore for food, nutrient 'stress' combined with water and temperature stress will reduce growth. As a result, cropping and farming systems will require alteration.

American Clean Energy and Security Act of 2009

- Requires electricity suppliers to generate a percentage of power from wind, biomass, solar, geothermal and other renewable sources
- Promotes technologies to capture and store CO_2 from coal-fired power plants
- Provides financial aid to auto companies to retool their plants to build electric vehicles
- Creates a smart electricity grid that encourages the development of energy efficient buildings, appliances and vehicles
- Establishes a cap and trade mechanism to reduce global warming pollution from industrial sources and creates programs to reduce emissions of hydrofluro carbons and black carbon (soot)
- Promotes green jobs with grants and worker retraining programs.

U.S. electricity use is projected to increase 45% by 2030 vs. 85% of U.S. energy production today by coal and other fossil fuels. Renewable electricity mandate requiring 5% of electricity to come from such sources as wind, biomass, solar and geothermal by 2012 and 25% from renewable sources by 2025.

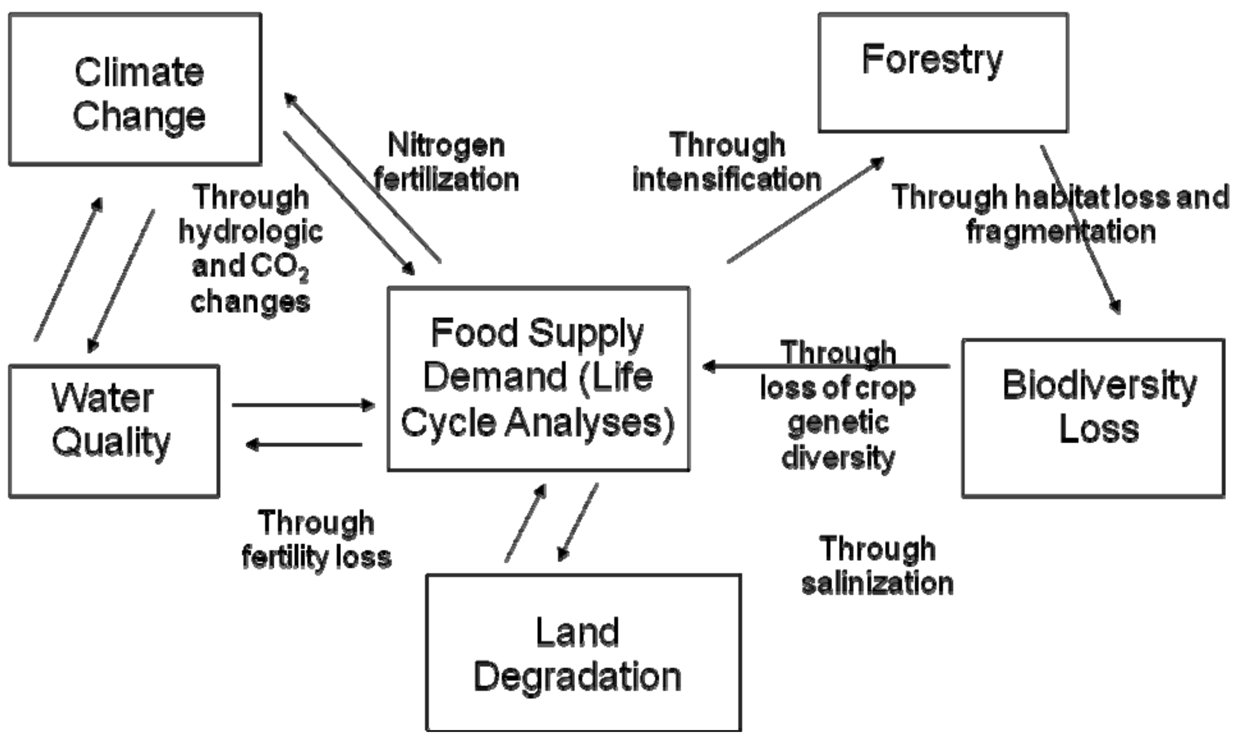


Figure - 2

Life Cycle Assessment (LCA)/Analysis (LCA)

LCA is a technique to assess the environmental aspects by analyzing the potential impacts of a good process or service from cradle to grave. It is a comprehensive accounting of a product's flows both material and energy-wise to and from the environment. Based on a LCA study and using a modified version of 'GREET' model software developed by Argonne National Laboratory (ANL), California Ethanol & Power (CE&P) could reduce 95% of GHG emission from an ethanol process and export electricity to grid. It produces 66 million gallons of low carbon ethanol and generates 800,000 million cu ft of gas per year to supply 50% of the electricity to the investor-owned grid from a 49.9 MW electrical power plant.

Table 7

From	GHG Emission (LB/MM Btu)
Sugarcane farming	32.72
Fuel production delivery	8.35
Electricity credit	(-) 30.40
Total	**10.67**

Table 8

Energy Requirement and GHG Equivalent

	Energy Requirement MM Btu/MM Btu	Total GHG Requirement lb eqv. CO_2/MM Btu
Bio-ethanol from Wheat	0.465	0.673
Bio-ethanol from Sugarbeet	0.496	0.928
Bio-diesel from Rape Seed Oil	0.437	0.951

The above table shows that bio-ethanol technology requires more energy input per unit of bio-ethanol energy output. However, bio-diesel has the highest primary energy input of three options, mainly due to increased energy input from nitrogen fertilizer manufacture and natural gas and methanol required for the esterification process.

Carbon Capture and Sequestration (CCS) to Minimize GHG Emissions in Atmosphere

Coal fired power plants generate about half of the electricity in the U.S. Presently, worldwide, more than 22 billion tons of CO_2 are released every year from human related activities. The existing coal fired power plants emit about 2 billion tons of CO_2 annually.

The two general approaches for reduction of carbon dioxide emissions from the existing plants are post-combustion capture and oxy-combustion. The proven MEA-based CCS will decrease the power plant's net efficiency by 30% and increase the retrofit project cost by more than 85%. Again, the economic benefit of oxy-combustion using pure oxygen is limited due to capital cost and energy consumption. Several R&D projects under DOE/NETL focus on membranes, solvents and sorbents for post-combustion, oxy-combustion and chemical looping combustion systems.

A list of current CO_2-capture technology-based R&D programs is shown in Table 9 to lower CO_2 emissions. The electric power sector accounted for 41% of energy related CO_2 emissions in 2007 compared to 4% by the chemical industry.

Carbon sequestration in underground reservoirs and oceans including land in terrestrial ecosystems and in solid compounds e.g. magnesium carbonate and CO2 clathrate is being studied.

Table 9

CO_2 Emission from Various Fuels

Fuel	**CO_2 Emissions in lbs. per 10^6 Btu**
Natural Gas	117
LPG	139
Propane	139
Aviation Gasoline	153
Automobile Gasoline	156
Kerosene	159
Fuel Oil	161
Tires/Tire Derivative Fuel	189
Wood and Wood Waste	195
Coal (Bituminous)	205
Coal (Lignite)	215
Petroleum Coke	225
Coal (Anthracite)	227

Table 10

Estimated Emission and Storage Costs

	$ per short ton of carbon	**$ per short ton of CO_2**
Emission cost	45.45	12.40
Storage cost	33.64	9.17

The U.S. EPA has proposed a national system for annual reporting of greenhouse gas (GHG) emissions in 2010 for industries that emit more than 27,500 tons/year of GHG.

Table 11

Table 1: Current CO_2-capture technology R&D projects

Project Focus	Participant
Post-Combustion Membranes	
Biomimetic Membrane	Carbozyme, Inc.
CO_2 Membrane Process*	Research Triangle Institute
Membrane Process for CO_2 Capture*	Membrane Technology and Research
Novel Dual-Functional Membrane	Univ. of New Mexico
Novel Polymer Membranes	Membrane Technology and Research
Electrochemical Membranes	DOE/NETL's ORD
Post-Combustion Solvents	
High-Capacity Oligomers*	GE Global Research
Integrated Vacuum Carbonate Absorption Process*	Illinois State Geological Survey
Phase Transitional Absorption	Hampton Univ.
Ionic Liquids	Univ. of Notre Dame
Reversible Ionic Liquids*	Georgia Tech Research Corp.
Post-Combustion Sorbents	
Amine-Grafted Zeolites	Univ. of Akron
Dry Carbonate Process	Research Triangle Institute
Low-Cost CO_2 Sorbent*	TDA Research
Metal Organic Frameworks	UOP LLC
Carbon Sorbents*	SRI International
Solid Sorbents*	ADA-ES, Inc.
Reactor Design Studies	DOE/NETL's ORD
Carbon-Supported Amine Sorbents	DOE/NETL's ORD
Supported Amine Sorbent Modeling	DOE/NETL's ORD
CO_2 Capture Sorbent-Based Device Simulation	DOE/NETL's ORD
Surface Immobilization Nanotechnology for Sorbents	DOE/NETL's ORD
CO_2 Sorbent Development	DOE/NETL's ORD
O_2 Supply	
Oxygen Transport Membrane-Based Oxy-Combustion	Praxair, inc.
Compression	
Novel Concepts for CO Compression	Southwest Ressearch Institute
Supersonic Shock Wave Compression Technology	Ramgen Power Systems
Oxy-Combustion	
PC Oxy-Combustion Pilot Testing	Babcock & Wilcox
Oxy-Combustion Impacts in Existing Coal-Fired Boilers*	Reaction Engineering International
Oxy-Combustion Boiler Development for Tangential Firing*	Alstom Power
Oxy-Combustion Boiler Material Development*	Foster Wheeler NA Corp.
Oxy-Combustion CO_2 Recycle Retrofit	Southern Research Institute
Pilot-Scale Oxy-Fuel Research	Canada Centre for Mineral and Energy Technology (CANMET)
PC Oxy-Combustion with Integrated Pollutant Removal	Jupiter Oxygen Corp.
Evaluation of CO_2 Capture/ Utilization/Disposal Options	Argonne National Laboratory
Fluegas Purification using SOx/NOx Reactions During CO_2 Compression*	Air Products and Chemicals, Inc.
Near-Zero Emissions Oxy-Combustion Fluegas Purification*	Praxair, Inc.
Oxy-Combustion with CO_2 Capture	DOE/NETL's ORD
Oxy-Fired Combustion Simulation	DOE/NETL's ORD
Materials Performance in Oxy-Combustion Environments	DOE/NETL's ORD
Oxy-Fuel Flame Property Measurement	DOE/NETL's ORD
Wireless Sensing in Oxy-Fuel Environments	DOE/NETL's ORD
Chemical Looping Combustion (CLC)	
CLC Prototype*	Alstom Power, Inc.
Coal Direct Chemical Looping*	Ohio State Univ.
CLC Oxygen Carrier Studies	DOE/NETL's ORD
CLC Model Development	DOE/NETL's ORD
Laboratory-Scale CLC Combustor	DOE/NETL's ORD
Design and Control of CLC Systems	DOE/NETL's ORD
* New projects announced in 2008.	

Hydrogen Economy and Choice of Feed Stocks

Hydrogen economy has been considered under few assumptions that

(a) oil peak production will occur between 2005 – 2015. After the peak, oil production will decline and price will increase due to increasing demand for oil by Asia and other developing countries.
(b) The threat to global warming due to greenhouse gas (GHG) emissions and its impact on acidification of the oceans and agriculture with respect to crop growth and its nutrition uptake from soil due to water and temperature stress.
(c) Heating value of hydrogen is higher i.e. 51,329 Btu per lb against either crude oil, natural gas or coal (Ref Table 9)
(d) Water electrolysis has a 'zero' CO2 emission if the energy source is from 'the renewables' (wind, solar, biomass, hydro, atomic energy).

From feed stock reaction stoichiometry, natural gas has the least CO2 emission potential of all other feed stock choices e.g., propane, naphtha, coke on coal. Coal releases much more CO2 per unit of hydrogen or electricity produced than methane or even petroleum. The cost of adding a carbon capture system to a coal gasification plant is about 10% of the cost of the hydrogen produced or $1.72 per lb of hydrogen vs. $0.91 per lb of hydrogen with steam reformation of natural gas or $2.12 per gallon of gasoline equivalent (GGE).

Hydrogen Technology Advancements

Fossil fuels (natural gas, liquid hydrocarbons and coal) are currently in use in the world for 96% of total hydrogen production. The remaining 4% is produced by electrolysis.

Several advanced techniques are being developed to produce hydrogen in the future. Two new methods are being developed that would use either solar or nuclear heat for dissociation of sulfuric acid and SO_3 at a temperature lower than 850°C and using membrane separation at a higher pressure in order to improve efficiency and lower capital cost.

Dissociation reaction

$$2H_2SO_4 \xrightarrow[\text{heat}]{850^\circ C} 2H_2O + 2SO_3 \ (1); \quad 2SO_3 \rightleftharpoons 2SO_2 + O_2 \ (1a)$$

The hybrid sulfur process (also known as Westinghouse GA 22 and ISPRA Mark II) has a single electrolysis step that completes the cycle.

$$SO_2\,(aq) + 2H_2O\,(l) \rightarrow H_2SO_4\,(aq) + H_2\,(g) \text{ at } 80^\circ C \ (2)$$

The ISPRA Mark III process has one chemical reaction followed by an electrolysis step.

$$Br_2\,(aq) + SO_2\,(aq) + 2H_2O\,(l) \rightleftharpoons 2HBr\,(g) + H_2SO_4\,(aq) \text{ at } 77^\circ C \ (3)$$

$$2HBr\,(g) \rightarrow 2Br_2\,(l) + H_2\,(g) \text{ at } 77^\circ C \ (4)$$

Also PEM (Polymer Electrolyte Membrane) electrolyzer is developed to convert HBr to bromine and hydrogen.

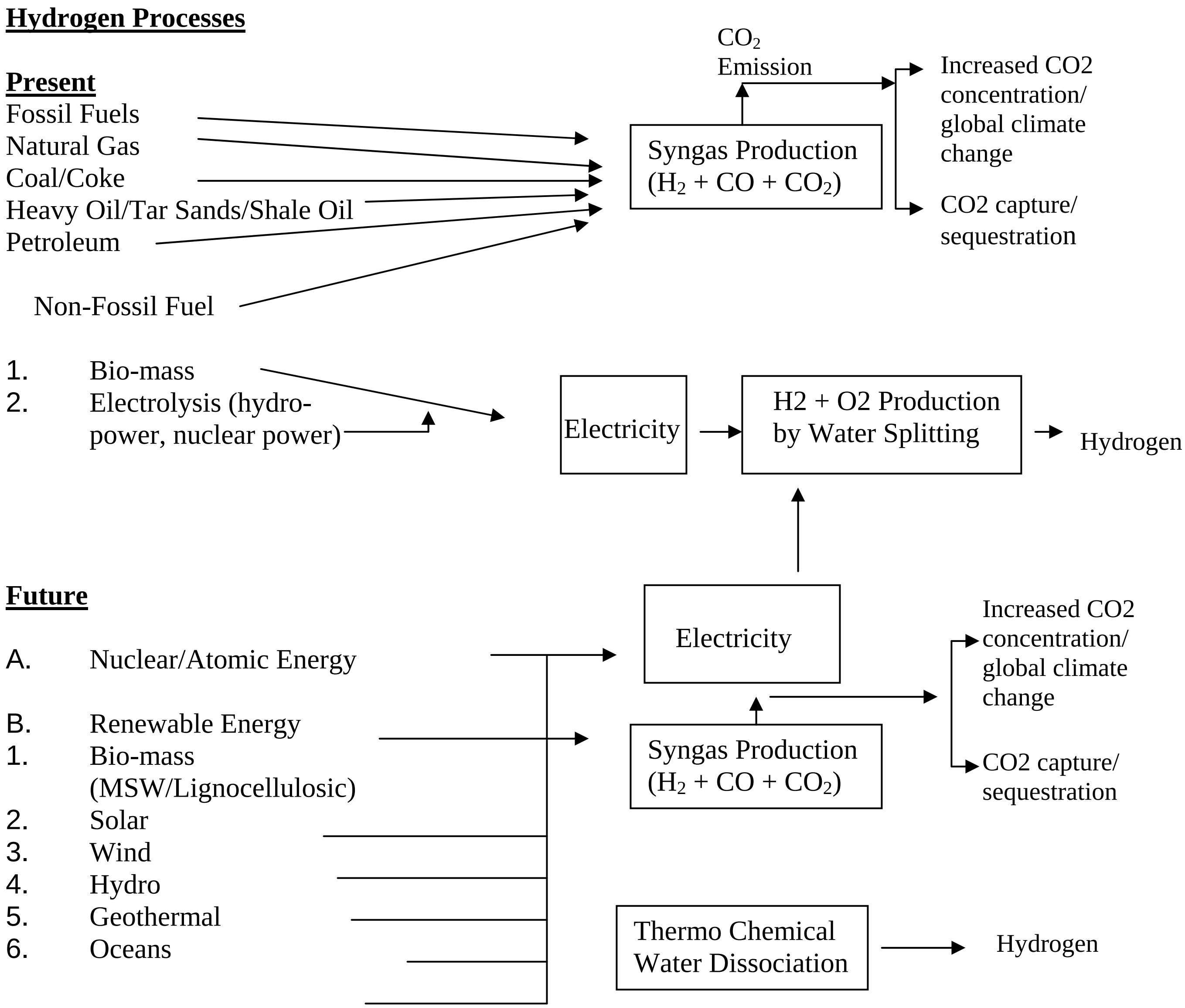

Hydrogen Processes
Present
Fossil Fuels
Natural Gas
Coal/Coke
Heavy Oil/Tar Sands/Shale Oil
Petroleum
Non-Fossil Fuel
1. Bio-mass
2. Electrolysis (hydro-power, nuclear power)
CO_2 Emission
Syngas Production (H_2 + CO + CO_2)
Increased CO2 concentration/ global climate change
CO2 capture/ sequestration
Electricity
H2 + O2 Production by Water Splitting
Hydrogen
Future
A. Nuclear/Atomic Energy
B. Renewable Energy
1. Bio-mass (MSW/Lignocellulosic)
2. Solar
3. Wind
4. Hydro
5. Geothermal
6. Oceans
Electricity
Syngas Production (H_2 + CO + CO_2)
Increased CO2 concentration/ global climate change
CO2 capture/ sequestration
Thermo Chemical Water Dissociation
Hydrogen

Figure – 3

Centralized hydrogen production from biomass gasification has been developed with the following steps:

- Biomass feed preparation
- Gasification/reformation
- Gas cleaning and synthesis gas production
- Shift reaction (HTS/LTS)
- CO_2 removal followed by pressure swing adsorption (PSA)
- Hydrogen gas storage

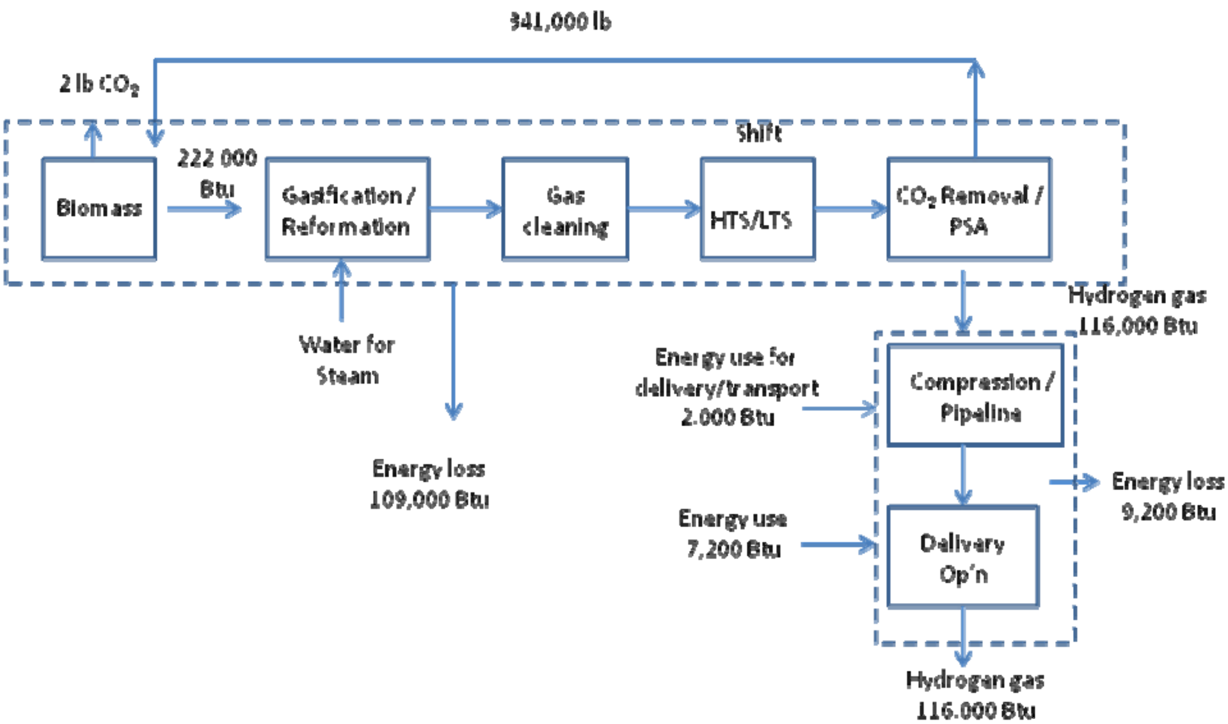


Figure - 4

<u>Overall Energy Balance (2030)</u>

	Energy In	**Energy Out**
Biomass	222,000 Btu	-
Electricity	3,000 Btu	-
Delivery/Transport/Operation	9,200 Btu	-
Hydrogen production	-	116,000 Btu
Energy losses	-	118,200 Btu
Total	**234,200 Btu**	**234,200 Btu**

Hydrogen cost for central steam methane reforming is estimated to be reduced from the current amount of $0.83/lb to $0.78/lb without carbon capture. Also, gasification-based fuel cell combined system concepts are underway under DOE/NREL five year strategic programs that are considering 'coal + 15% bio-mass' mix in addition to petroleum coke and waste product to produce electric power and hydrogen and transportation fuels.

Table 12

Hydrogen Production Costs for Various Commercial Processes

Capacity: 92,655 tons of hydrogen per year

Process	**Steam Reforming**	**Partial Oxidation**	**Texaco Coal Gasification**	**Water Electrolysis**	
Feed stock	***Natural gas***	***Refinery oil***	***Coal***	***Water + Electricity***	
Consumption per ton of hydrogen	150 x 10^6 Btu	139 cu ft	8.87 tons	46,540 kwh	
By-product per ton of hydrogen	13 lbs. steam	243 lbs. sulfur	567 lbs. sulfur	2.658 tons	
Capital cost $MM	**250**	**650**	**850**	**400**	
Variable cost, ($/100 lb. of hydrogen) Feed	26.25	48.65	22.18	81.44	58.17
Catalyst/Chemicals/ Utilities	1.50	1.50	3.00		
Subtotal A	***27.75 @ $3.5/MM Btu***	***50.15 @ $7/cuft***	***25.18 @ $50/ston***	***81.44 @ 3.5 cents/kwh***	***58.17 @ 2.5 cents/kwh***
Fixed cost, ($/100 lb. hydrogen) Operating labor	20.17	20.17	25.00	20.17	
Maintenance/labor/materials	9.70	18.00	22.80	11.47	
Administration	1.35	1.35	1.35	1.35	
Interest and taxes	8.01	21.04	27.51	12.95	
Insurance	0.70	1.75	2.56	1.08	
Depreciation	13.49	35.07	45.86	21.58	
Miscellaneous	0.13	0.35	0.51	0.26	
Construction cost	0.81	2.10	2.75	1.30	
Interest on working capital	0.40	1.05	1.36	0.65	
Subtotal B	***54.76***	***100.88***	***129.70***	***70.81***	
Total A and B	***82.51***	***151.03***	***154.88***	***152.25***	***128.98***
By-product credit	-	(-) 0.36	(-) 0.85	(-) 14.01	
Manufacturing cost, $/100 lb. hydrogen	82.51	150.67	154.03	138.24	114.97
Manufacturing cost, $/million Btu of hydrogen	16.10	29.35	30.00	26.93	22.40

Table 13

U.S. DOE Goals for Future Hydrogen Cost

Technology	Goal	Target Year
Hydrogen from Natural Gas and Liquid Fuels	Delivered cost of $1.50 kg ($0.68/lb)	2010
Electrolysis	Delivered cost of $2.50/kg ($1.14/lb)	2010
Photo-electrochemical Water Splitting	Delivered cost of $5/kg ($2.27/lb)	2015
Biomass	Delivered cost of $2.60/kg ($1.18/lb)	2015
Biological System	Delivered cost of $10/kg ($4.54/lb)	2015
Thermo-chemical Cycles Using Nuclear Heat	Demonstration of technical capability with gasoline	2015
Other	Evaluate new production technology	2015

Table 14

Lower Heating Value (LHV) of Feed Stocks

Fuel	LHV Million Btu per s.ton	Btu per lb
Hydrogen	102.658	51,329
Natural Gas		14,409
Crude Oil	37.400	18,700
Ethane	41.450	20.725
Coal	24.000	12,000
Coke	26.500	13,250
Coke Oven Gas	30.530	15,266
Methane	42.866	21,433
Sewage or Bio-gas	20.368	10,184

With increased global demand of 4% per year for natural gas, production is expected to peak by 2030 and Liquified Natural Gas (LNG) is expected to represent about 15% of the world's gas demand. Worldwide, reserve to production ratio of natural gas is an estimated 63 years compared to 48 years for oil and about 200 years for coal.

Hydrogen production from 'biomass' adds a few more steps before gasification and gas cleaning that increases the final manufacturing cost than from natural gas under current natural gas price at this time. At $39.15/ton of dry wood delivered, electricity cost would be $0.05-$0.06 per kwh energy for a 50 MWe electric power plant or a methanol plant for conversion to hydrogen. Also, bio-fuels e.g. ethanol and bio-diesel are produced from woody or agricultural crops such as eucalyptus, cottonwood or switchgrass, bagasse and others.

Ammonia Plant Energy Efficiency and CO_2 Emission

Improvements in energy efficiency of ammonia plant can reduce CO_2 emission with the use of a feed stock with the highest hydrogen to carbon ratio such as methane and natural gas vs. propane or butane.

Table 15

Comparative CO_2 Emission per Unit of Hydrogen Production from Feed Stocks of Different Processes

Feed Stock	Process	C:H in Feed	Ton CO_2/Ton H_2 in Product	% H_2 Derived from Steam/Water
Water	Electrolysis	0:1	0	100
Natural Gas	Catalytic Steam Reformation	1:4	0.25	50
Naphtha	Partial Oxidation/Reforming	1:2	0.33	66
Propane	Reforming	1:2.6	0.30	60
Coal	Gasification	1:0	0.50	100

Ammonia plant energy efficiency is calculated from energy input for endothermic reactions, heating and compression and purification vs. energy output from cooling and exothermic reactions.

Table 16

Overall Energy Efficiencies of Ammonia Production in Previous Years

Year	Technology	Efficiency in Million Btu/ton Ammonia (LHV)
1940	Wood/Coke Gasification	69 – 77.5
1953-1955	Steam reformation at low pressure	40.5 – 45.7
1965-1975	Steam reformation at 440 psia/-515 psia	28 – 39
1975-1984	Low energy	25 – 29.5
After 1990	New concepts and advancement	< 24

Table 17

Ammonia Plant Energy Efficiency vs. CO_2 Emission
(Based on Feed + Fuel Consumptions and Overall with Power + Steam)

Region	**Energy Efficiency (Feed + Fuel Consumption)**	**Energy Efficiency (Overall) including power import (*1) + steam import (*2)**	**CO_2 Emission without Steam Export Credit**	**CO_2 Emission with Steam Export and Power Import with Credit (*3)**	**CO_2 Emission with Steam Export and Power Import without Credit**
	Million Btu per ton Ammonia		*Tons of CO_2 per ton Ammonia*		
World	35.85	33.89	1.99	1.87	2.03
North America	32.66	30.70	1.81	1.69	1.85
Europe	30.16	28.20	1.67	1.56	1.72
USA	33.00	31.04	1.83	1.71	1.87
	29.00	27.04	1.61	1.50	1.62

(Stoichiometric requirement 18.00 million Btu per ton of ammonia based on pure methane)

(*1) - Electrical power import 0.082 MWH/ton of ammonia or 0.723 million Btu/ton of ammonia
(*2) – Steam export credit 2.413 million Btu/ton of ammonia
(*3) – Less CO_2 emission 0.16t per ton of ammonia (w/ credit)

Some of the improvements of ammonia plant energy efficiency have been obtained from proprietary and confidential technologies available from each vendor and new CO_2 recovery processes including more efficient turbines and better integration processes. However, if the U.S. can improve ammonia plant efficiency from 33 to 29 million Btu/ton of ammonia, CO_2 reduction can be lowered 12% in addition to increased ammonia production. A modernization of a 2000 ton per day ammonia plant can expect to pay off its capital investment within a period of 3-6 years even at a natural gas price of $3.50 or $7 per million Btu.

A. $\frac{4\times10^6 \text{ Btu of natural gas}}{\text{ton of ammonia}} \times \frac{\$3.5}{10^6 \text{ Btu of natural gas}} \times \frac{710{,}000 \text{ tons of ammonia}}{\text{year}} = \$9.94 \frac{\text{MM}}{\text{year}}$

B. $\frac{4\times10^6 \text{ Btu of natural gas}}{\text{ton of ammonia}} \times \frac{\$5.0}{10^6 \text{ Btu of natural gas}} \times \frac{710{,}000 \text{ tons of ammonia}}{\text{year}} = \$14.20 \frac{\text{MM}}{\text{year}}$

C. $\frac{4\times10^6 \text{ Btu of natural gas}}{\text{ton of ammonia}} \times \frac{\$7.0}{10^6 \text{ Btu of natural gas}} \times \frac{710{,}000 \text{ tons of ammonia}}{\text{year}} = \$19.88 \frac{\text{MM}}{\text{year}}$

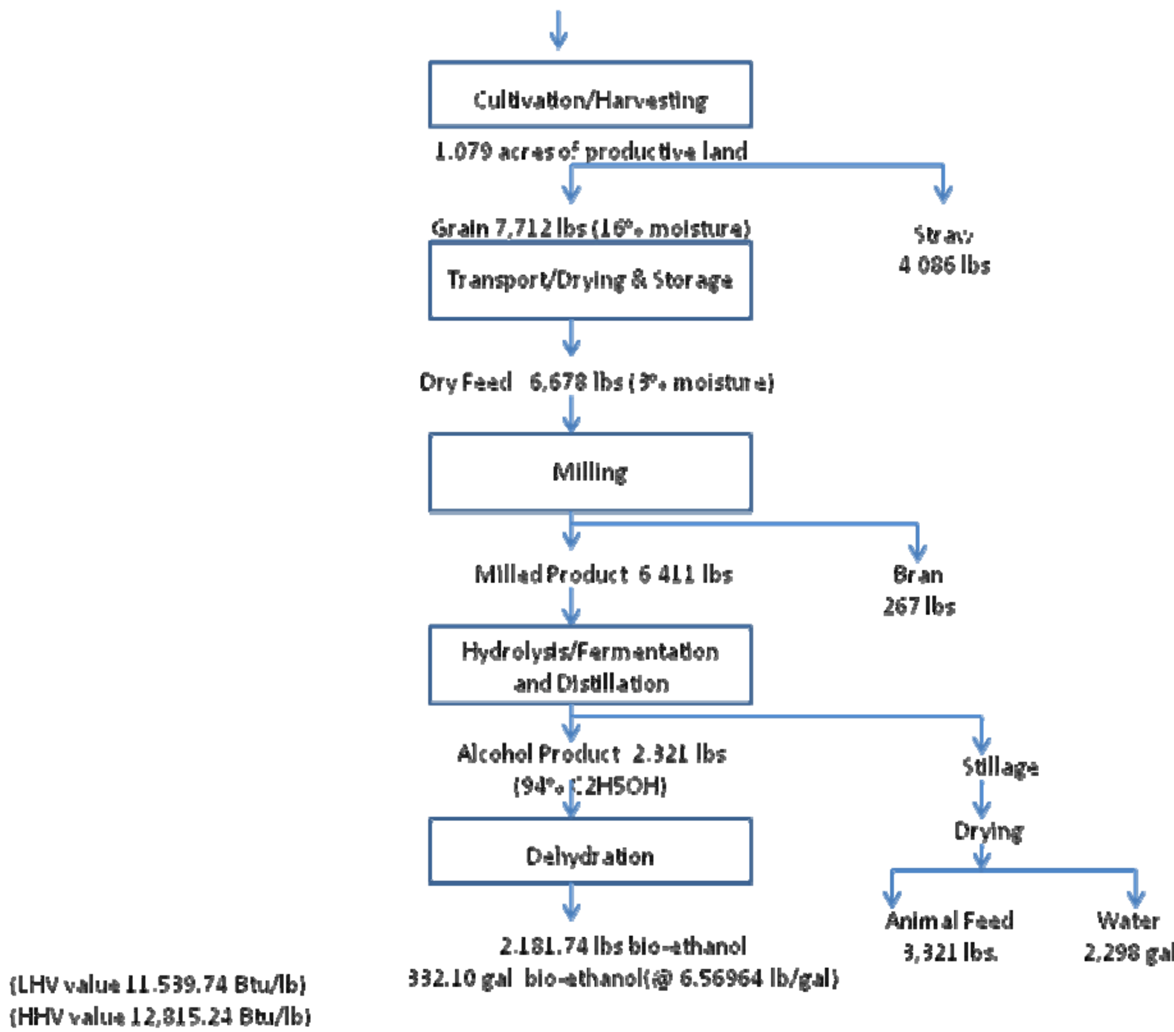
Biomass & Bioenergy

Biomass use has been increasing either for electricity and/or liquid fuels e.g. ethanol, methanol, or bio-diesel. It provides more than 3% of the total energy consumption in the United States compared to 12% worldwide. It is envisioned to replace 30% of the current petroleum consumption with bio-fuels by 2030. The supply of biomass will be available from forest land and agricultural land to produce 1.3 billion in dry tons of biomass potential.

Bio-fuels (Bio-ethanol and Bio-diesel)

Corn, wheat etc. are known as first generation bio-fuels. Lignocellulosics e.g. corn stover, switchgrass etc. or short rotation woody crops are known as second generation bio-fuels.

Material Balance for Ethanol Production from Wheat



(Ref. 5)

Table 18

Economics of ‘Bio-mass’ Conversion from Eucalyptus Tree Crop
in Silivicultural Energy Farm; Central Florida

1. Land Area (Clay Settling Area) — 25,000 acres
2. Bio-mass Wood Yield — 12 dry ton/acre per year
3. Annual feed — 250,000 ODT
4. Annual ethanol production — 18 million gallons
5. Annual lignin production (by-product) — 39,600 tons
6. Annual electricity production — 95,000 MWH
7. Total capital investment — $100 million (MM)
8. Working capital — $10 million (MM)

A. Operating Cost ($ MM)

- Feed @ $39.15/ODT	9.80
- Chemicals/catalysts	1.50
- Utilities	1.50
- Maintenance/labor	4.50
- Operation/labor	4.50
- Supervision	1.50
- Environmental	1.50
- Miscellaneous	0.50
Subtotal A	***25.30***

B. Capital Charges ($MM)

- Amortization @ 6.5%	6.50
- Interest on working capital @ 3%	0.30
- Interest on construction @ 6%	1.20
- Taxes & insurance	1.50
- Start-up cost	1.50
Subtotal B	***11.00***

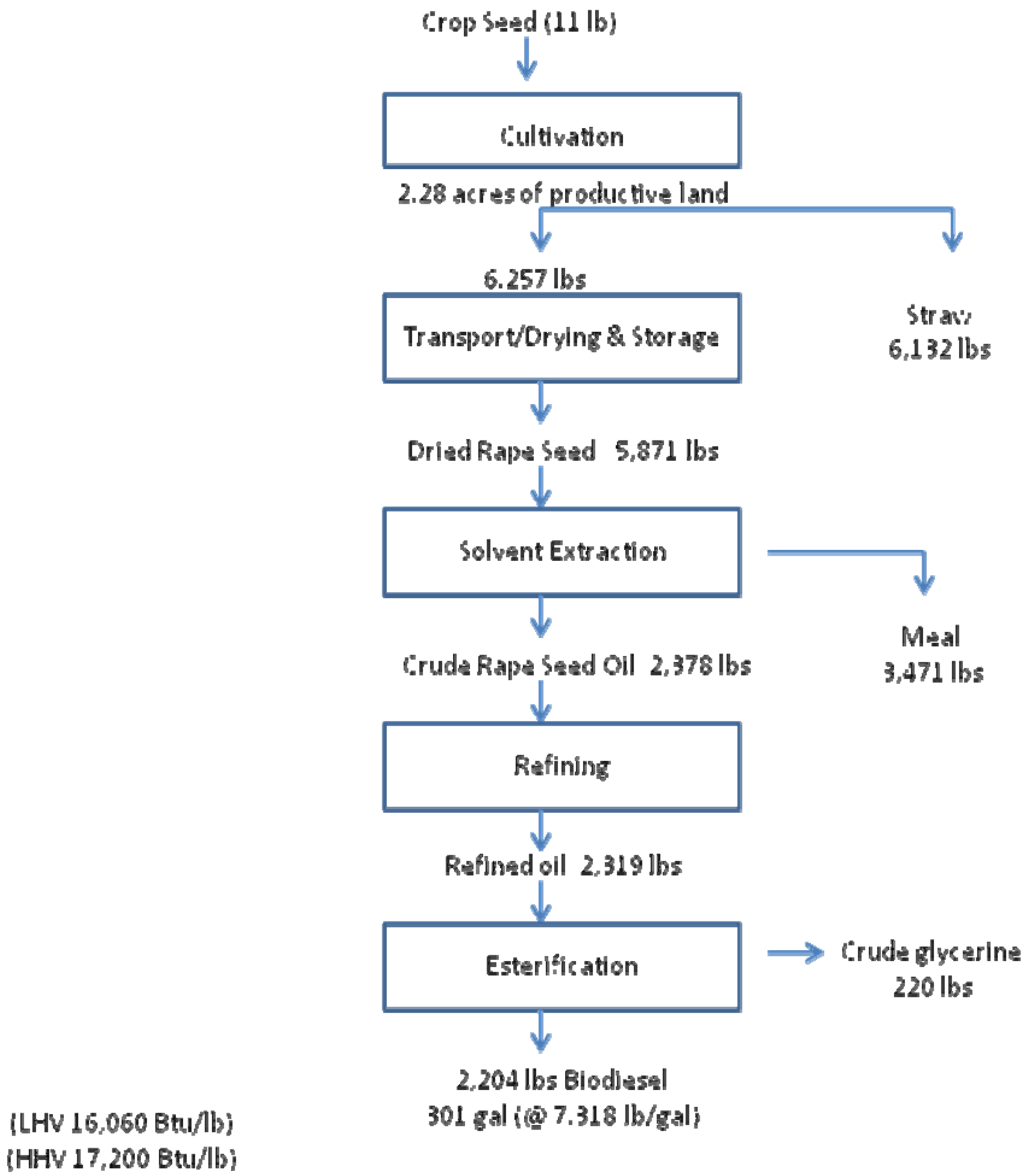
C. Annual Income From:	w/ Electricity ($MM)	w/ Lignin ($MM)
* Ethanol @ $2.50/gal	45.00	45.00
* Electricity @ $0.06/kwh	5.70	-
* Lignin @ $0.25/lb		19.80
Total C	***50.70***	***64.80***
D. Return on Investment (ROI) %	13.09	25.90

Total manufacturing cost (A + B) $36.30 MM ($2.02/gal)

Ethanol manufacturing cost with

- **Electricity credit @ $0.06/kwh** $36.30
  (-) 5.70
  $30.60 ($1.70/gal)

Material Balance for Bio-diesel Production from Rape Seed



(Ref. 5)

Fertilizer Outlook

The primary nutrient demands are expected to increase due to increasing population, food, feed and bio-fuel demands in the future. Fertilizer demands for nitrogen, phosphate and potash have slowed down considerably in 2009 since the global economic crash began in September 2008. The global capacity for each nutrient in 2009 is estimated below in Table 19.

Table 19

Global Capacity (2009) for Primary and Secondary Nutrients
(Million tons/year)

Primary			Secondary
Nitrogen	Phosphate	Potash	Sulfur
130	175	64 (Present operating rate 55)	79 (Fertilizer use 14)

Fertilizer Prices

Fertilizer prices declined after October 2008 and are beginning to show an upward trend indicating that this downturn is a short-term situation.

Table 20

(All figures are in U.S. $ per short ton FOB price)

Period	Ammonia	Urea	UAN	10-34-0	DAP	MAP
April ‘09	285	265-272	180-185	575-725	300-310	310-325
December ‘08	120	190-210			275-300	285-310
April ‘08	610	460-490	330-350	850-875	980-1000	980-1000

Lowering CO_2 emission is envisaged by improving phosphoric acid P_2O_5 efficiency with the use of high quality process water as shown in Table 21.

Table 21

Phosphoric Acid Process Water Quality Improvement of First Stage
Lime Treatment by Electro-Coagulation Method

Components	**Untreated Process Water**	**1st Stage Lime-Treated Process Water**	**1st Stage 'E/C' Treated Water**
Total P_2O_5 (PPM by Wt)	18,460	456	192
CaO (PPM by Wt)	1,541	820	60
F (PPM by Wt)	4,800	64	33
H_2SO_4 (PPM by Wt)	7,054	4,645	4,410
Fe_2O_3 (PPM by Wt)	240	-	20
Al_2O_3 (PPM by Wt)	-	-	30
MgO (PPM by Wt)	862	382	151
Na_2O (PPM by Wt)	3,390	2,419	2,419
K_2O (PPM by Wt)	351	260	251
SiO_2 (PPM by Wt)	215	-	83
Total Dissolved Solids (PPM by Wt)	40,218	12,658	7,620
PH	1.78	4.47	6.77

Silvicultural Energy Farm with a Short Rotation Woody Crop (Eucalyptus)

Silvicultural energy farms or production entities are devoted to the production of wood exclusively for its fuel or feed stock values. It is a long term program of twenty years or more requiring large investments on land and commitment for supply of wood on a regular basis under forest management.

Short rotation tree farming is generally combined with close spacing of the trees in order to achieve full site utilization within the rotation period between 3 – 6 years for eucalyptus or 20 years for slush pines etc.

Design parameters for a silvicultural tree farm of 25,000 acres of productive land

- Annual production: 250,000 ODT (oven dry ton) of wood
- Productivity: 12-16 ODT/acre per year
- Rotation: 3-6 years; 30 year plantation lifetime
- Land acquisition:
- Land clearing/preparation:
- Planting: Initial seedlings planted in first year and coppices in second and third year
- Irrigation: Drip irrigation or automatic sprinkler
- Fertilization: Annual NPK applications with lime if needed in first year
- Weed/pest control: Mechanical/manual as needed
- Harvesting: Use of harvester for tree crop
- Transportation: Chip handling or wood 'trucking'
- Work roads: For harvester and truck movement
- Miscellaneous operations: Planning, supervision/management and field supplies

Estimated Operational Costs for a Silvicultural Energy Farm

Items	$ per ton of ODT wood
Planning & Supervision	1.50
Land lease/purchase	1.00
Land preparation	1.50
Roads	0.25
Planting @ 25,000 acres	7.00
Irrigation	5.00
Fertilization	5.00
Weed control	1.40
Harvesting	3.50
Handling/Transportation	10.00
Interest @ 6%	0.60
Taxes	1.00
Return to Investor @ 12%	1.20
Salvage value	(-) 0.10
Depreciation @ 10%	0.20
Miscellaneous	0.10
Wood production cost, $/ODT	39.15

Table 22

Energy Balances for Silvicultural Eucalyptus Tree Crop Farm
(Basis: 250,000 ODT/year)

	Energy x 10^6 Btu/year	**% of Total Energy Input**
Supervision	1,670	0.04
Harvesting/supplies, etc.	8,400	0.21
Bio-mass handling/transportation	26,100	0.61
Fertilizer manufacture, urea, tsp, potash, etc.	125,000	2.94
Fertilizer transportation/application	1,000	0.02
Irrigation	115,000	2.70
Total Energy Consumption	277,170	6.52
Total Energy Input	4,250,000	100.00
Net Energy Yield	3,972,830	93.48
Net Energy Efficiency		93.48

Conclusions

1. Notwithstanding the differing views on the ultimate causes of climate change, the increasing CO_2 concentration in the earth's atmosphere as determined by 'IPCC' scientists cannot be ignored, nor the melting ice cap, rising sea levels, temperature increases and their effects on future food supply. The challenges for food and energy security as well as environmental sustainability are well undertaken worldwide by gradual shifting from 'imported' oil to bio-fuels and bio-diesels and renewables (wind, solar, geothermal and bio-mass) and nuclear power.

2. CO_2 emission by the U.S. has been lowered by 4% during the past six years (2000-2006) and the rate of increase of CO_2 emission is expected to slow in the future due to growing renewable share from 8% in 2007 to 14% in 2030.

3. More developments in hydrogen technology, including storage and transportation, will improve the world economy by lowering hydrogen production cost on a gasoline gallon equivalent (GGE) energy basis with improved efficiency and/or feed-mix (coal + bio-mass or solar/pv powered electricity and water).

4. Increase in ammonia plant efficiency reduces CO_2 emission and lower nitrogen cost to fertilizers.

5. Increase in phosphoric acid plant efficiency lowers energy use and cost to fertilizers.

6. Utilization of second generation lignocellulosic bio-mass from tree and other energy crops grown in marginal lands (clay settling areas) and reclaimed lands contributes future bio-energy demand economically with a 13% - 26% rate of return.

7. In summary, utilizing mined phosphate land with eucalyptus tree crop (SRWC) plantation would minimize global warming and eliminate cogongrass, provide renewable energy at $1.70/gallon of ethanol and $0.06/kwh of electricity and make fertilizer business more economically attractive.

Acknowledgements

The author would like to acknowledge Tracey Cayson for providing the administrative support for this presentation.

References

1. Annual Energy Outlook 2008 with projections to 2030. U.S. DOE/EIA
2. Beyond Oil and Gas: The Methanol Economy by George A. Olah, Alain Goeppert and G.K. Surya Prakash
3. Hydrogen and Fuel Cells. Rebbeca L. Busby.
4. Biomass Conversion Processes for Energy and Fuels. Edited by Samir S. Sofer and Oskar R. Zaborsky.
5. Energy and Carbon Balances of Bio-Fuels Production: Bio-diesel and Bio-ethanol. R.E. Horne, N.D. Mortimer and M.A. Elsayed. Proceedings No. 510, IFS London.
6. Wood to Energy Biomass Ambassador Guide, UF, IFAS Extension.
7. ‘Energy-Mix’ for Sustainable Environment in View of Fertilizer/Agricultural/Utility Industries. Paper presented at the annual AIChE (Central Florida) Clearwater Convention at Sand Key, Clearwater, Florida. June 8-9, 2007. P.K. Bhattacharjee and Dr. Donald Rockwood.
8. Biotechnology of Biomass Conversion Fuels and Chemicals from Renewable Resources. Morris Wayman, Sarad R. Parekh.
9. Ammonia Production: Energy Efficiency, CO_2 Balances and Environmental Impact by J.D. Pach, The International Fertilizer Society, Proceedings No. 601, London.