Sustainable Development Engineering

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Abstract: Sustainable Development Engineering (SDE) is addressed based upon System Theory(ST). SDE is a subsystem of Sustainable Development(SD). SDE is one step ahead of Environmental Engineering(EE) which is a subsystem of SDE and the other subsystem is Renewable Raw Materials (RRMs). The paper addresses using an Integrated System Approach(ISA) analyzing the different subsystems and their relations to each other and to the economy in general . Sustainable Energy(SE) is a subsystem of SDE and both should be discussed in an integrated manner. It is now essential to combine both experimental and mathematical modeling techniques to optimize the development and use of equipment and flow sheets for SD. The utilization of RRMs makes it necessary to introduce novel units; processes and control techniques. SDE applies to all branches of engineering, however this lecture will concentrate on Chemical and Biochemical Engineering.

Sustainable Development(SD) and Hydrogen

- **Hydrogen(H2) is at the heart of SD**
- **SD and SDE are more general systems than EE which**

is a subsystem of SDE and other sub-system is Renewable Raw Materials(RRMs)

- **Hydrogen is only locally clean and not globally clean when produced from fossil fuel.**
- **Globally clean hydrogen is that produced from RRMs.**
- ***There are other sources of ENERGY, e.g.: Solar, Wind, Falling Waters , Nuclear , etc. energies ; but are not addressed in this plenary lecture which covers only :(H2), Bio-Fuels(BFs) and Integrated Bio-Refineries (IBRs)***

Main Research Approaches and Methodology for Hydrogen:

a- Novel auto-thermic Circulating Fluidized Bed Membrane Reformer (CFBMR)

b- Hydrogen from Biomass (gasifier)

SD: Sustainable Production and Consumption (SP&C)

- **SD emerged as a key issue at the United Nations Conference on Environment and Development (UNCED) in Rio de Janeiro in 1992. The conference called on governments, business and others to play major roles in implementing measures to promote efficiencies in production and sustainable patterns of consumption, with developed countries taking the lead.**
- **The United Nations Commission on Sustainable Development (UNCSD) has called specifically upon business to:**

1) integrate environmental criteria in its purchasing policies;

2) design more efficient products and processes;

3) increase life spans for durable goods;

4) improve after sales service; reuse and recycle;

5) promote sustainable consumption through advertising, marketing, and product information.

Some Basic Concepts
Eco-efficiency

- Eco-efficiency is reached by the delivery of competitively priced goods and services that satisfy human needs and bring quality of life, "while progressively reducing ecological impacts and resource intensity throughout the life cycle, to a level at least in line with the earth's estimated carrying capacity."

- This can be achieved through:

1-taking account of the entire life-cycle of goods and services - design and engineering, purchasing and materials management, production, marketing, distribution and waste management;

2- applying the principles of eco-efficiency to create increased value for customers through the sustainable use of resources;

3- procuring and requesting products and services that have less environmental impact.

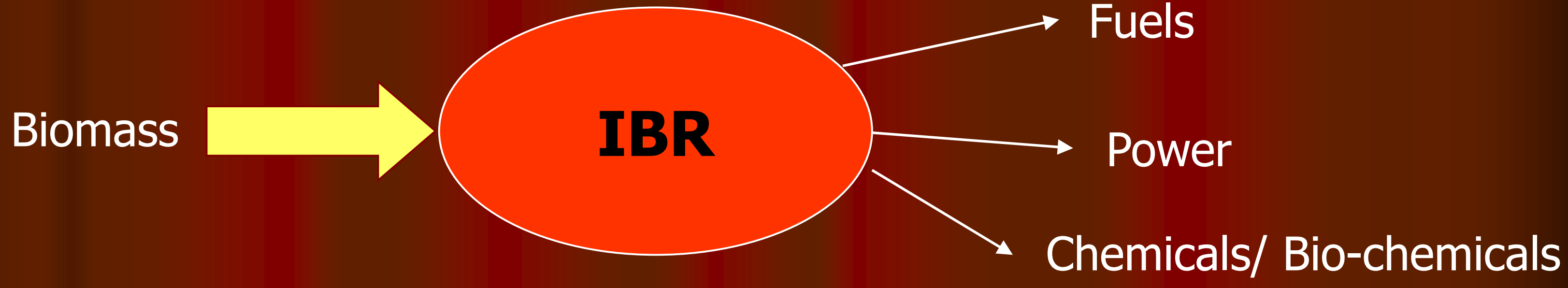
4- making accurate, scientifically sound environmental information available to customers and the public so that they can make informed decisions about purchasing, use and disposal.

Industrial Ecology(IE)

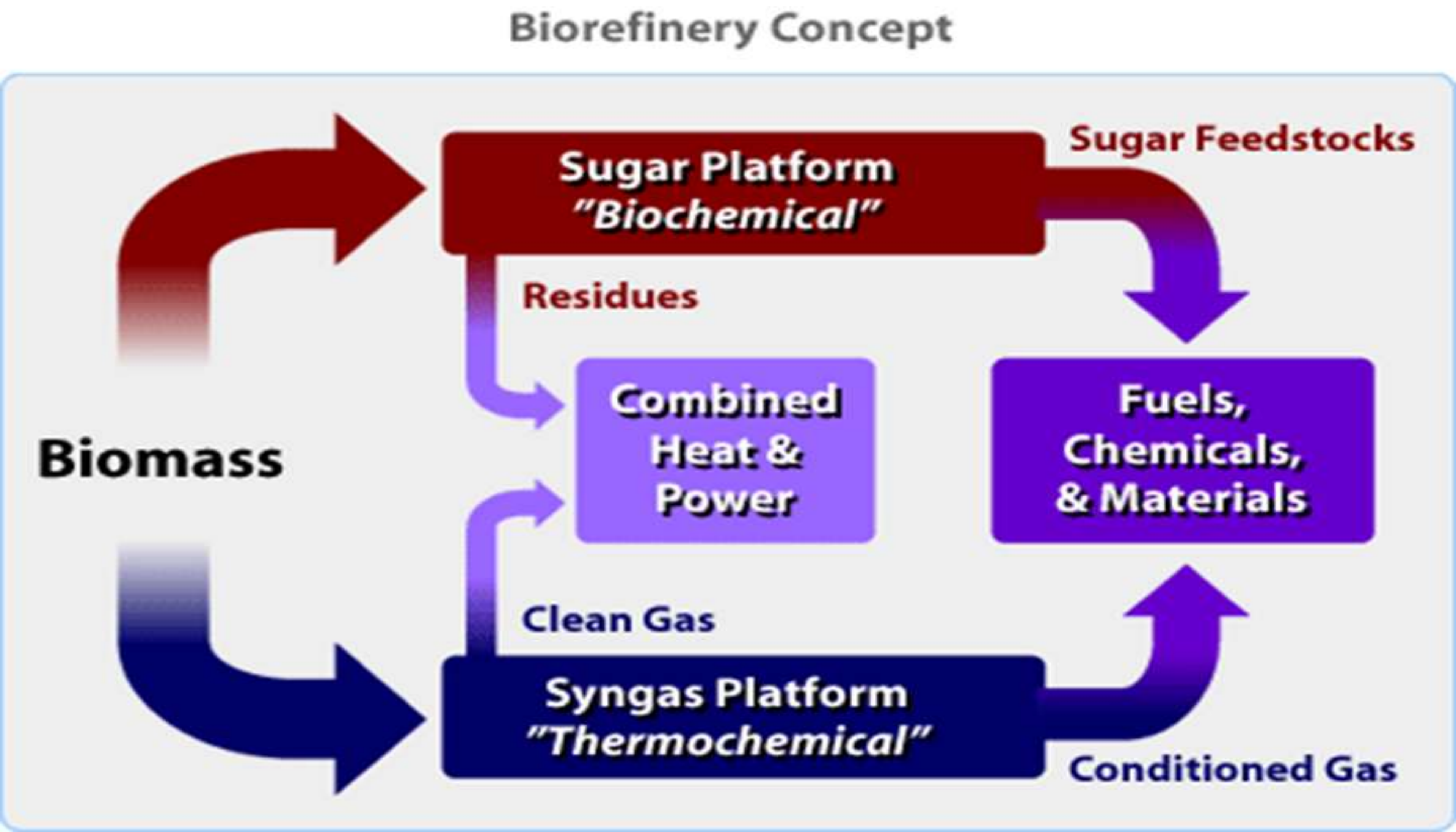
- Efficient Use of Resources
- Extending the Life of Products
- Pollution Prevention
- Recycling and Reuse
- Eco-Industrial Parks

Integrated Bio-Refineries (IBRs)

- **IBR is a complex facility that integrates biomass conversion processes and equipment to produce fuels, power, and chemicals/bio-chemicals from biomass. Hydrogen and bio-hydrogen can be among the important products of IBRs**
- **The bio-refinery concept is analogous to today's petroleum refineries coupled to petrochemical complexes, that produce multiple fuels and products from petroleum. Industrial IBRs have been identified as the most promising route to the creation of a new domestic and distributed bio-based industry.**



Typical IBR with two platforms, one is Sugar biochemical platform and the other is Syngas Thermochemical-Catalytic Platform



Integrated Bio-Refineries(IBRs)

- IBRs = Bio-equivalent of the following industries based on non-renewable raw materials:

  Petroleum Refineries

  +

  Petrochemical Complexes

  +

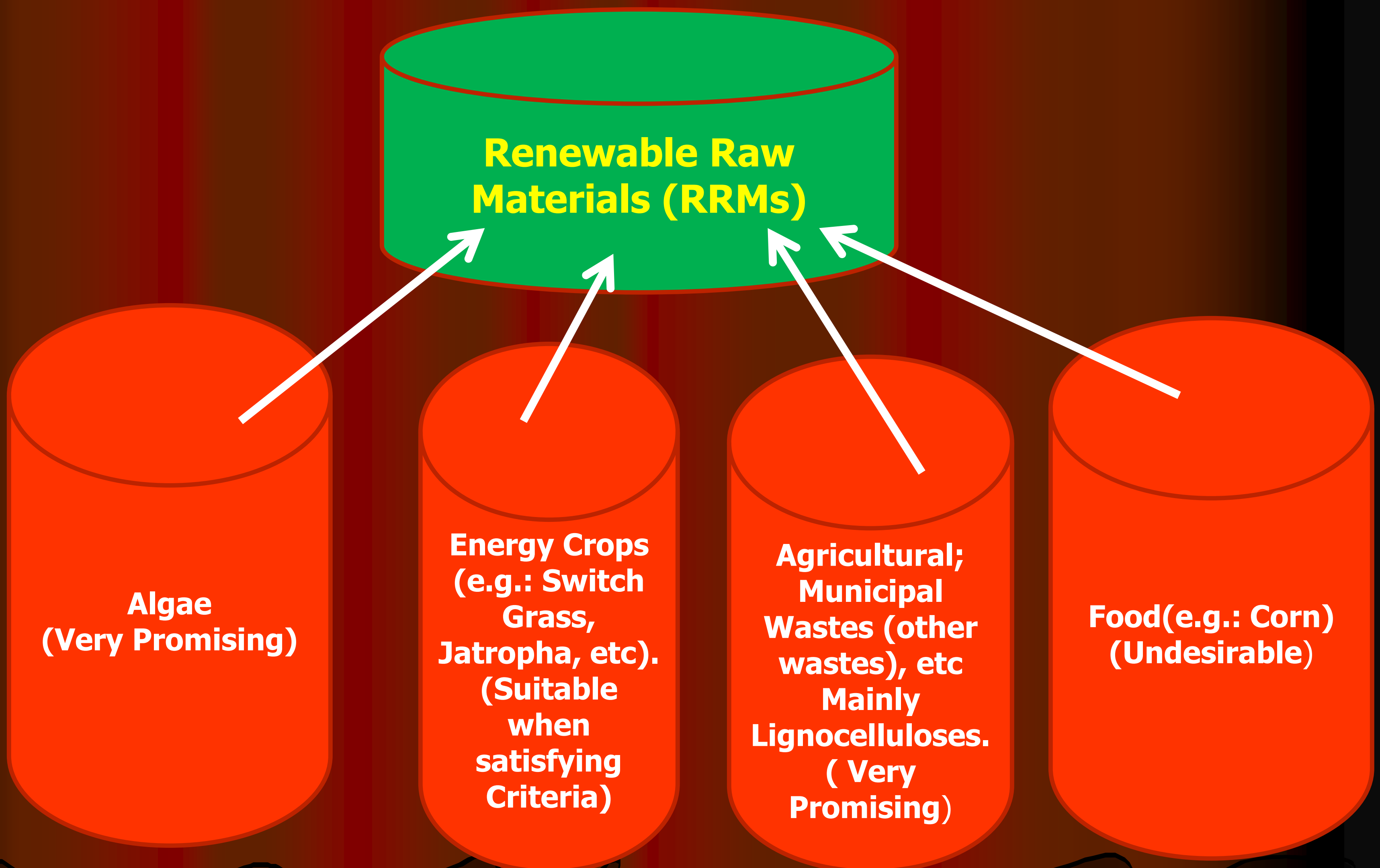
  Some other Chemical Industries

SD Requires Renewable Raw Materials (RRMs)

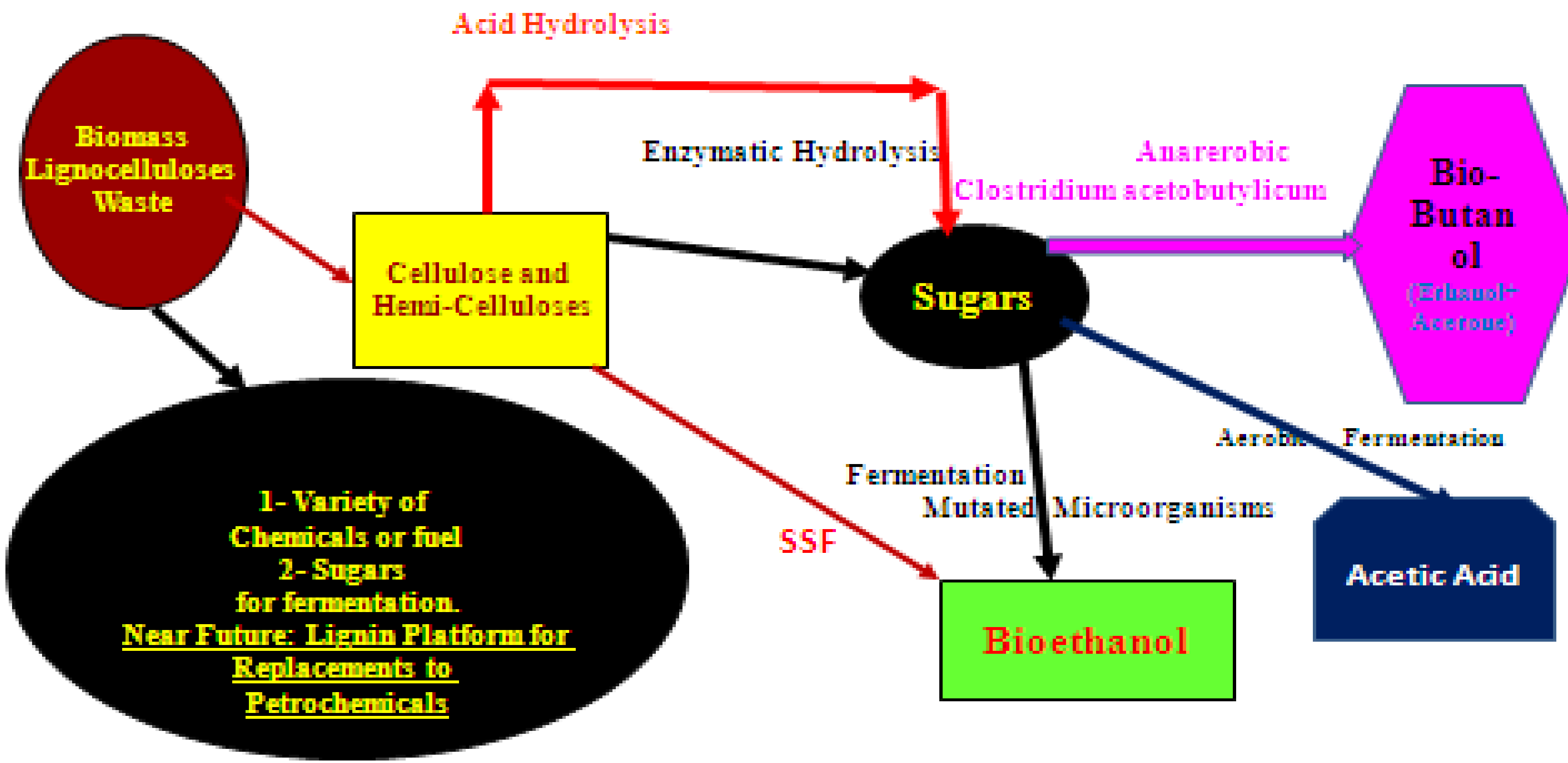
- **Main difference between SDE and EE is related to RRMs.**
- **RRMs have a life cycle of about 6-18 months and include 4 main groups as shown in the next slide.**
- **Feedstock used now, in PRs and PCCs are non-RRMs.**
- **The life time of these non-RRMs is 20-35 years.**
- **The life time of these non-RRMs can be extended a few years through performance improvements to achieve Maximum Production- Minimum Pollution (MP-MP) ; specially through catalysts and reactors improvements.**
- **Life time can be extended further by the use of RRMs.**
- **They can be eventually replaced by RRMs.**

The Main 4 RRMs Pillars

- **System Classification**



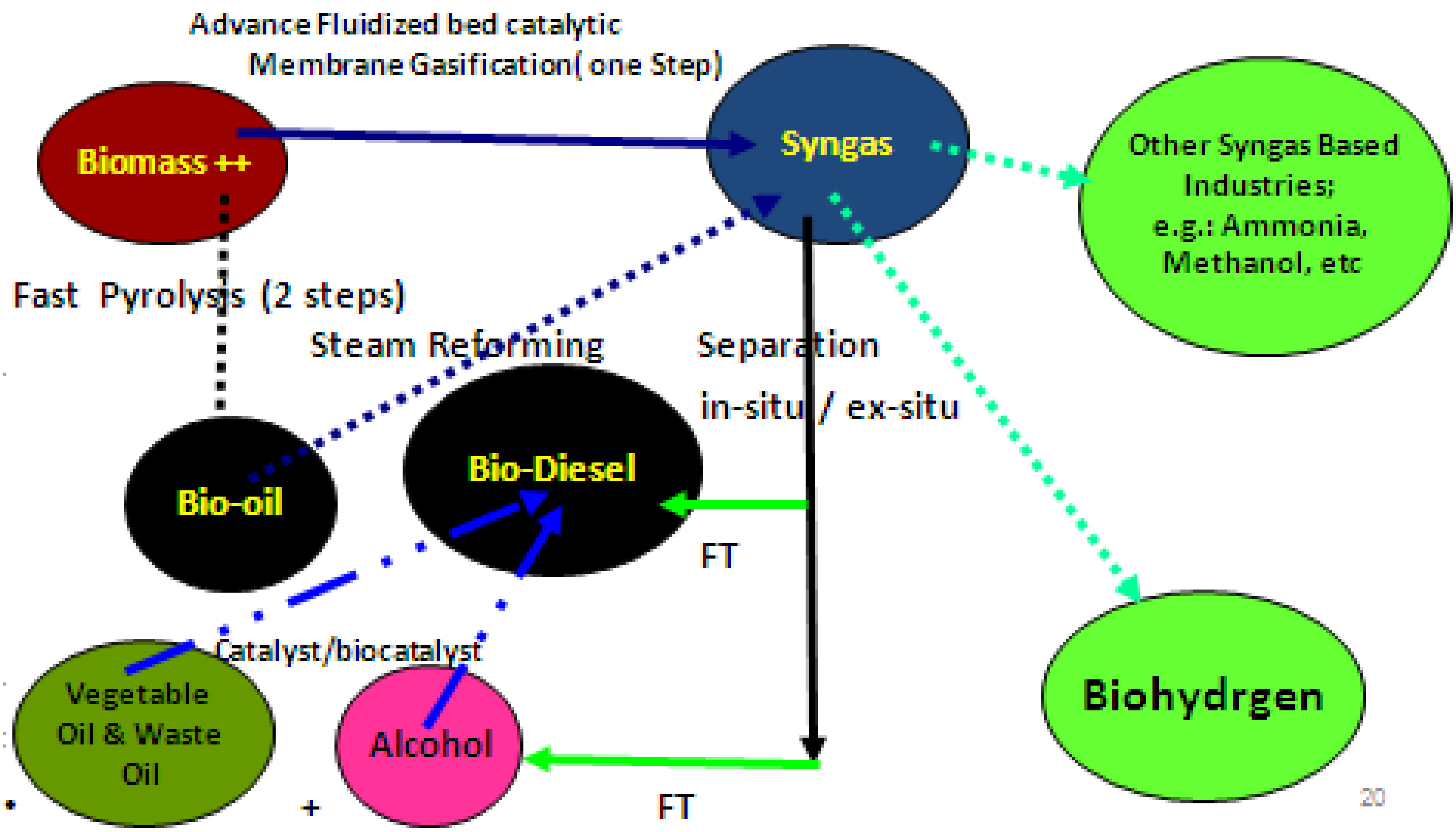
Critical evaluation of the different routes to bio-ethanol and bio-butanol from biomass



SSF=Simultaneous Saccrification/Fermentation

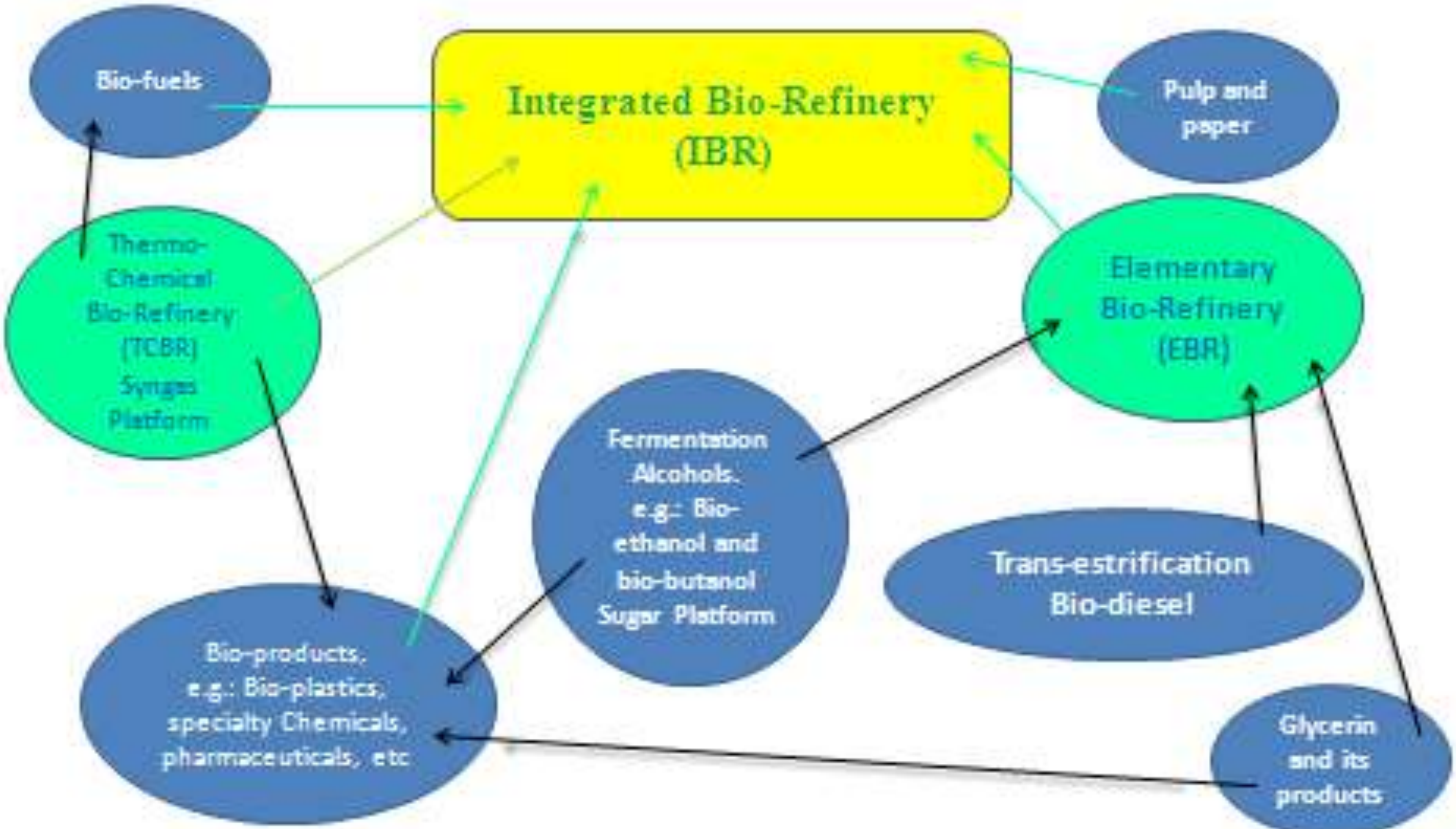
Syngas Platform to Fischer-Tropsch Bio-Diesel(FT-BD), Bio-Hydrogen (BH) and the Vegetable Oil Bio-Diesel(VO-BD)

EBR with SG platform



Elementary and Integrated Bio-refineries

- **Integrated System Approach (ISA)**



Some IBRs Promising Products(1)

- IBRs need to give attention to BPs and not only BFs; to achieve sustainability. Examples of Multidisciplinary work for new BPs:
- High-value (up to $25/lb) specialty chemicals, pharmaceutical precursors and flavorings as "side stream" chemicals from the ethanol process.
- Solvent techniques like use of near-critical water (e.g.: pressurized water at 250°C to 300°C), gas-expanded liquids (e.g.: CO_2 in methanol) and supercritical fluids (e.g.: CO_2 under high pressure).
- Cytochrome P-450 designer enzyme technology that applies specific enzymes as biocatalysts for the conversion, in a single step, of relatively low value substrates into high value chemicals.
- Potential market embraces more than 15,000 commercially available chemicals, including various alcohols, aldehydes, ketones and carboxylic acids.

Some IBRs Promising Products(2). Bio-Plastics

- The production of plastics from renewable resources provides another example of how green technologies could change the face of the chemical industry.
- 2006, first commercial plant , 40,000 t/year to produce PHAs (poly-hydroxyl-alkanoates) , a family of bio-degradable high performance plastics that can be used in many applications currently served by petrochemical plastics, e.g., coatings, film and molded goods.
- 2008 , 50,000-ton/yr plant of PHAs, the plant will take starch from the mill as its raw material.
- 2009, 20,000 t/year New Xenoy iQ resins, for automotive applications, are made from recycled PET(Poly-Ethylene Terephthalate).
- A subsidary offers a biodegradable plastic. Its poly-lactic acid (PLA) polymer is produced from corn at a 140,000-metric-ton/yr plant in Blair, Neb.
- PLA has won a significant place in biodegradable packaging; Wal-Mart switched to PLA packaging for its fruits/herbs in 2005.

Some IBRs Promising Products(3). Wind Energy to Produce Bio-polymers

- NatureWorks Co., uses Wind Energy for all its energy needs in its PLA plant therefore its PLA is the world's first and only greenhouse-gas-neutral polymer.

- PLA polymers fall more within the definition of compostable rather than bio-degradable materials at least in the U.S. (The difference is one of timescale and the ambient conditions required for each.) They can, however, also be recycled, which for the moment is arguably one of the few ways for petrochemical- based plastics to carry a "green" label

Some IBRs Promising Products (4). Plastic-waste feedstock

- SABIC Innovative Plastics, developed new use for recycled PET waste. It also has developed new route to polybutylene terephthalate (PBT) based resins and polyester based elastomers that uses PET waste — mainly from plastic bottles. Their PET is first depolymerized and then chemically upgraded so it can be reacted with butanediol (BDO) — one of the main feedstocks in the conventional process — to produce PBT.
- Annual global production capacity for biodegradable materials amounts to only around 300,000 metric tons, with the NatureWorks plant accounting for almost half of that.
- With retail giants like Wal-Mart already in the market for biodegradable packaging, this level of capacity undoubtedly only scratches the surface of the potential for this particular green chemistry.

Some IBRs Promising Products(5). Commercialization of renewable-resource-based routes to chemicals

- Bio-feed-stocks can play a wide role for producing many bulk chemicals.
- Studies focused on 15 chemicals, e.g.:

acetic acid, acrylic acid, adipic acid, butanol, caprolactam, ethanol, ethyl lactate (EL), ethylene, lactic acid, lysine, 1,3 propanediol (PDO), polyethylene terephthalate (PTT), polyhydroxyakanoates (PHA), polylactic acid (PLA) and succinic acid.

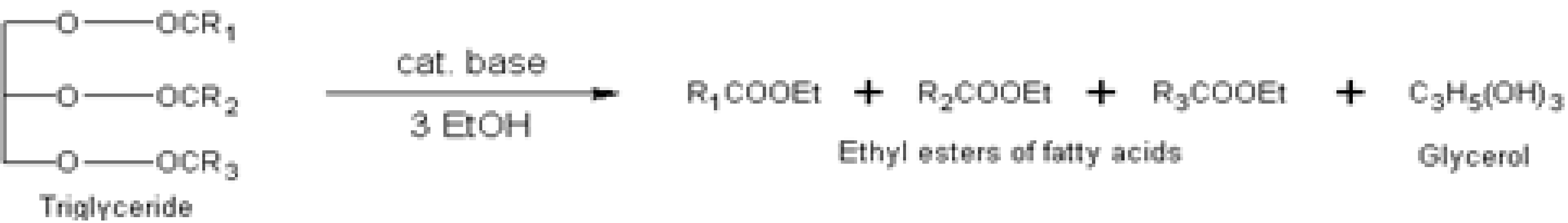
- All 15 products can realistically be produced via fermentation and they all have substantial potential consumption, e.g.: at least 200,000 metric tons/year in Western Europe.

Some IBRs Promising Products(6). Highlights on Economics

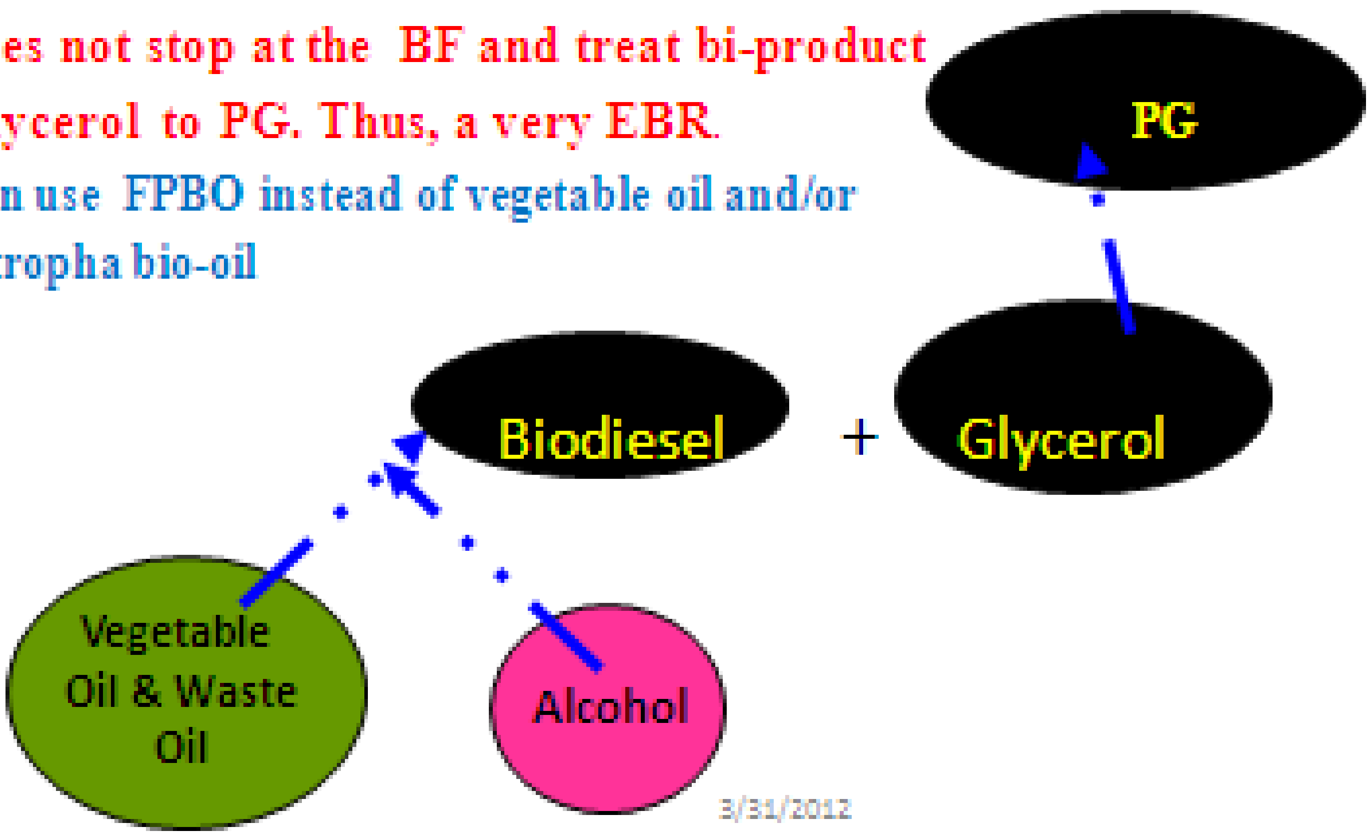
- Utrecht Univ. supported by an industrial consortium, formed of: BP, Degussa, DSM, DuPont, NatureWorks, Novozymes and Shell carried out a first economic study and published it in Applied Biochemistry and Biotechnology, 2007 regarding economics of production using bio-feed-stocks versus oil or natural gas.
- Sensitivity analysis was carried out to varying prices for sugar (70€/mt, 135€/mt, 200€/mt and 400€/mt) for different kinds of sugar sources , e.g.: sugar cane, lignocelluloses and corn starch and two crude oil prices ($25/bbl and $50/bbl); and different plant sizes (100,000 mt/y, as well as 200,000 mt/y and 400,000 mt/y for some of the products).

- The results showed that making many of the chemicals with bio-feed-stocks is already economically viable.
- With today's oil prices over $100.0/bbl the answer is obvious.

Elementary Bio-Refineries (EBRs) Producing Glycerine&PG



- Does not stop at the BF and treat bi-product Glycerol to PG. Thus, a very EBR.
- Can use FPBO instead of vegetable oil and/or Jatropha bio-oil



Glycerol (Glycerin), Economics of Trans-esterification Bio-diesel and PG

- The economics of trans-esterification Biodiesel strongly depend on the market for the byproduct glycerol.
- The U.S. biodiesel industry is expected to introduce 1 billion pounds of additional glycerol into a market that currently only has an annual demand for 600 million pounds. So, the industry clearly needs to find a high-value use for its glycerol.
- Propylene glycol (PG), a less toxic alternative to ethylene glycol for antifreeze and other uses, could be the answer.
- Producing it from glycerol, says Suppes, can reduce the cost of bio-diesel manufacture by as much as $0.40/gal.

Important Example: Menu of Glycerol (Glycerin) Bio-Products(1)
First Catalytic Breakthrough

The 2006 Presidential Award winner, Galen Suppes, Professorof Chemical Engineering at the University of Missouri –Columbia:

- He developed a catalytic process for converting glycerol (glycerin) into Propylene Glycol (PG)

- This process could change the economics of the burgeoning biodiesel (from Vegetable oil or FPBO) through trans-esterification (alcoholysis) industry.

Glycerin to PG

- Suppes' award-winning process couples a new copper-chromite catalyst with reactive distillation and offers a number of advantages, such as: lower operating temperature and pressure, more efficient conversion and less byproduct, compared to previous more conversion routes.

Nano-catalysts and Trans-esterfication Bio-Diesel

- Researchers at Oak Ridge National Laboratory, Oak Ridge, Tenn., have developed a series of solid acid nano-catalysts that promise to avoid some post-reaction steps in the production of biodiesel.
- Pore sizes boasted of 5-10 nanometers to provide improved catalytic performance, and an average surface area of 400 m2/g, which is about 20 times higher than that of other heterogeneous catalysts.
- Also membrane catalysis can revolutionize the trans-esetrification process.

Algae Bio-diesel

- Among the most photo-synthetically efficient plants are various types of algae.
- Some species of algae are ideally suited to bio-diesel production due to their high oil content (some well over 50% oil), and extremely fast growth rates.
- From the results of some research, algae farms would supply enough bio-diesel to completely replace petroleum as a transportation fuel in the US (as well as its other main use - home heating oil)
- Algae's single-celled structure is extremely efficient in use of light and absorption of nutrients. So much so, that algae's growth and productivity is 30 to 100 times higher than crops like soybeans

Some Basics about Algae Bio-diesel

- NREL's research showed that one quad (7.5 billion gallons) of biodiesel could be produced from 200,000 hectares (roughly 500,000 acres) of desert land.
- Algae farms could also be constructed to use waste (human or animal) streams as a food source, excellent way of spreading algae production around the country.
- Nutrients extracted from the algae for production of a fertilizer high in nitrogen and phosphorous.
- Using waste streams (agricultural, animal waste, human , etc.) as the nutrient source, these farms essentially also provide a means of recycling nutrients from fertilizer to food to waste and back to fertilizer.
- Extracting the nutrients from algae provides a far safer and cleaner method of doing this than spreading manure or wastewater treatment plant "bio-solids" on farmland.

- **Diesel fuel has an energy density (ED) of 1,058 kBtu/cu.ft. BD has an ED of 950 kBtu/cu.ft, and hydrogen stored at 250 times atmospheric pressure only has an ED of 68 kBtu/cu.ft. So, highly pressurized to 250 atmospheres, hydrogen's volumetric ED is only 7.2% of that of BD.**
- **Micro algae present the best option for producing BD in quantities sufficient to completely replace petroleum. While traditional crops have yields of 50-150 gallons of BD per acre per year, algae can yield 5,000-20,000 gallons per acre per year. Algae grow best of waste streams .**
- **DOE is also investigating the possibility of using the algae mush (what is left after extracting the oil) as a fertilizer. It is also mainly lignocelluloses can be used for the bio-ethanol process and similar processes.**
- **The future is for photo-bio-reactors for the efficient production of algae and BD from it. It is the most promising route for BFs.**

MD research, sequential de-bottlenecking, innovation and optimal configurations

Main Feature of Modern "Chemical/Biological" Engineering Research Should Be Based On:

1- **Multidisciplinary:** different engineering and scientific disciplines as well as humanities.

2- **Innovative:** novel units and processes development utilizing sequential de-bottlenecking

3- **Widen the scope of RRMs:** to replace non-RRMs and include all possible wastes , special plants, etc..

3- **Combined processes in single units**, e.g., membrane reactors for breaking thermodynamic barriers.

4- **Integrated designs, e.g.,** Integrated auto-thermal membrane coupled reactors

5- **Utilization of fundamental research into applied research** (e.g., Chaotic Fermenter)

6- **Optimal combination of experimental and mathematical techniques**

7- **Close co-operation with industry**

8- **Minimum data collection** (extensive utilization of published and industrial data)

Next is Novel Techniques for Hydrogen Production Coupled to Production of Other Products

Autothermicity

- It is a concept developed by Elnashaie and other researchers in order to achieve optimal thermal efficiency for important industrial processes which are highly endothermic requiring large amounts of external heat inputs.
- The same concept is applicable to the overall energy needs of certain communities, specially remote communities where the fuels are supplied from far centers and the disposal of waste is quite a problem.
- The success of this concept is very useful to different remote areas and is a step forward towards wider application of the concept to different cities and states/provinces and the integration of the concept to the IBRs and eco-industrial parks concepts.

Once again on the Definition of SD

- **Many sustainable development definition are "catch" phrases not real ones, an example is: "It is the form of technological, economical and social strategy for development that provides a mode of development so that future generations will have at least the same opportunities to live and prosper that the present generation enjoys"**
- **Does this mean that we are happy with the present situation, locally, state wise, national wise and international wise?,**
  - **of course not**
- ***Sustainable development definition should be more concrete and specific than that. The definition should be formed of a number of components and not a "catch phrase". I will have a modest trial on such definition:***

I- For Present Generation:

1- **Develop novel clean technologies capable of producing Minimum Pollution coupled to Maximum Production (MPMP)**

2- **Develop Technologies Capable of using RRMs to achieve sustainability (and may be growth) of raw materials rather than the present situation associated with the continuous and critical depletion of raw materials.**

3- **The use of natural distributed RRMs in contradistinction to the present depleting raw materials concentrated in certain parts of the world causing continuous conflicts and wars.**

4- **Produce environmentally friendly products easy to degrade and/or reuse.**

5- **Develop clean and environmentally friendly housing, office buildings and shopping centers.**

6- **Develop efficient technologies for waste treatment and recycle. " DO YOUR BEST THEN TREAT THE REST"***

7- **Building socio-economic and political frameworks to apply the above (including the necessary non profit tendencies and change of consumer habits, etc.) in order to achieve sustainability of: raw materials, capacity of our ecosystem for waste without being negatively affected and more national and international distribution of raw materials, products and wealth.**

II- Future Generations:

- A considerable percentage of the present population belong to future generation (s) And have strong interest in the well being of what we call future generations.

- The role of the present generation (us) with regard to future generations can be summarized in two main pillars one is good and the other is bad:

1- Good one is that “future” generations inherit from us more advanced technologies and accumulation of knowledge and, hopefully, “wisdom” !

2- Bad one is that they inherit from us: more pollution, Weapons of Mass Destruction (WMD) and humanly un-necessary political/social/military conflicts.

- The best we can do to future generations is to :

Maximize 1 in quantity and quality by leaving them : more advanced and clean technologies using renewable raw materials, more knowledge about good and useful things and the wisdom of avoiding racism and wars.

Minimize 2 by: decreasing pollution, getting ride of WMD all over the world and not only from the “bad” guys and resolve political/military conflicts.

Sustainable Development. Multidisciplinary by Its Very Nature

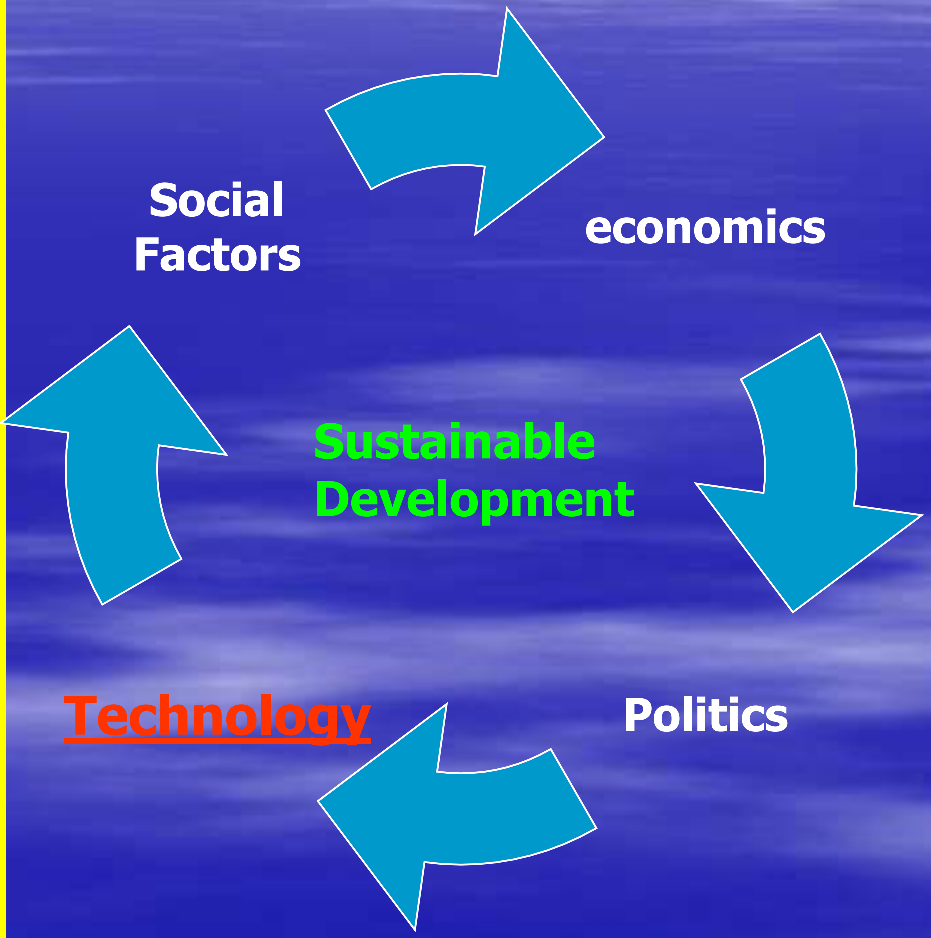
- **Main Components of Sustainable development:**

1- Political: e.g.: Legislations and strategic decisions…..

2-Economical: e.g.: Investment in novel new technologies……

3-Social: e.g.: Consumption Trends, acceptance of novel clean technologies and products...

4-Technological: e.g.: Novel efficient clean technologies, efficient utilization of renewable feedstocks, new environmentally friendly products, In-process Modification for MPMP, efficient waste treatment…….



Sustainable Engineering

- It Includes in an Integrated manner all engineering disciplines, e.g.:

1-Chemical/Biological , 2-Architect , 3- Mechanical, 4-Civil, 5-Planning, 6-Electrical , 7-Aerospace, etc.

It also include Physical-Chemical Sciences, e.g.:

1)Chemistry, 2)Biochemistry, 3)Physics, 4)Microbiology, 5)Ecology, etc.

As well as Socio-economic sciences and political Sciences.

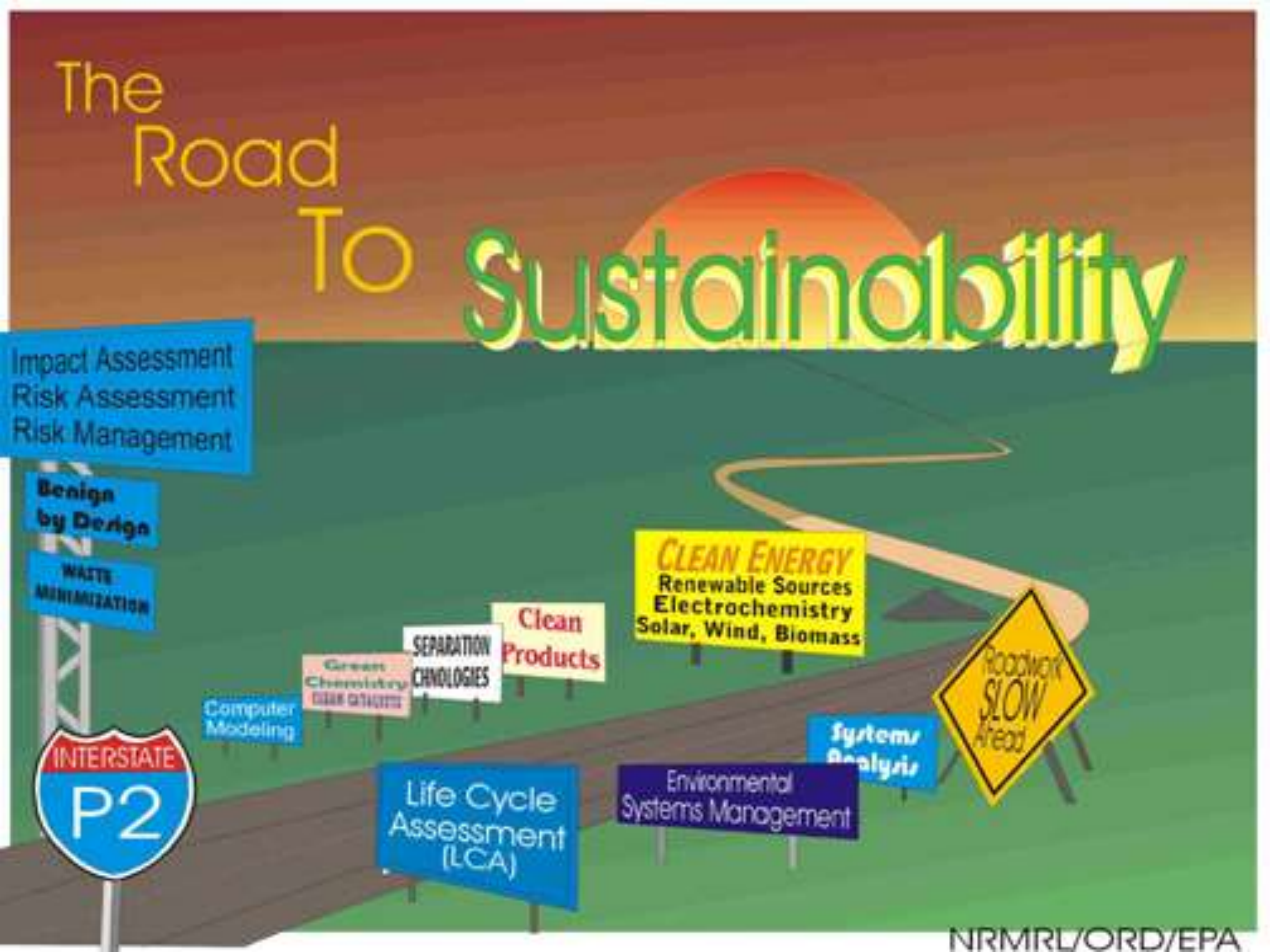
Thus it is Multidisciplinary By Its Very Nature. Best Approach is the

UTILIZATION of SYSTEM THEORY

in a

MULTIDISCIPLINARY FRAMEWORK


Carbon Dioxide
Biomass
Mineral Recycle
Fuel/Power/
Heat and New
Bioproducts
New Biomass Crops
Conventional Biomass
Recycling
Agricultural
Residues
Sludge
Use
Mineral
Recycle
Residues
Products
Fossil Energy
Wood Products
and Energy or
Food/Feed
Chemicals


The Road To Sustainability
Impact Assessment
Risk Assessment
Risk Management
Benign by Design
WASTE MINIMIZATION
CLEAN ENERGY
Renewable Sources
Electrochemistry
Solar, Wind, Biomass
Clean Products
SEPARATION
CHNOLOGIES
Green Chemistry
Computer Modeling
Roadwork SLOW Ahead
Systems Analysis
Environmental Systems Management
Life Cycle Assessment (LCA)
INTERSTATE
P2
NRMRL/ORD/EPA

Some Typical Promising Research Issues

1- **Bio-Fuel Cells for the Efficient Simultaneous Production of Energy and Single Cell Protein (SCP) for Animal Feed :**

- The process is quite clean and promising, producing not only electricity but also SCP while consuming a good part of the CO_2 produced from the reforming process thus decreasing the overall CO_2 emission and replacing it with useful Single Cell Protein SCP.

2- **Bio-hydrogen Production :**

- It is a very serious challenge to combine different research disciplines to intensify the naturally slow processes for the production of bio-hydrogen. Success in efficient production of bio-hydrogen will have very positive impact on sustainable development and the environment.

IBRs, Bio-oils and their Reforming

3- IBRs Development, Modeling, Simulation &Optimization :

- **Bio-refineries will contribute greatly to a bio- and sustainable development and will require a truly multidisciplinary efforts to develop the necessary technologies and their optimal integration and will also require strong economical and political well to implement it against opposing economical and political interests.**

4- Biodiesel and the Steam Reforming of Bio-oils:

- **Bio-diesel as an energy carrier has many advantages regarding the environment compared with diesel fuel from hydrocarbon sources, it also has many advantages over hydrogen with regard to ease of storage and handling. Efficient process for production of bio-diesel from biomass represents a great contribution for SD and clean environment.**

5- Multilayer Compact Steam Reformer Coupled to Bio-Fuel Cell:

- This is a new project funded by ENSERC and is joint between UBC and UOW. It is based on developing a compact multilayer reformer to supply hydrogen to a bio-fuel cell, where hydrogen is used at the anode; the ferric ions are used at the cathode. Ferrous ions are regenerated to ferric ions at a bioreactor utilizing CO_2 CO2 to produce SCP for animal feed.
- The development of the compact multilayer reformer is complete and the student got his PhD and the work is now on combining it to the bio-fuel cell

6-Steam Reforming of Bio-oil:

Many studies suggest that bio-diesel from renewable raw Materials(e.g.: micro-algae) is the most promising bio-fuel of the future. When not from micro-algae which produces bio-diesel directly it can be from other sources producing bio-oil not bio-diesel (e.g.:Jatroffa energy plant directly or pyrolysis of biomass to syngas). If not from something like Jatroffa. The emphasis is one producing it from biomass rather than vegetable oil. The process of producing it from biomass consists of three steps:

1. Fast pyrolysis of biomass to produce bio-oil
2. Steam reforming of bio-oil to produce syngas
3. Fisher-Tropsch process for the production of bio-diesel from syngas

The first and third steps are relatively well developed, while the second step is not well developed . This is a project with Professors John Grace and Jim Lim at UBC Funded by CIF (Canadian Industrial Fund)

Hydrogen Production

1. **Novel Autothermic CFB Membrane Reformer for Natural Gas (Dr.Paradeep, Professors: Faisal Abdelhady (Auburn Univ.), , S.Elnashaie(Auburn University), Giovani(Univ. of Western Virginia) and Ritchie (Univ.of Alabama))**

2. **Novel Autothermic CFB Membrane Reformer for Higher Hydrocarbons. Model Component Heptane, aiming for Gasoline, Diesel and Bio-oils (Dr. Chen, Professors: S.Elnashaie , Faisal, Giovani and Ritchie)**

3. **Novel Transport Membrane Reactor for the direct production of hydrogen from biomass (Transport Membrane Reactor Hydrogen Producer (TMRHP)). Hydrogen membrane extraction from syngas (Mr. John Tourtellotte & Professors: Elnashaie, Faisal, Giovani and Ritchie)**

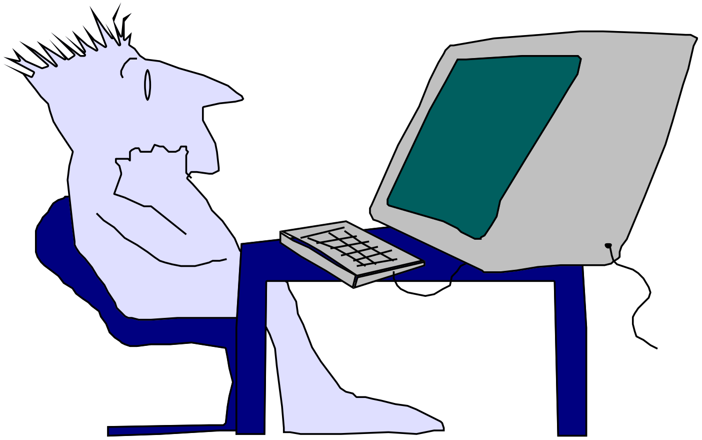
4. **Fluidized bed membrane gasification for hydrogen production (Dr.Wan Azlina, Prof.S.Elnashaie (UPM, Malaysia), Mr. Tony (Noram Co., Vancouver, Canada)**

5. **Bio-hydrogen Production using biochemical methods (Prof. Gamal Ibrahim, Menoufia Univ.,Egypt and Dr. Zurina, Prof.Elnashaie (UPM , Malaysia), Dr. Nour Elgendy (EPRI, Egypt))**

Main Research Approach and Methodology

- ***Sequential De-bottlenecking from Philosophy to Technology***
- ***Optimal Configuration and optimal design/operation***
- ***Optimal utilization of Modeling, simulation and experimentation***
- ***Multidisciplinary Teaming and Research***

Process Simulation and Enterprise Modeling



"A model should be as simple as possible and no simpler" – Albert Einstein

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The Right Model is the One with the Optimum Degree of Sophistication

Prof.Dr.Rutherford Aris

Late Professor Aris (an Englishman) was a Professor of Mathematics in University of Edinburgh , Scotland. On the early 1950's he became a Professor of Chemical Engineering (CE) and joined the department of CE at University of Minnesota (May be the best one in the world). He and Prof. Amundson (originally from Scandinavia) in Minnesota established the top/leading school of mathematical modelling in CE.

Main Bottlenecks and Sequential De-bottlenecking (I)

Bottleneck 1: Very low E.F. (η) as low as 0.001 to 0.01:

Cause: Strong Diffusional Resistances due to large particles.

Cure: Use of fine particles where η =1.0

Obstacles: Not Possible in a Fixed Bed.

Solution: Different Contact equipment, e.g.: Bubbling Fluidized Bed.

New difficulties, such as:

- **More difficult to design and operate than fixed bed.**
- **Limitation on flow rate, much lower flow rate than in fixed bed**
- **Needs additional equipment, e.g.: Cyclone.**

Main Bottlenecks and Sequential De-bottlenecking (II)

Thermodynamic Equilibrium of Reactions Causing Conversion limitations:
Cause: Main Reactions are Reversible.
Cure: Break thermodynamics barrier by product removal.
Possible Techniques:
1- Hydrogen removal by membrane,
2- CO2 removal by adsorbent (e.g. CaO or CaO/MgO).
Obstacles :
Material Science Challenges for Membranes
Regeneration/recycling challenges for CO2 adsorbents.
Solutions:
1- Membrane development.
2- CO2 adsorbent development
2- Use of solid continuous circulation configuration, e.g.: Circulating Fluidized Bed (CFB).
New difficulties, such as:
1. Membrane difficulties
2. Continuous circulation difficulties
3. More difficult to design and operate

2nd Generation: Bubbling Fluidized Bed Reformer.
Membrane Reactor Technology(MRT)

Main Features

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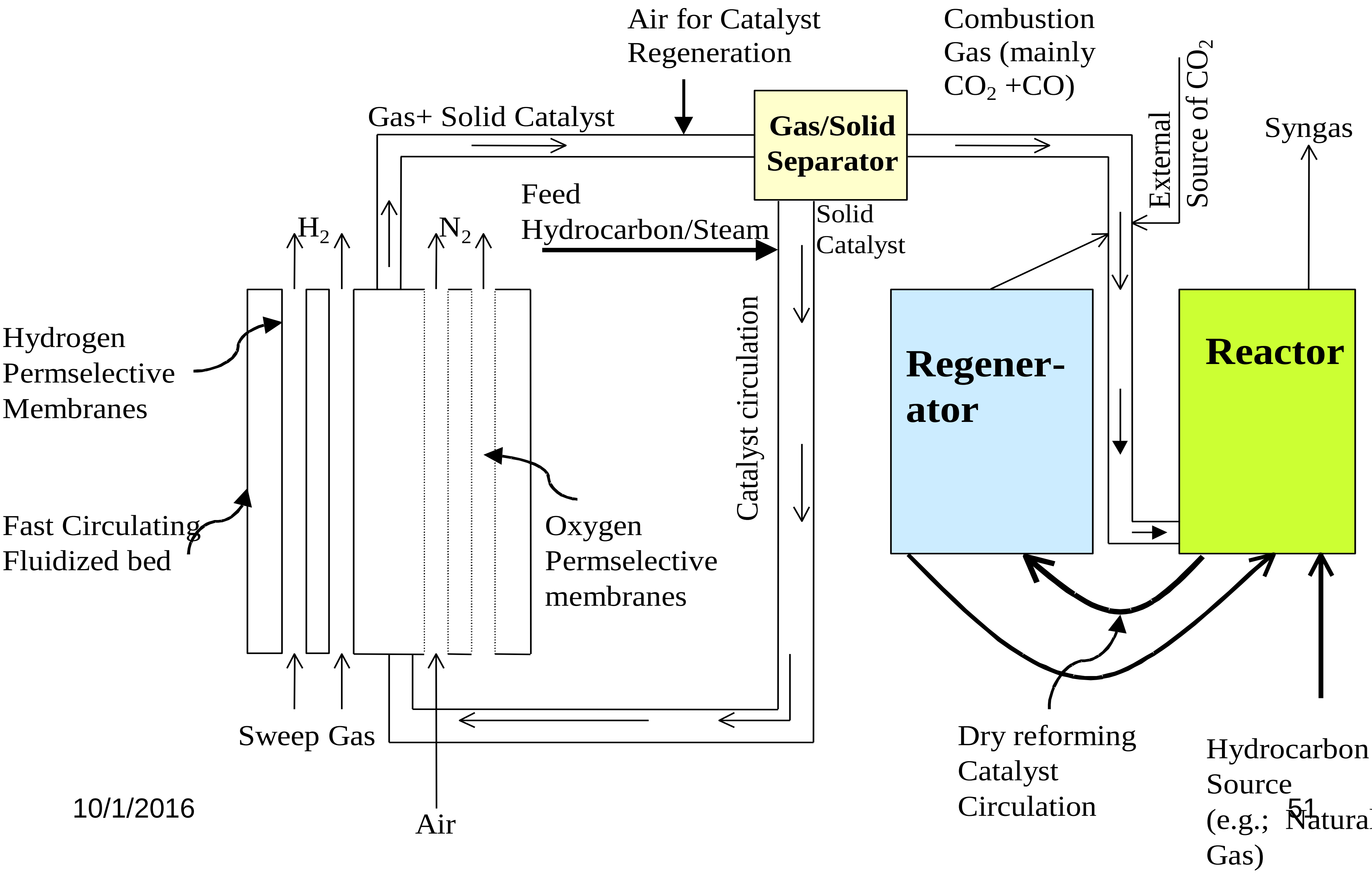
- **Powdered catalyst particles (η= 1)**
- **Hydrogen perm-selective membranes for "shifting" THD equilibrium.**
- **Oxygen feed for efficient in-situ heat supply.**
- **More details, MRT ,not to be disclosed.**

*__*Early references*__***: Elnashaie and Adris(1988), Grace et al & Adris et al (1991 ,1997), Roy et al (1999)***

Novel Autothermic Integrated Circulating Fluidized Bed Reformers (AICFBRs)

Schematic Diagram for Novel AICFB Membrane Reformer (AICFBMR)

MHS=Membrane Hydrogen Separator . Before Catalyst Regeneration



Three main Types of Membranes

- Pd, Pd/alloy Porous Stainless Steel (PSS) and other types for in-situ hydrogen removal in the reformer. (Giovani, UWV)
- Zirconium based and Perovskite membranes, as well as Ion Transport Membranes (ITM) and others for in-situ oxygen supply in the reformer. (Giovani, UWV).
- Polyethersulfone (PES) thermally stable polymers mixed matrix membranes containing an inorganic phase to enhance selectivity for hydrogen permeation to separate residual hydrogen in exit gas from reformer. (Elzanati, NRC, Egypt and Ritchie, Univ. of Alabama USA)

Industrial Reformer Data. Basis For Comparison with CFB

Reformer		***Inlet conditions per tube***	
Furnace dimensions (m)	**21.834 × 35.49 × 13.72**	Process gas (kgmol/hr)	3.953
Furnace type	Top-fired	Temperature (K)	760
Reformer Tubes:		Pressure (kPa)	2837.1
		H_2O/CH_4	3.5610
Heated length	13.72 m	H_2/CH_4	0.2432
Inside diameter	0.0978 m	CO_2/CH_4	0.1209
Number of tubes	897	N_2/CH_4	0.0204
Catalyst pellet shape	Raschig rings	Composition (mol %):	
Catalyst bulk density	1362 (kg/m^3)	***CH_4***	20.22
		H_2O	72.00
		H_2	4.92
		CO_2	2.44
		N_2	0.42

Comparison with Fixed Bed Reformer

	Fixed Bed	FFMSR		
		Case I	Case II	Case III
Exit Methane Conversion	0.8527	0.8675	0.913	0.9375
Exit Steam Conversion	0.3405	0.3226	0.3524	0.3721
Total Hydrogen Yield (per mole of methane introduced)	2.812	2.884	3.081	3.200
Methane Feed Rate (mol/hour)	3953	3953	3953	3953
Process gas exit temperature (K)	1130	1130.57	1130.79	1130
Pressure (kPa)	2200	2200	2200	2200
Length (m)	13.72	0.2	2	2
Total Reactor Volume (m^3)	0.1031	0.0018	0.018	0.018
Membrane Diameter (mm)	-	9.78	9.78	9.78
Membrane Surface Area (m^2)	-	0.123	1.229	1.229
Hydrogen Yield per m^3 of reactor	27.27	1602.2	171.2	177.8

Membranes and/or Sequestration

-Membrane are suitable for all configurations, including fixed beds.

-Sequestration(CaO or Dolomite) most suitable for CFB

-Sequestration much slower than reforming. Exploit slip velocity.

-Optimum seems to be CFB with an optimal combination of Membranes and sequestration.

-Sequestration solid like CaO has the severe limitation of being batch, if there is no on-line regeneration of CaCO3.

Auto-thermal operation using carbon formation combustion

Carbon formation - combustion

- **Methane Cracking**

$CH_4 \rightleftharpoons C + 2H_2$ [$\Delta H(298C) = 75$ kJ/mol] Endothermic

- **Carbon burning**

$C + O_2 \rightarrow CO_2$ ($\Delta H(298) = -393.5$ kJ/mol) Exothermic

- ***Net heat production: 159.25 kJ/mol H_2 formed***
  (318.5 kJ/mol CH_4 reacted)
- ***Maximum Hydrogen Yield: 2 mol H_2/mol CH_4***

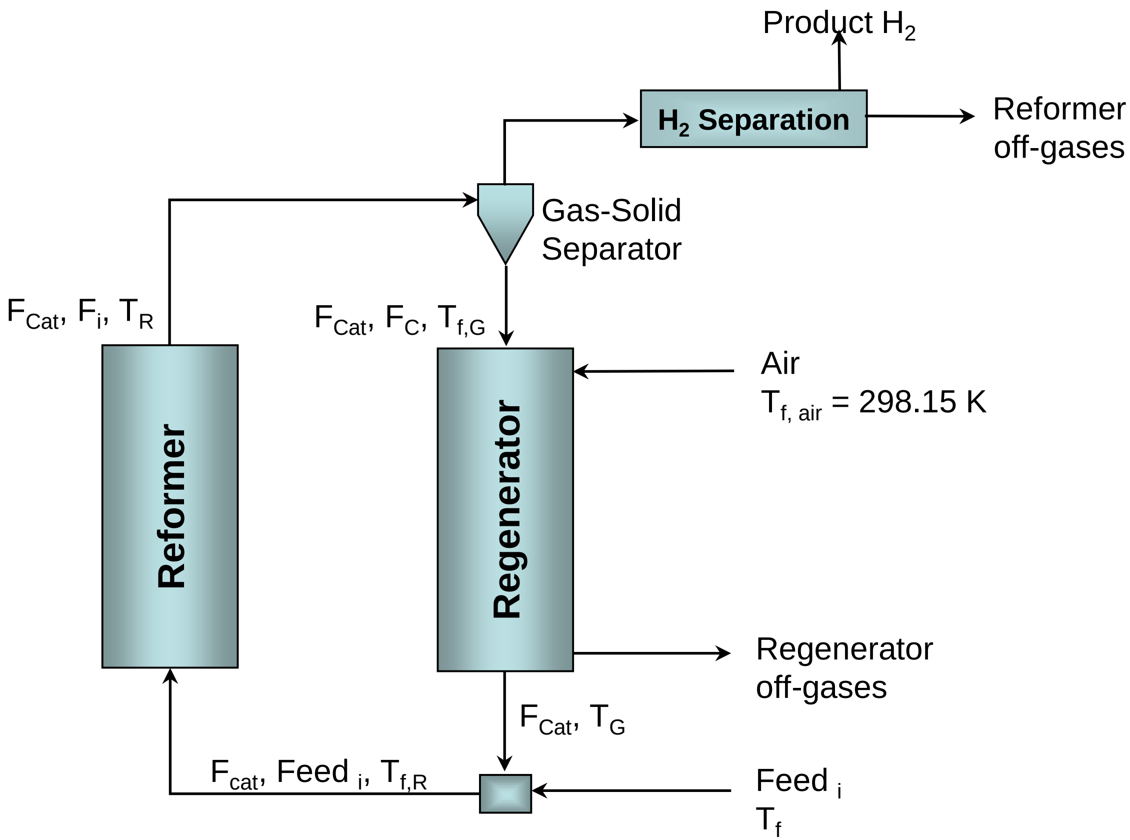
ADDITION OF STEAM

$CH_4 + 2H_2O \rightleftharpoons CO_2 + 4H_2$ ($\Delta H(298) = 165$ kJ/mol) {4 *mol H_2/mol CH_4*} Endothermic

Autothermal operation

Maximum Hydrogen Yield = ~ 3.32 mol H_2/mol CH_4

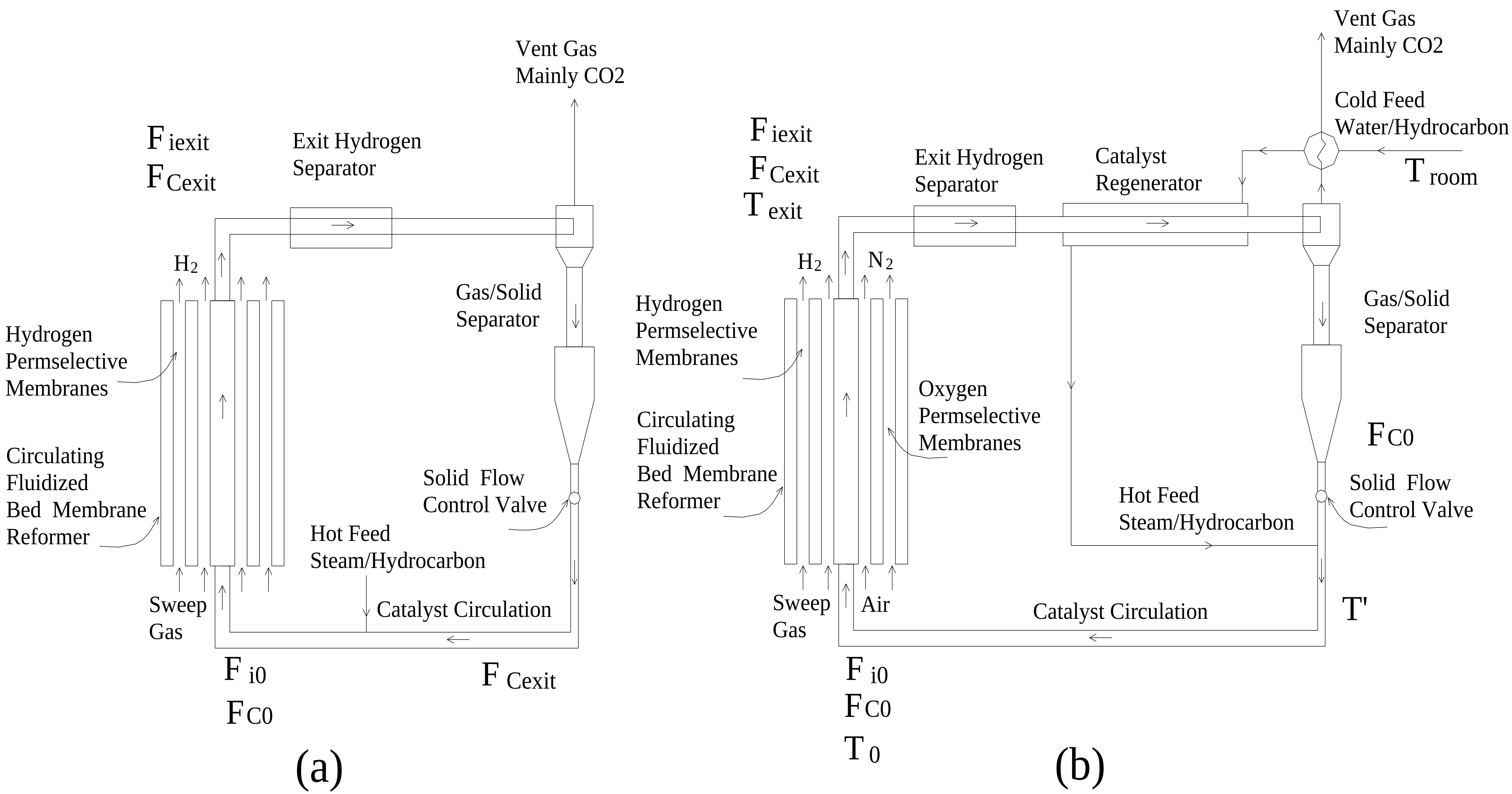
Reformer – Regenerator (Configuration A)



- Boundary Value Problem
- Bifurcation phenomenon

Higher Hydrocarbons. Heptane as a Model Component.

<u>Aiming At</u> : Gasoline, Diesel and Bio-Oils



Schematic of the circulating reformer-regenerator system
a). For pseudo-steady-state cases without catalyst regeneration
b). Autothermal system with catalyst regeneration

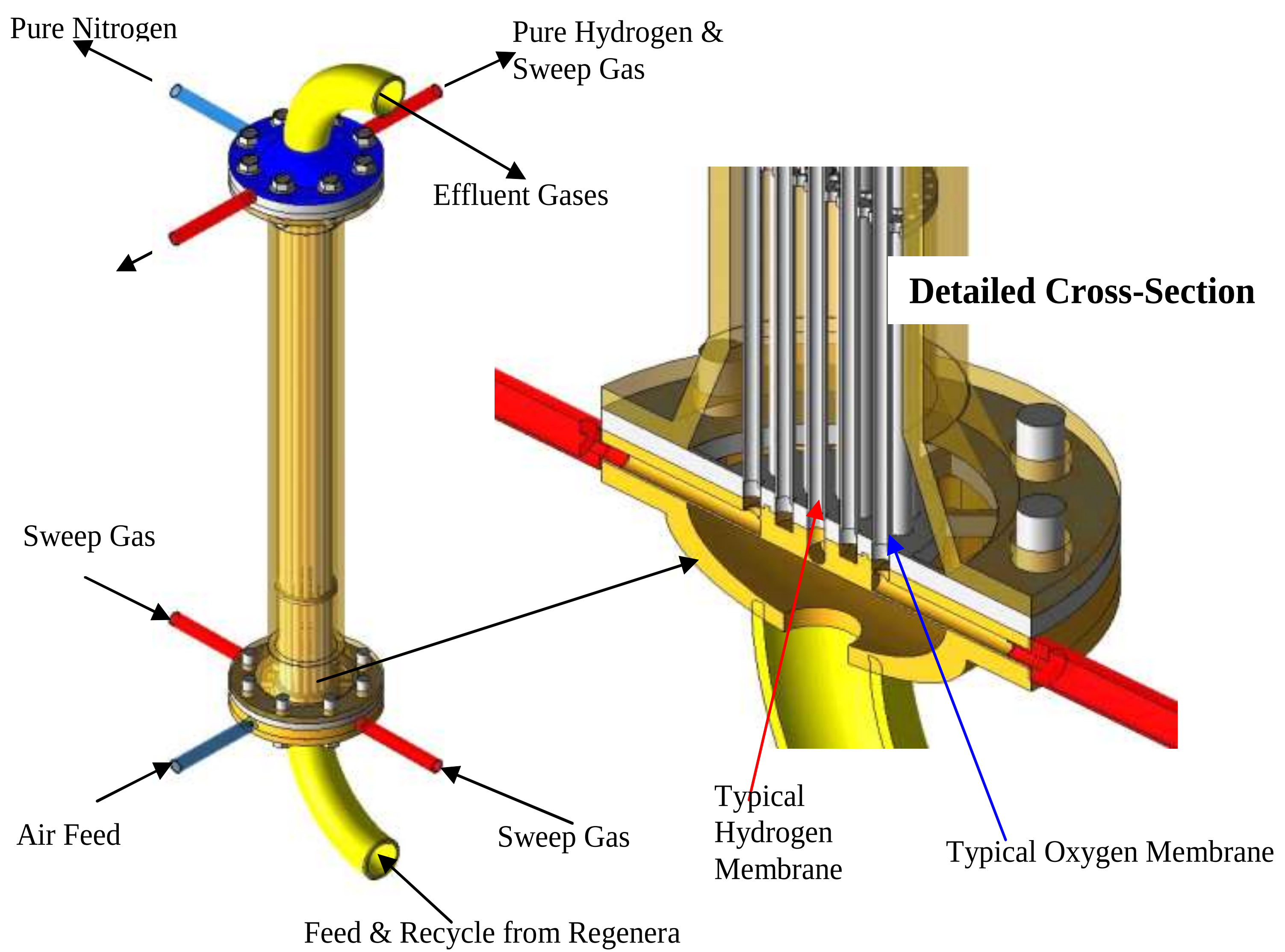


Fig. 2: Preliminary Design of the Fast Fluidized Bed Membrane Reformer

A Novel Transport Reactor for the Direct Production of Hydrogen from Biomass

Elnashaie Group at Auburn University,Auburn, AL (Now at UBC) Jointly with

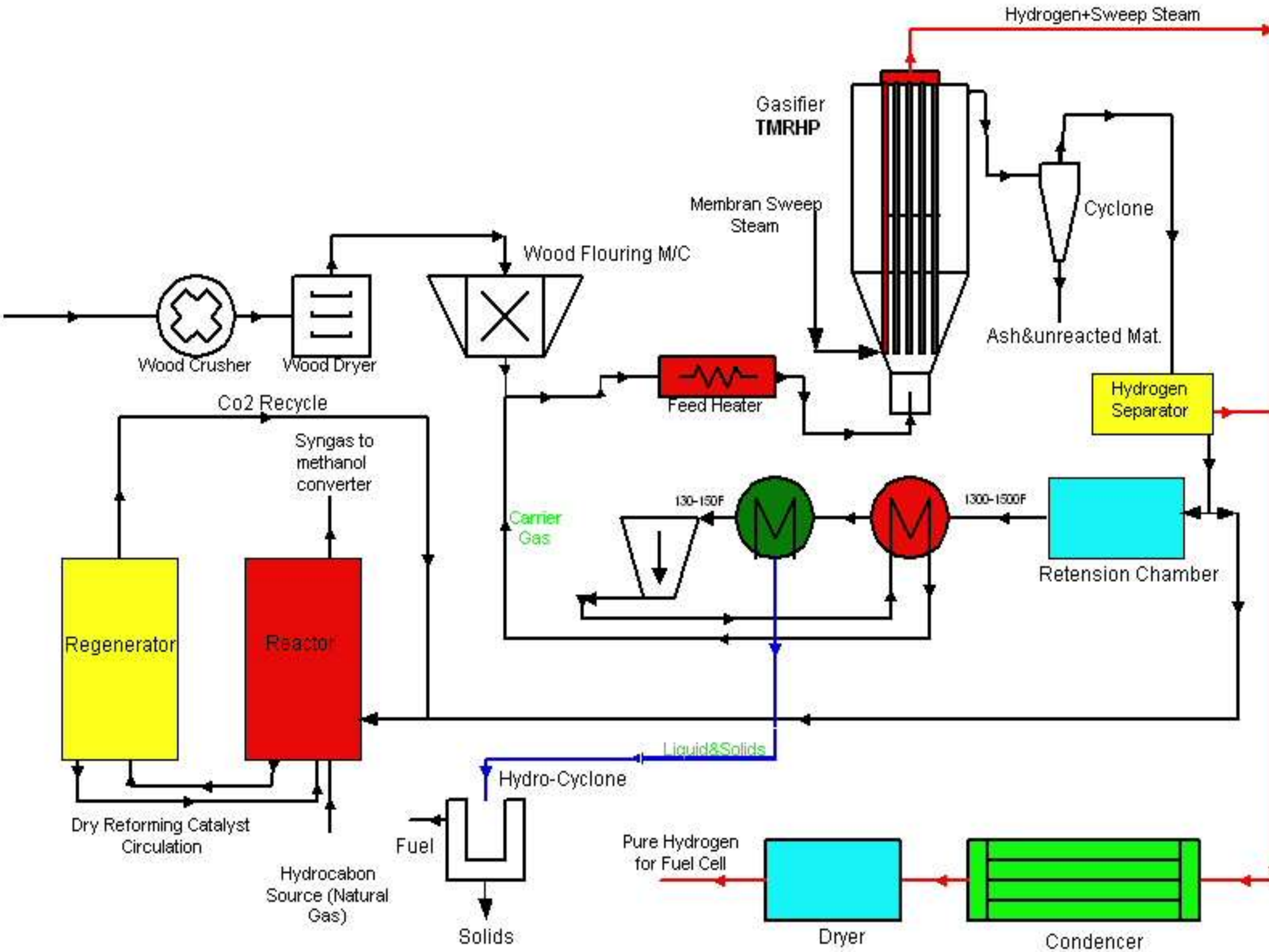
Tourtellotte & Associates, Birmingham, Alabama

Continued now with Dr. Wan Azlina, UPM, Malaysia

Transport Membrane Reactor Hydrogen Producer (TMRHP)

Objectives of the research include:

- improving performance by optimizing gasifier configuration and fundamental processes.
- use of small amount of Nickel based catalyst to promote reforming and water-gas-shift reactions for maximization of hydrogen and minimization of CO production.
- use of hydrogen permeable membranes and CO2 sequestration to “push” the thermodynamic equilibrium towards maximum hydrogen production.



Hydrogen+Sweep Steam
Gasifier
TMRHP
Cyclone
Membran Sweep Steam
Wood Flouring M/C
Ash&unreacted Mat.
Wood Crusher
Wood Dryer
Feed Heater
Hydrogen Separator
Co2 Recycle
Syngas to methanol converter
130-150F
1300-1500F
Carrier Gas
Retension Chamber
Regenerator
Reactor
Liquid&Solids
Hydro-Cyclone
Dry Reforming Catalyst Circulation
Fuel
Hydrocabon Source (Natural Gas)
Pure Hydrogen for Fuel Cell
Solids
Dryer
Condencer

Bio-hydrogen Production

- **Hydrogen from fossil sources is locally clean but not globally clean**
- **Bio-hydrogen is the true clean fuel both locally and globally and it is obtained from bio-RRM, whether the processes used are bio, or non-bio.**
- **Thermo-chemical processes based on biomass: is gasification of biomass to produce syngas (H_2, CO, CO_2); or fast pyrolysis of to bio-oil followed by steam reforming of the bio-oil to high quality syngas (rich in H_2). Syngas can then go through the catalytic FT process to produce any thing from methanol up to diesel; they are Bio-Fuels (BF) from RRMs, although the processes are all not bioprocesses. This is one route, another route is the extraction of hydrogen from this syngas using suitable technique, e.g.: Membrane Separation (MS), Pressure Swing Adsorption (PSA), etc, this hydrogen is also a bio-hydrogen from RRMs.. The extraction of this bio-hydrogen can be complete or it can be an extraction of any excess hydrogen above the % necessary for the FT process and the rest is used in the FT process to produce one of the other BFs, e.g.: bio-diesel. This bio-diesel is different than the present bio-diesel produced from vegetable oils and some alcohol through trans-esterification. In order to distinguish between the two we will call the above the FT-bio-diesel, which is more strategic bio-diesel than the trans-esterification one and does not use food nor alcohol in the process of its production.**

Light driven processes:

Three main bio-processes can utilize light to produce hydrogen:

a- Bio-photolysis of water using algae and cyano-bacteria; This method uses the same processes found in plants and algal photosynthesis, but adapts them for the generation of hydrogen gas instead of carbon containing biomass.

b- Photodecomposition (photo-fermentation) of organic compounds based on phototrophic bacteria which have high theoretical hydrogen yield and the ability to consume organic substrates derivable from wastes and then, for their potential to be used in association with wastewater treatment.

c- Water Gas Shift (WGS) reaction: $CO + H_2O \longleftrightarrow CO_2 + H_2$ catalyzed by a microorganism (e.g.: *Rhodospirillum ruburm*) at low temperature in the liquid phase, in contradistinction to the classical process using iron based solid catalyst at high temperatures in the gas phase. The hydrogen produced is bio-hydrogen although the feed can be from non-biological sources but the process is a bio-process. The feed, in this case, can be from a bio-source if the CO comes from something like the gasification of biomass.

U.S. DEPARTMENT OF ENERGY | Energy Efficiency & Renewable Energy BIOMASS PROGRAM

- **Renewable Fuel Standard (RFS) mandates biofuel use to improve energy security in all countries, even oil producing countries.**
- **The standard for USA, as an example, requires 36 billion gallons of renewable fuels production by 2022, of which 21 billion gallons will be advanced biofuels.**
- **RFS will require technological innovation, private investment.**
- **Success will depend on development of efficient new systems and networks to sustainably produce, harvest, and transport large quantities of diverse feed-stocks; advanced technologies to cost-effectively convert biomass to fuels; and expanded and improved distribution and end-use infrastructure to deliver these fuels to consumers across the country**

Strategic Approach by USA DOE Adopted by Many Countries in the Last Few Years

- U.SA DOE Biomass Program works with industry, academic, and laboratory partners to develop advanced technologies and real-world solutions to reduce costs and spur market growth.
- By multidisciplinary research, development, and demonstration (RD&D) , DOE facilitates technology advancements accelerating sustainable production of clean, affordable energy.
- Unlocking potential of diverse, non-food biomass resources: e.g.: switch-grass, Jatroffa, agricultural and forest residues, municipal waste, and algae, yields advanced biofuels including cellulosic ethanol and renewable gasoline, aviation, and diesel fuels. These resources also produce bio-power and bio-products (IBRs)

SD

- **SD efforts by DOE address environmental, social, and economic issues along the entire bioenergy/bio-products supply chain.**
- **The Biomass Program is committed to maximizing environmental benefits based of RRMs to ensure SD.**
- **Through field research, modeling, and advanced analysis, the program investigates the Life-Cycle(LC) impacts of bioenergy/bio-products production**

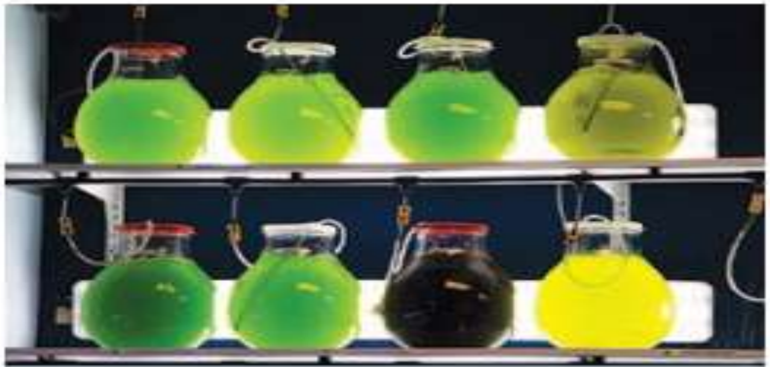
The program is currently supporting development of cellulosic ethanol as well as renewable gasoline, diesel, and jet fuels.
Photo from BCS Incorporated

IBRs

- **BFs /BPs are produced in IBRs that efficiently convert a broad range of biomass feed-stocks into affordable BFs/BPs, and heat and power.**
- **Biomass Program focuses its efforts on key supply chain challenges, including development of replicable feedstock supply systems and innovative conversion technologies, both result in lower production costs.**

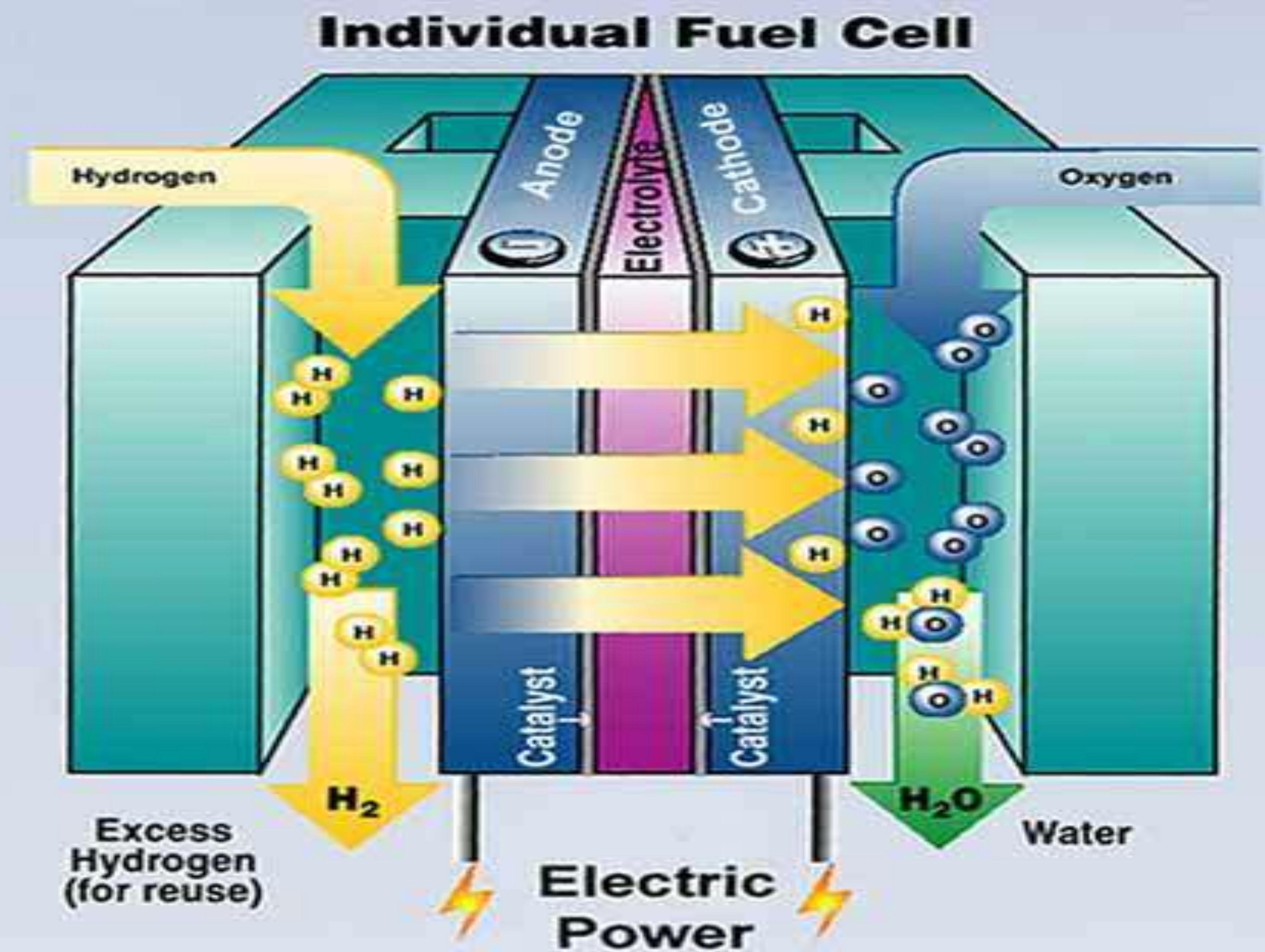
Conversion Processes

- **The Biomass Program is exploring new ways to convert feed-stocks into cost-competitive liquid renewable transportation fuels. It conducts collaborative multidisciplinary R&D to explore biochemical and thermochemical conversion as well as processes that combine the two methods, specially in IBRs.**
- **Biochemical Conversion : It entails breaking down biomass to make carbohydrates available for conversion into sugars, which can then be converted into BFs/BPs using microorganisms and other catalysts. Many researchers at DOE and around the world are working to drive down the cost of pretreatment and enzymatic hydrolysis processes. They are also exploring robust new fermentation microorganisms. Future research will explore biological and chemical catalysis integration to produce a wider range of advanced BFs/BPs.**



Algae R&D focuses on genetics, strain development, cultivation strategies, and harvesting and dewatering, as well as sustainability and siting considerations.
Photo from iStock/5312772

Example: Schematic for Hydrogen Fuel Cell (HFC). Single or Stack



Hydrogen as Feed for Fuel Cells

- **Hydrogen is the most plentiful and simplest of all elements in the universe. Despite its simplicity and abundance, hydrogen doesn’t occur naturally as a gas on the Earth and is always combined with other elements, because of its high reactivity.**

-Hydrogen is the basic component of water and is also found in many organic compounds, notably the hydrocarbons that make up many of our fuels, such as gasoline, natural gas, methanol, and propane.

-Hydrogen is not an energy source itself but can be called an energy carrier as it takes a great deal of energy to extract it from water and other hydrocarbons and is therefore used in fuel cells and batteries.

-The hydrogen fuel cells are just like traditional batteries. When a chemical reaction occurs between air and hydrogen, three things are produced namely electricity, which in turn propels the vehicle, a small amount of steam is emitted as a by product instead of pollution causing gases which are produced by other traditional fuels like coal, petroleum etc. and some heat.

- **Can this be better?**

Hydrogen& Hydrogen Fuel Cells (HFs)

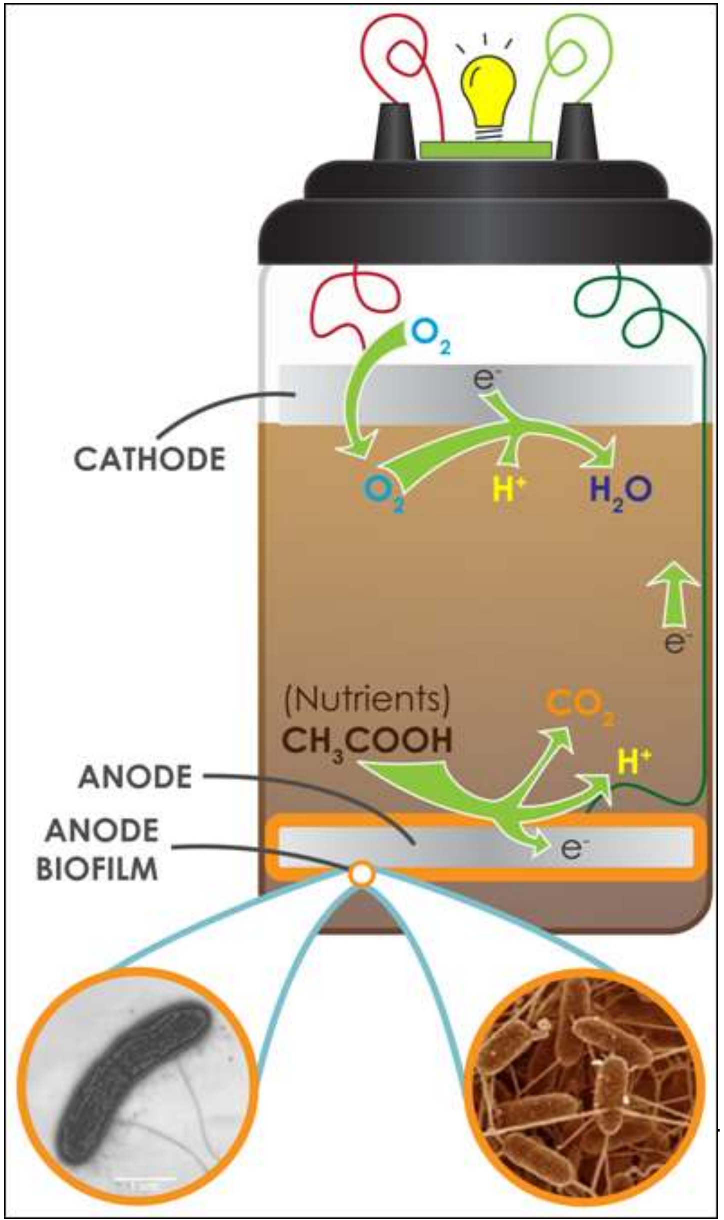
-Companies are accelerating research and development of hydrogen fuel cells. Production, storage, and delivery infrastructure technologies needed to support hydrogen fuel cells for use in vehicles and electricity that many of the fuel cell producing for cities. The usage of hydrogen fuel cells in everyday life would also minimize transportation costs and expensive wiring and may be even develop to large power plants in near future.

-Besides being a non-polluting resource and the only emission is water vapor, hydrogen fuel cell has its disadvantages and obstacles to overcome before it can become widely available, and accepted. The foremost being its high cost. As the popularity of using hydrogen propelled vehicles is increasing the demand of hydrogen fuel is becoming higher than its production. And therefore the price of hydrogen fuel is quite high.

-Since non-bio hydrogen has to be produced using coal, natural gas and oil, it does not really solve the dependency issues and its storage and transportation may indirectly lead to pollution.

Microbial Fuel Cell (MFC)/biological FC is bio-electrochemical system deriving current using bacteria mimicking bacterial natural interactions.

MFCs can be grouped into two general categories, those that use a mediator and those that are mediator-less. The first MFCs, demonstrated in the early 20th century, used a mediator: a chemical that transfers electrons from the bacteria in the cell to the anode. Mediator-less MFCs are a more recent development dating to the 1970s; in this type of MFC the bacteria typically have electrochemically active redox proteins such as cytochromes on their outer membrane that can transfer electrons directly to the anode. Since the turn of the 21st century MFCs have started to find a commercial use in the treatment of wastewater.



A soil-based MFC (shown in previous slide)

- **Soil-based MFC is a typical special case. Soil acts as the nutrient-rich anodic media, the inoculum, and the proton-exchange membrane (PEM). The anode is placed at a certain depth within the soil, while the cathode rests on top of the soil and is exposed to the oxygen in the air above it.**
- **Soils are naturally teeming with a diverse consortium of microbes, including the electrogenic microbes needed for MFCs, and are full of complex sugars and other nutrients that have accumulated over millions of years of plant and animal material decay. Moreover, the aerobic (oxygen consuming) microbes present in the soil act as an oxygen filter, much like the expensive PEM materials used in laboratory MFC systems, which cause the redox potential of the soil to decrease with greater depth. Soil-based MFCs are becoming popular educational tools for science classrooms.**

Mediator and Mediator-less MFC

- **Mediator MFC: Most of the microbial cells are electrochemically inactive. The electron transfer from microbial cells to the electrode is facilitated by mediators such as thionine, methyl viologen, methyl blue, humic acid, neutral red and so on. Most of the mediators available are expensive and toxic.**
- **Mediator-free MFC: These fuel cells do not require a mediator but use electrochemically active bacteria to transfer electrons to the electrode (electrons are carried directly from the bacterial respiratory enzyme to the electrode). Among the electrochemically active bacteria are, *Shewanella putrefaciens*, *Aeromonas hydrophila*, and others. Some bacteria, which have pili on their external membrane, are able to transfer their electron production via these pili. Mediator-less MFCs are a more recent area of research and due to this, factors that affect optimum efficiency, such as the strain of bacteria used in the system, type of ion-exchange membrane, and system conditions (temperature, pH, etc.) are not particularly well understood. Mediator-less MFCs can, run on wastewater, also derive energy directly from certain plants. This configuration is known as a plant MFCs. Possible plants include reed sweetgrass, cordgrass, rice, tomatoes, lupines, and algae.**

Microbial electrolysis cell

A variation of the mediator-less MFC is the microbial electrolysis cells (MEC). Whilst MFC's produce electric current by the bacterial decomposition of organic compounds in water, MEC's partially reverse the process to generate hydrogen or methane by applying a voltage to bacteria to supplement the voltage generated by the microbial decomposition of organics sufficiently lead to the electrolysis of water or the production of methane.

A complete reversal of the MFC principle is found in microbial electrosynthesis, in which carbon dioxide is reduced by bacteria using an external electric current to form multi-carbon organic compounds.

- **Thank You**

I will Be Happy to Answer any Questions and Discuss Any Topics

- **E-mail: selnashaie@gmail.com**

If you wide like to have a copy of this PP slides please e-mail me

This is not the end. It is not even the beginning of the end. But it is the end of the beginning.

Winston Churchill