

# **A Biochemical Approach to Attributing Value to Biodiversity – The Concept of the Zero Emissions Biorefinery\***

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## **Abstract**

Since the National Forum on Biodiversity held in Washington in 1996 biodiversity has become a central scientific and political problem world-wide. Deforestation, plantation industries and monoculture orientated agriculture with pest problem, chemical pollution, habitat fragmentation, etc., are factors increasing ongoing extinction of biodiversity. Biodiversity can be characterized not only as a variation of genes, diversity of higher plants, number of species but also as a sheer weight of biomass and variety of its biocomponents. The plantation core business utilizes maximum 10% of biomass and only few its components (for example, sugar cane juice, oil from oil palm, fibers from sisal, pineapple fruits, coffee, etc.). The loss of materials and biochemicals is the loss of value and diversity. A total conversion of plantation and agricultural waste materials into value added biochemicals like sugars, vitamins, citric acid, furfural, lipids, waxes, xylitol, medicals and many other products means applying a strategy of replacing petroleum products with biochemicals from biomass and it should facilitate an indirect biodiversity conservation. It has been shown that the substitution of petroleum refinery with biorefinery modifies 3R approach (reduce, reuse, recycle) to 4R approach (replace, reduce, reuse, recycle). Strategies of replacing petroleum products with chemicals from biomass need an integration of industries in the clusters with Zero Emissions. Besides environmental benefits there are economical benefits from biorefinery. Biorefinery creates new economy - lignocellulosics (in the narrow sense "carbohydrate") economy similar to petrochemical economy. The progress of new and conventional biorefinery technologies such as steam explosion, solid state extrusion, pyrolysis, etc. together with biotechnologies has been demonstrated. Issues of biodiversity protection and conservation and a variety of value added biochemicals from biomass are tightly connected with the value of world's ecosystem services and natural capital, including natural resources and environmental conditions, problem.

## **INTRODUCTION**

Eco-restructuring for sustainable development involves shifts in technology, economic

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activities and lifestyles needed to harmonize human activities with natural systems [1]. An important element for eco-restructuring is the Zero Emissions concept, which literally means there is no waste in air, water and land. The Zero Emissions scientific program ZERI (Zero Emissions Research Initiative) was first launched at the United Nations University, Tokyo, in 1994. In the UNU/ZERI Feasibility Studies Report C-G. Heden emphasized the importance of biomass biorefinery [2]. Biorefinery was used in two meanings:

- as an industrial system for value added chemicals and materials;
- as a part of knowledge system which can be disseminated and learned through "virtual university" using networking and new teaching concepts.

UNU/ZERI is not the waste minimization but the waste utilization program to achieve more with less. According to Gunter Pauli [3] we need new Generative Science which could shift our activities from the Homo non sapiens with linear thinking to Homo sapiens with management concept based on analogy with decentralized immune system. It considers every core element of the system is intelligent. Generative Science starts from the embedded intelligence of nature, and searches for the maximization of wealth of earth (principle of cooperative biodiversity). Biodiversity includes variation of genes, diversity and number of species and also variety of biomass and its biocomponents. Today the worlds industry is utilizing not more than 5% to 10% of the biomass of raw materials from plantation [4]. At the same time only 1% of all materials disposed in landfills could not be readily recycled by a process already available. An important component of biorefinery breakthroughs is material separation technologies [5].

## WHAT IS OIL REFINERY?

The crude oil is a mixture of many different organic hydrocarbon compounds, the building blocks of petroleum. In the process of oil refinery the first is to remove water and other impurities from the crude oil, then distill the crude oil into its various fractions as gasoline, diesel fuel, jet fuel, kerosene, lubricating oils, tars and asphalt. Then, if necessary, these fractions can be chemically changed further into various industrial chemicals and final products. In total the petroleum refinery operates with more than two thousand hydrocarbon compounds.

## WHAT IS BIOREFINEFRY?

Biorefinery separates the plant biomass, so called lignocellulosic materials, into

building blocks - phenols and sugars. Biorefinery technologies produce value-added products that might range from basic food ingredients to complex pharmaceuticals and from simple building materials to complex industrial composites. Products such as ethanol, biodiesel, glycerol, lipids, oils, citric acid, lactic acid, acetic acid, methanol, isopropanol, vitamins, sugar and protein polymers, etc., could be produced for use as fuels in food, cosmetic and pharmaceutical industries. The crucial for biorefinery is products - special fibers, new adhesives, biodegradable plastics, degradable surfactants, biodetergents, specific polymers and enzymes, etc. - development with a target to fill particular niches. Recently almost 50 percent of all detergents in the USA contain enzymes and the market share in Europe and Japan for enzyme based detergents is over 90 percents. The cost of enzymes has dropped by more than 75 percent in the last 10 years [6]. Biorefinery utilizes organic waste materials from agriculture, forestry, fishery, etc., converts biomass into value-added products and cleans environment as an interconnected-closed system (see Fig.1).

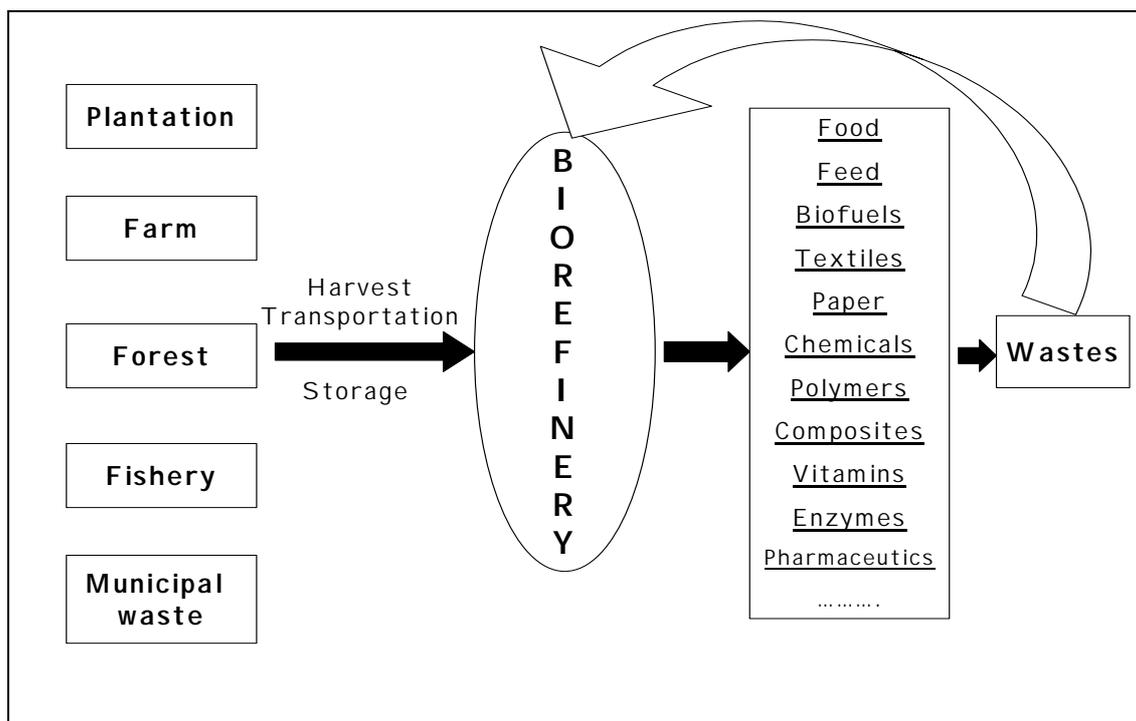


Figure 1. Closed loop: biomass - biorefinery - value added products - disposed waste - biorefinery.



## WHY BIOREFINERY WILL REPLACE OIL REFINERY?

It is clear that the industry based on petroleum is not sustainable. The limited nature of fossil resources, particularly oil, and environmental pollution resulting their use create a demand for alternative sources. The global oil production peak and 1970s-style oil shocks will begin between 2005 and 2010 [8,9]. The forecast of global upcoming energy crisis illustrates bell shaped curves (Fig.3). Hence, the rise of biorefinery will come faster than expected. Recently the energy sector is the largest handler of materials in economy. Current global emissions of carbon as a main fuel now are about 6 billion tons, or more than 1, 000 kilograms per person on the planet. In comparison, the global steel industry produces about 700 million tons per year, or about 120 kilograms per person [10]. The sources alternative to oil should be renewable, photosynthetically based biomass. Biomass in natural cycles conserves mass but dissipates energy. Fortunately for this energy we shouldn't "pay". Oil refineries discharge lot of wastewater containing waste oil and toxic by-products from the refinery process. Some impurities such as heavy metals, sulfide, and phenols are in the crude oil. Toxic compounds such as cyanide, dioxins and furans are generated during the refining process. Refineries also discharge large amounts of pollutants to the air and generate hazardous solid waste. Most of the oil refinery sites groundwater is contaminated with refinery toxic chemicals as phenols, cyanide, dioxins, furans, etc. These compounds, for example, migrated towards Lake Ontario at the rate of 10 meters per year [11]. The oil refinery pollution creates a new problem - bioremediation. Some of bioremediation methods are also biorefinery. For example, tailored microbes to break down phenols were used in many contaminated sites. The petroleum refinery starts with a receipt of oil for storage, refining operations and shipping the refined products from the refinery. Oil companies use catastrophic event risk management (as environmental health and safety acceptable risk levels) at the oil refinery. Chemicals produced from biomass generally require production processes with less intensive conditions of temperature, pressure or solvent. So biorefinery reduces or eliminates the risk. Biomass refinery in contrary to oil refinery, if produced and used on sustainable basis, recycles carbon dioxide and sequesters it. Hence biorefinery implies positive effect for global warning. If harvested wood is used to displace coal in electric power generation then 1 kg of carbon C in wood is equivalent to 0, 6 kg of C in coal [12]. The efficiency of power plant can be characterized as an amount of carbon dioxide emissions per kwh. So, wood-fired plant efficiency is about 60% of the coal-fired plant. At the same time as

shown in the Graz/Oak Ridge Carbon Accounting Model (GORCAM) report [12] the total carbon benefit of fuelwood plantation on agricultural land is 520 t Carbon/ha after 100 years or 5,2 t Carbon/ha annual C sequestration.

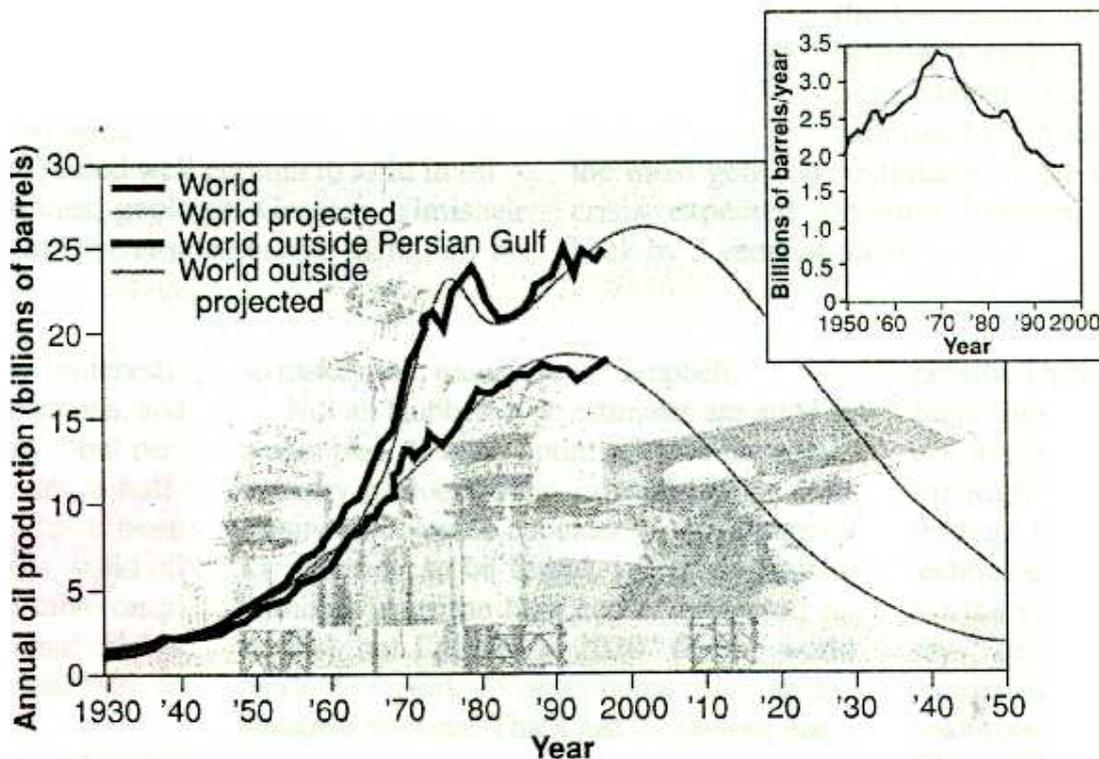


Figure 3. Predicted peak in world oil production. Upper right - U.S. oil production in the lower 48 states peaked in 1970, as was predicted by the geologist M. King Hubert (Nature, 1998, vol. 281, N 5380, 1128 -1131).

#### THE PRESENT CONSUMPTION OF PETROLEUM AND PLANT BIOMASS

Today the USA consumes 19 million barrels of oil per day and 72 million barrels a day are used worldwide. The USA, German, Japanese and Dutch economies require 45 to 85 metric tons of natural resources per person per year, over 40% of which is the result of energy derived from fossil fuels [13]. In the USA renewable sources still contribute only about 1% of the total energy generating capacity [14]. Presently the production of same products, except pulp and paper, from petroleum is much cheaper than from lignocellulosics, starch and vegetable oil. In 1989, 172 million tons of fossil fuels were used in the USA for making industrial products (excluding construction products like asphalt). The same time, aside of papermaking (80.9 million tons), only 6 million tons

of plant matter consumed in the USA are used for industrial purposes [6]. Hence the ratio of fossil fuels to plant materials are 30:1. At the same time there are great facilities for lignocellulosic materials biorefinery. Only in the USA there are approximately 350 million tons of agricultural waste currently disposed each year [6]. Unused, residual biomass from tropical plantations is enormously high. So, different organic waste materials can be used for biorefinery without damaging forest and without soil erosion. Only 40% or less of the organic matter is actually removed from farm fields for biofuel-ethanol production. The rest is returned to the soil as organic matter, increasing fertility and reducing soil erosion [15]. This soil organic substances represent a net removal of carbon dioxide from atmosphere. An increase of only 1% in the soil organic substances is equivalent to reduction of over 40 tones of carbon dioxide per hectare of land [15]. Energy use for transportation is responsible for over 25% of total US greenhouse gas emissions. Ethanol is now replacing over a billion gallons of gasoline, and providing 35% to 46% fewer emissions. However, for bio-fuels to reach their full potential, a greatly expanded biorefinery industry and improved engine designs will be required [16].

## MATERIAL FLOW ANALYSIS AND NEW ECONOMIC ACTIVITIES MEASURE INDEX

Material inventory and material flow analysis are important for estimation of systems material utilization efficiency. Economic activity also depends on the intensity of material flows. That is the reason why many researchers use material flow diagrams. As a typical example is material flows in the USA forest industry [10]. Forest products waste materials (Fig, 4) are potential raw materials for biorefinery. However not all material chains have positive influence on industrial and environmental system. Measures such as the Gross Domestic Product (GDP) do not include the movement or processing of large quantities of materials that have no or even have negative economic value. Hence, the World Resources Institute (WRI) starts [13] to use a new index Total Material requirement (TMR) which measures the total consumption of natural resources (in monetary value) that national economic activity requires. The ratio- TMR/GDP provides an overall measure of the efficiency of country's economy. For developed countries the foreign proportion of TMR ranges from 35% to 70%, with the larger percentages in smaller countries. The researchers of the WRI concluded that "these high- income countries gain the benefits of consuming imported resources, but the environmental cost of producing them falls on others, often developing countries, that

supply them". In the context with the "Factor 10" the target for developed countries can be expressed as 30 kg of materials per 100 \$ of GDP, instead to the present value of about 300 kg per 100 \$ of GDP [13].

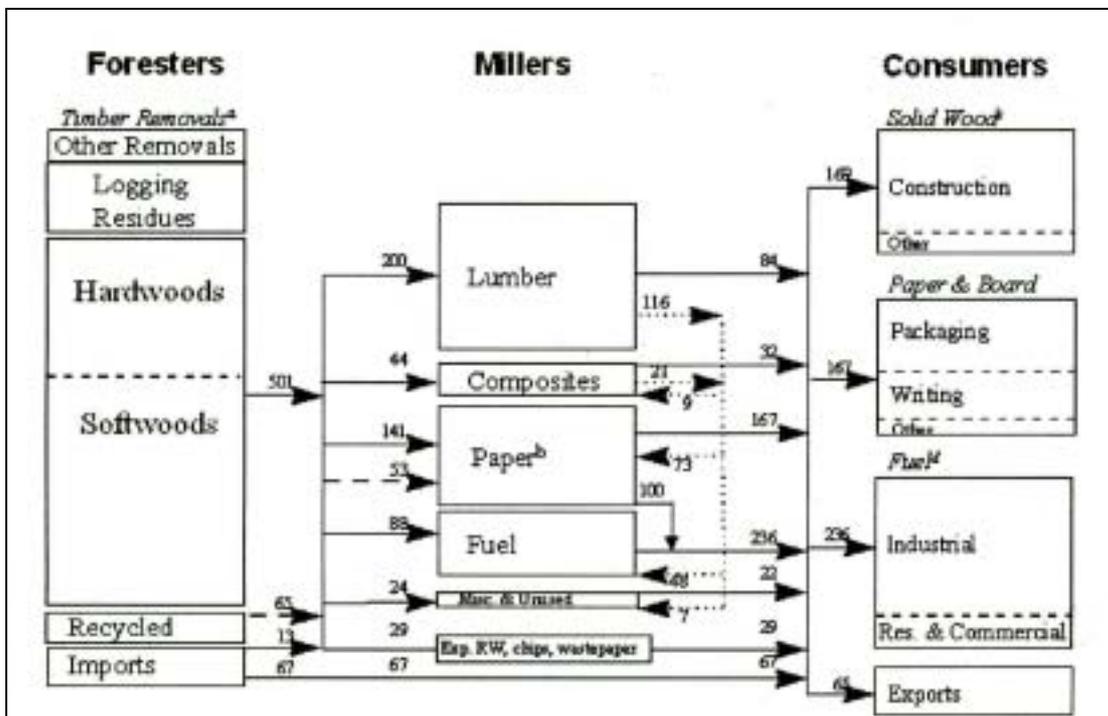


Figure 4. Material flows in the USA forest products industry. Box heights are to scale. Values are in million cubic meters. One metric ton to be equivalent to two cubic meters. a) based on the ratio of logging residues (15,1%) and "other removals" (6,6%) to all removals for 1991; b) the dashed lined entering paper represents the inputs from "recycled"; c) construction includes millwork such as cabinetry and moldings. "Other" includes industrial uses such as materials handling, furniture, and transport; d) the ratio of end uses relies on Btu data from the USDOE Energy Information Administration [10].

#### SPECIFIC DEMANDS TO BIOREFINERY

Biomass distribution density as well as energy is low in comparison with existing fossil resources. Hence the economic value per unit weight of the materials is also low and consequently the value added becomes low. As consequences the development of biorefinery technologies should be based on the principle of local uses in small areas. Biorefinery technologies should be compact and mobile, oriented to apply in rural areas and generate new jobs. Particularly it is important for developing countries because

about 90 percent of the growth in world population will occur among people living in these countries with traditional village-based ways of life. The biorefining conversion of biomass would be considered not only as a substitute of fossil resources but also as an integrated use of living organisms, microorganisms and enzymes in a cycle of food-stuffs, feeds, value added chemicals and industrial materials. Biorefinery technologies should not adversely affect the environment, living things and the life of people in community. The system approach needs analyses of such four important agricultural and forestry cycles as carbon (respiration, photosynthesis, organic matter decomposition), nitrogen (N fixation, mineralization, denitrification), phosphorus (fungi mutualistic symbiotic relationships with plant roots-mycorrhizae) and water (precipitation, evaporation, infiltration, runoff) and their interdependence. Soil degradation elimination and biodiversity conservation are the dominating factors in biomass biorefinery. Principles of ecological conservation and the balance between production and utilization of biomass resources should be used in applying biorefinery technologies. The global target for biorefinery technologies is eco-efficiency which can guarantee "resource productivity increase". For instance "by a factor of four, the world could enjoy twice the wealth that is currently available, whilst simultaneously halving the stress placed on our natural environment" [17]. For thermodynamic viewpoint, photosynthesis is the most important materially productive process on the Earth. The same time ecological productivity is limited. Biomass can not grow infinitely. Unfortunately photosynthesis efficiency (maximum amount of solar energy trapped as chemical energy in biomass) is low. The maximum efficiency which photosynthesis can occur is 26% [18] (some methods give only 8 to 15%). An agricultural crop in which the biomass (total dry weight) stores as much as 1% of total solar energy received on an annual area- wide basis is exceptional. Only some plants particularly sugarcane efficiency is as much as 3.5% [19].

## BREAKTHROUGH BIOREFINERY TECHNOLOGIES

A case study (Table 1) shows the advantages of new technologies in comparison with conventional pulping technologies of plant materials. Targets for these technologies are different. Cellulose and fibers are targets for the conventional pulping industry, for the steam explosion - fibers, cellulose, sugars, lignin and phenols, for the solid state extrusion - sugars and composite materials. In [19] the authors using series of process design and economy models calculate the process cost for several scenarios in steam explosion fractionation of wood. It was concluded that steam-explosion processing can

be operated on a small scale and be economical.

Table 1. Comparison of convention wood pulping, steam explosion and solid-state extrusion technologies.

<b>Wood Pulping (Pulp and Paper Industry)</b>	<b>Steam Explosion</b>	<b>Solid State Extrusion</b>
<ul style="list-style-type: none"> <li>• high water and energy consumption;</li> <li>• additional chemicals (sulfur and chlorine compounds);</li> <li>• high environmental pollution processing –</li> <li>• hours</li> </ul>	<ul style="list-style-type: none"> <li>• high temperature steam;</li> <li>• chemicals from biomass;</li> <li>• small emissions</li> <li>• minutes</li> </ul>	<ul style="list-style-type: none"> <li>• no water consumption;</li> <li>• no chemicals;</li> <li>• no pollution</li> <li>• seconds</li> </ul>

Another breakthrough technology is Simultaneous Saccharification and Fermentation (SSF) [20]. When enzymatic hydrolysis is employed after a pretreatment step, for instance after steam explosion (Fig.5) the enzymatic hydrolysis and 6- carbon atoms containing sugars fermentation can be combined into one process. Next breakthrough in biomass to ethanol technology was simultaneously fermentation of both xylose (5- carbon sugars) and glucose (6- carbon sugars) by using genetically- engineered bacterium *Zymomonas mobilis* [21]. These techniques eliminate need and cost of separate tanks for saccharification and fermentation of glucose and xylose.

#### MODIFICATION OF 3R APPROACH (REDUCE, REUSE, RECYCLE) TO 4R APPROACH (REPLACE, REDUCE, REUSE, RECYCLE)

Environmental issues as it was mentioned are significant in the conventional oil refinery. Petrochemicals linear production, use and disposal model is showed in Fig 6. In oil refinery about 80-90 percent of pollution is "upstream" and 10-20 percent is "downstream". By using plant biomass biorefinery derived biochemicals oil and

petrochemical companies avoid much of the "upstream" pollution and, in some cases, can significantly reduce the pollution generated by the "downstream" disposal. Otherwise these strategies are modification of 3R approach (reduce, reuse, recycle) to 4R approach (replace, reduce, reuse, recycle).

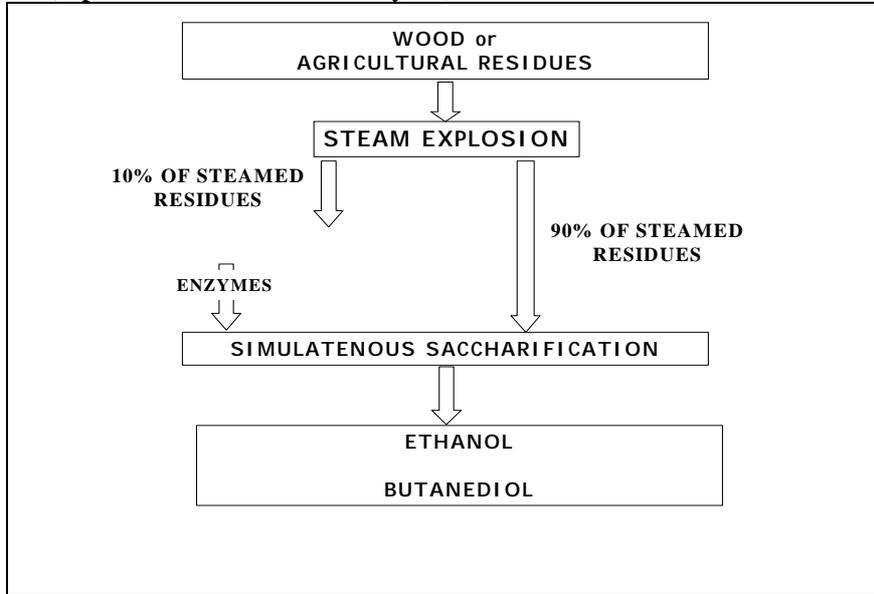


Figure 5. A simplified process of biomass conversion to ethanol or butanediol using steam explosion and SSF according to E.K.C.Yu and J.N.Saddler

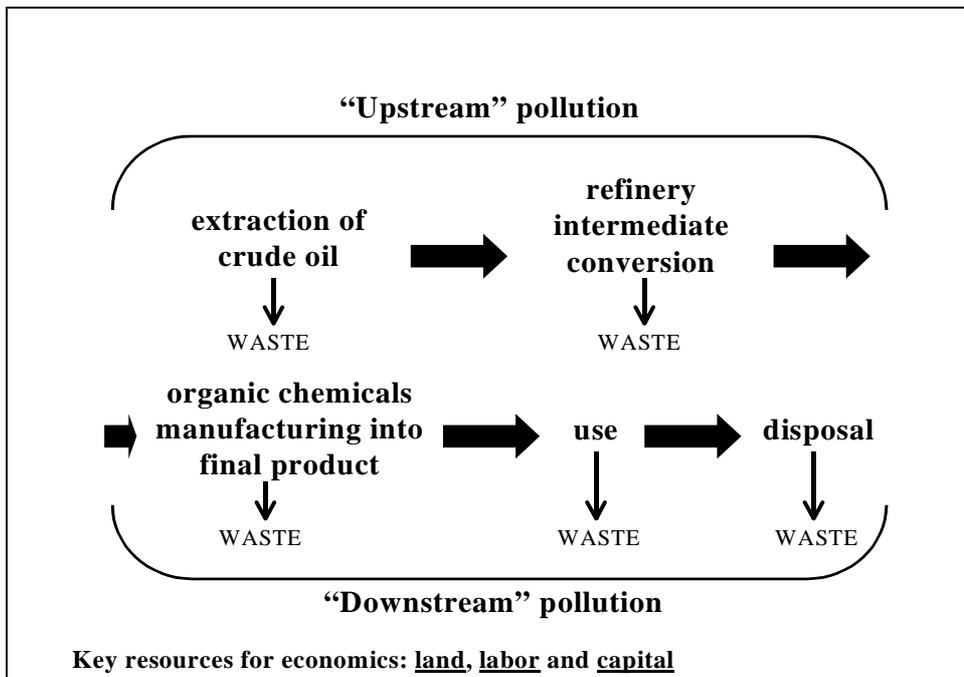


Figure 6. Petrochemicals linear production, use and disposal model.

## STRATEGIES OF REPLACING PETROLEUM PRODUCTS WITH CHEMICALS FROM BIOMASS

There are three strategies [6, 29] for replacing petroleum products with chemicals from biomass:

1. direct substitution petrochemical with the same compound from biomass;
2. indirect substitution with functionally similar but not chemically identical biochemical;
3. replacing petroleum based product with principally new bio-based product (for example, synthetic plastics with biodegradable polymers from starch).

An experience showed that petrochemicals substitution with biochemicals reduces "upstream" and "downstream" pollution to 30 percent [6, 29]. Hence for full elimination of pollution we need the fourth - Zero Emissions strategy.

### ZERO EMISSIONS STRATEGY

For the main part of the world the existing production system: resources - processing - products, is linear. The main components of linear economics are land, labor and capital (see Fig.6). However, the target "no waste" and eco-efficiency demand to use UNU/ZERI Integrate Industrial Cluster approach. In this cluster waste output from one industry becomes an input for another (Fig.7).

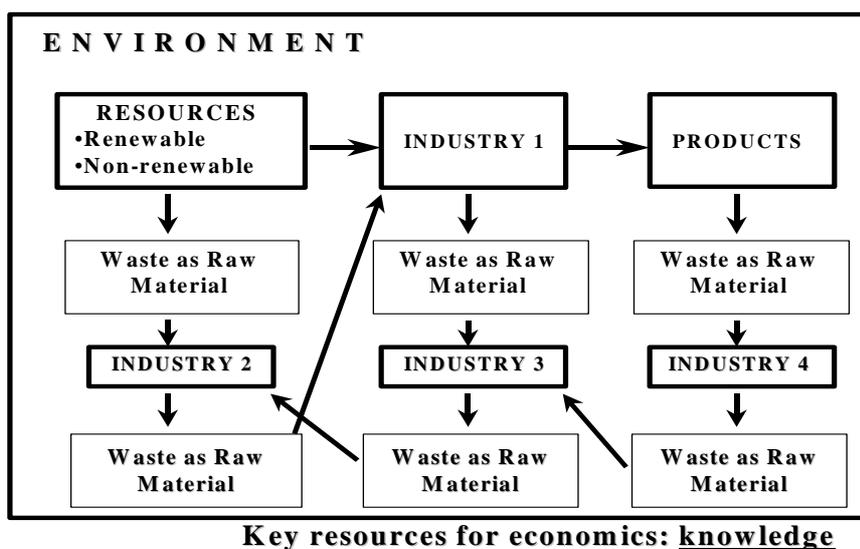


Figure 7. Zero Emissions industrial cluster according to [23].

Zero Emissions industrial cluster imitates the Nature, and in principle eliminates waste targeting near Zero Emissions. From the economical viewpoint the integration is a shift from the core business to the diverse business by combination of high volume - low price and low volume - high price products from biorefinery. The problem is not only availability of material resources; rather the only relevant and essentially unlimited factor is man's knowledge. We should grow by knowledge to reach eco-efficiency for production with maximum efficiencies and small loses of materials. Instead of land, labor and capital the knowledge is the main driving force for Zero Emissions biorefinery. We will increase our knowledge to solve the main question how to organize the industrial cluster with Zero Emissions and maximal profit for companies. This complex question needs an additional research as well as computer simulation and believable input-output data. In principle Zero Emissions model is a replacement of input-output tables with output-input tables. However there does not exist a methodology for such approach. On the applied and technological level UNU/IAS studies demonstrated possibility to create a self-supporting with materials and energy industrial cluster, for example in oil palm and sugar cane industries (Fig.8).

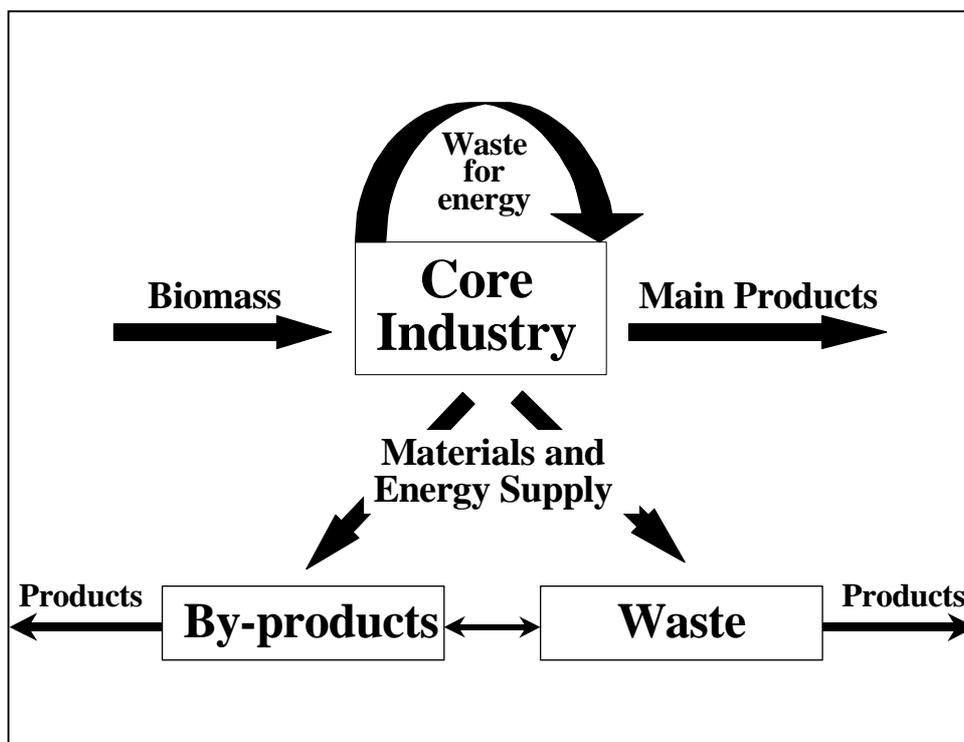


Figure 8. Self-supporting with materials and energy sugar cane mill and complementary industries cluster [23]. The main products from the core industry are sugar and/or alcohol; by-products are molasses; waste is sugar cane bagasse.

It was showed that using the energy co-generation approach, producing not only the steam but also electricity, it is possible to reduce bagasse burning from 10 to 20 percent. These 10 or 20 percent of bagasse could be used as a raw material for clustering around sugar mill complementary industries manufacturing such products as furfural, vitamins, citric acid, sugars, alcohol, charcoal, fiberboard, etc. Some part of remaining bagasse can be used as a raw material for pulp and paper industry. The sugar cane is one of the most efficient vegetable converters of solar energy to chemical energy. According to [24] CO<sub>2</sub> gas balance of ethanol is 112 percent positive considering CO<sub>2</sub> released during the production and burning in car engines against the consumption for the growth of the corresponding sugar cane. That means the consumption of the sugar cane's ethanol cleans the atmosphere of CO<sub>2</sub> at the rate of 12 percent. One component of cluster is self-sufficient charcoal production technology development at the Latvian State Institute of Wood Chemistry (LSIWC, Riga, Latvia) with energy cascading and total energy efficiency about 75 percent, and near Zero harmful Emissions (Fig.9).

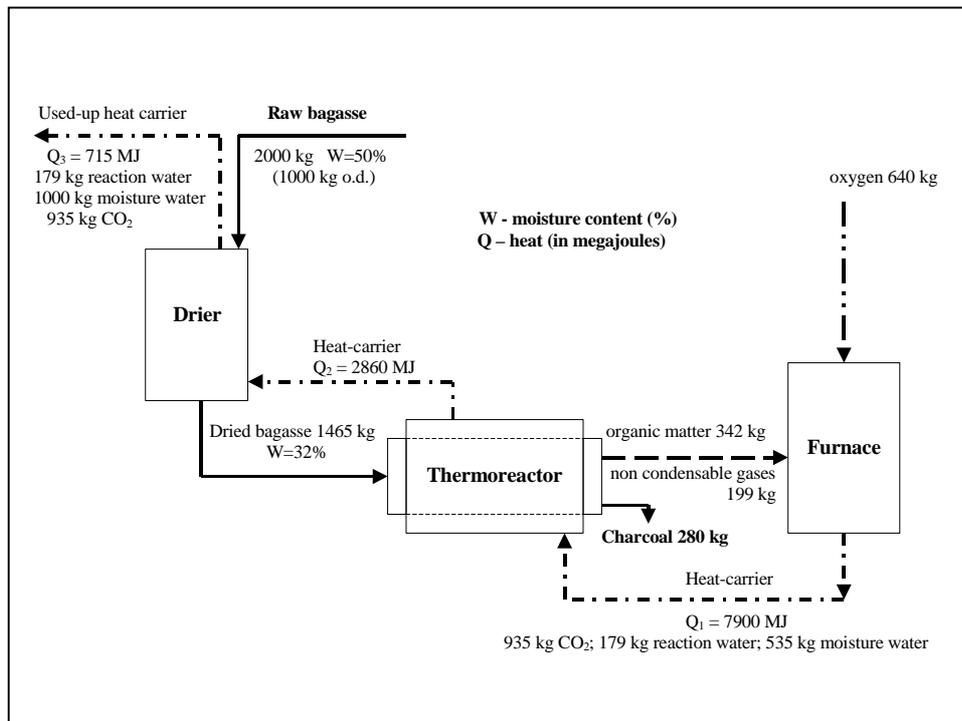


Figure 9. Material and energy flows using LSIWC charcoal energetically self - sufficient production technology as case study [25].

## LIGNOCELLULOSICS ECONOMY

Besides environmental benefits there are economical benefits from biorefinery. Biorefinery at first separates plant biomass materials - lignocellulosics - into the main "building blocks": cellulose (sugars) and lignin (phenols). Hence, biorefinery creates new economics - lignocellulosics or carbohydrate (sugars) economics similar to petrochemical (or hydrocarbon) economics. As it was showed by Brazilian Bioethanol program (Proalcool) the significant factor is a price of bioethanol and a price of gasoline [26]. The price of gasoline in the USA is 1.10 - 1.40 \$ per gallon. Bioethanol produced with the best biorefinery technologies with the price 1.10 - 1.20 \$ per gallon becomes competitive with gasoline [27]. It is interesting to note that the replacement of ethanol from corn with a system based on conversion of switch grass to ethanol will increase total energy ratio (total output energy/ total input energy) from ethanol from 1.21 to 4.43. But calculated carbon sequestration rates may exceed those of annual crops by as much as 20 - 30 times, due in part to carbon storage in the soil [28]. Solvents from the peels of citrus fruits (Inland Technologies) and biodegradable polymers from starch are the next examples as excellent substitutes for petroleum products in the meaning of properties and economy. Boeing's annual savings by replacing toxic solvents from petroleum with "Citra Safe" solvent from peels are 750,000 \$ [29]. Advances in biorefinery are lowering the cost of making biochemicals while environmental regulations are rising the cost of making, using and disposing of petrochemicals. Assessment results [30] show that, when externalities (consequences of a production process, imposed on society or the environment, which are not taken into account in the product price) are introduced into the cost analyses, the total cost of biomass electricity is lower than that of coal. So, quantification of environmental and social impacts using the "damage function" approach is important. Monetary valuation of the CO<sub>2</sub> emission was about 0.52 - 13.17 ECU per ton of CO<sub>2</sub> [30] emitted depending on the scenarios considered and on the discount rates used (from 0 to 10%). It is clear that the ratification of Kyoto agreement on global warming should facilitate strengthening of "lignocellulosics" (carbohydrate) economy.

## CONCLUSION

We have no other alternatives than substitution of industrial petrochemicals and fuels from petroleum with biofuels and biochemicals from plant materials. Energetical issues

will be solved combining biofuels with other renewable sources. The same time petrochemicals and synthetic materials can be fully replaced with chemicals and materials obtained from biomass. In the substitution of industrial petrochemicals with biochemicals a significant role is played by replacement of oil refinery with biorefinery. Biorefinery converts biomass components into value added products and will be targeted towards Zero Emissions using the integrated industrial cluster approach. Lignocellulosics economy demonstrated that more and more products from biorefinery become competitive with products from petroleum. The main target for biorefinery is eco-efficiency without environment damage and biodiversity conservation. Sustainable conversion of biomass using biorefinery is the key for biodiversity protection. Biomass is a renewable resource but it is not infinite.

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