

Biofuels: Dream Or Reality - Enthalpic, Exergetic And Socioeconomical Analysis

Luciano Zanderighi Department of Physical Chemistry and Electrochemistry –
University of Milano – Via Golgi 19 20137 Milano

Some aspects of bio fuel production, as a renewable source of energy, are analysed in terms of EROI (Energy Returned On energy Input). Actually EROI can be evaluated in terms either of enthalpy (first thermodynamic axiom) or of exergy balance (second thermodynamic axiom). The two approaches are analysed and discussed. Bio fuel production competes with food production; moreover a large extension of land must be dedicated to bio fuel production. These and other factors influence the socio-economical conditions and the development of the countries overall the world.

Are bio fuels the right way to the solution of the energy for the world development?

Introduction

Many philosophers and thinkers of the ancient time had a dream: to build-up a device or an engine that could self produce work without any external contribution, which is a “perpetuum mobile”. The investigation of such a marvellous engine was alive until 1775 (actually some patents on that subject are claimed also today) when the Académie Royale des Sciences de Paris decided not to publish any memory on whatever argument, design or project, dealing with “perpetuum mobile”. This decision was the end line of a long discussion among the scientists, which started with Leonardo da Vinci (1452-1519), Cardano (1501-1576), Stevin (1548-1620), Huygens (1629-1695), and many other scientists, and stated for good the impossibility to produce work from nothing.

The modern version of the “perpetuum mobile” is the dream of the “renewable energy”, an inexhaustible source of available energy.

Actually the world has a natural and inexhaustible source of energy in the sunlight that arrives continuously on the earth surface, and distributes in various forms, such as heat, wind, evaporation of water, photosynthesis, etc., some of which may be accumulated and utilized.

Unfortunately solar energy has certain characteristics that do not allow its easy use, such as for instance:

- a) high dispersion on the earth surface (mean value 1000 w/m^2);
- b) wide spectra of light frequencies (visible radiation is about 41% of all solar radiation with a wavelength in the range 400 e 700nm).
- c) the sunlight arrives continuously but it is not continuously available.

For these reasons solar energy must be concentrated and stored. One natural and spontaneous way to store solar radiation is the photosynthesis process that transforms radiation energy into chemical energy.

It is well known that many forms of energy exist, and, according to the first axiom of thermodynamics, all these energies are equivalent and generally treated in terms of enthalpy. Actually not all energies have either the same characteristics nor the same capability to produce useful work. This capability can be assumed as a parameter to measure the quality of the energies.

In thermodynamics the useful work is measured in terms of exergy. According to Gaggioli [1] exergy is defined as the maximum amount of work that can be done by a subsystem as it approaches thermodynamic equilibrium with its surroundings by a sequence of reversible processes. In other words exergy is the amount of energy (enthalpy) that can be transformed in useful work, the other part is called anergy (useless energy).[2,3]

While enthalpy and the sum of exergy and anergy are subject to a conservation law, exergy exempts from it.

All processes dealing with concentration or storage of solar energy, including agriculture production, are analysed in terms of material and energy in- and out-flows, and the efficiency in storing energy is measured in terms of EROI: (Energy Returned)/(Energy Input). However, in many of these balances, the humane work, the energy for plant maintenance and the depreciation of the energy used for the machinery productions and for the plant buildings, are not considered, mainly since it is difficult to evaluate the weight of these energies in the total balance.

Moreover EROI may be evaluated either in terms of enthalpy or in terms of exergy: in the first case it is based on the classical concept of the energy conservation in a process flow sheet, and the difference between in and out enthalpy is a measure of the gain in energy (i.e. solar energy stored); in the second case the energy flows are weighted according to their capability to produce useful work: actually the aim is not to make an energy balance but rather to evaluate the amount of the obtained useful energy with respect to the one used.

Agronomical aspects of bio fuel

As a preliminary information the carbon dioxide reaction rate in photosynthesis process is $800 \text{ kg/km}^2 \cdot \text{h}$, under optimal irradiation conditions and a fertile land. This means that, by considering a mean irradiation of 8 h/day the theoretical maximum productivity is $48 \text{ t/ha} \cdot \text{year}$ of dry biomass. Actually the productivity is about half of the theoretical value, since it depends on many factors such as soil fertility, water availability, solar radiation, etc.

Nevertheless reference values of soil productivity are important for making some evaluation of the different agriculture production for bio fuel productions.

In table 1 some data of agricultural crop for biodiesel production are reported.

The process of oil transformation into biodiesel is a simple trans-esterification reaction since, in the presence of basic catalysts, methanol substitutes glycerine in the aliphatic ester.

The yield of the process is about one (w/w), that is one ton of biodiesel is produced from one ton of oil. Researches are studying new plants (Sandbox tree, Sea mango, Jatropha, etc) or genetically modified known plants (molecular assisted breeding), in order to increase the yield in oil (t/ha).

Table 1: Mean values of crop yield (t/ha) in Italy. (1tep=6,841 barrels)

CROP PRODUCTION	BEAN/SEED t/ha	OIL t/ha
RAPESEED	2,5 - 2,6	1,1 - 1,2
SUNFLOWER	2,6 - 3,0	1,3 - 1,5
SOY	3,0- 3,5	0,6- 0,7

In India [4] a plant known as *Jatropha curcas*, that can be grown in wastelands, has attracted the interest of farmers, researchers and institutional investors since more than 1800 (l/ha) of oil can be produced.

Bio ethanol can be produced with a fermentation process of a sugar solution. The process is well known, but it is still under study with the aim of reducing the exergy duty.

Recently however, researches have started investigating the possibility to find an innovative process of ethanol production from cellulose competitive or even better, than from sugar.[5]

Table 2: Yield (l of bio ethanol/t of crop) of Bio ethanol from various crops.

BIOMASS	ETHANOL YIELD (l/t of crop)
SUGAR CANE	70
SORGHUM	85
BEET	100
CASSAVA	180
MAIS	360
WHEAT	340
RICE	430

EROI: E(n,x)ergy Returned / E(n,x)ergy Input

While the EROI evaluation in terms of energy (enthalpy) can be performed simply on the bases of a quantified flow sheet of the process, its evaluation in terms of exergy must consider the time and the place where the plant operates, and the final aim of the plant.

The subject of this presentation is the bio fuel production, so the analysis will be limited to this topic. The aim of bio fuel production is to get a fuel useful for feeding engine and vehicles as alternative to fuel of mineral origin.

The exergy returned can be easily evaluated from the process flow sheet. For the evaluation of the exergy input, all production steps from the land until the industrial plant must be considered.

While exergy input in terms of electric energy, gasoil, chemicals, fertilizers, that is all contributions related to material balance, are easily evaluated, on the contrary it is difficult to evaluate it for other inputs, not related to material balance, such as, for instance, human work, machinery, buildings and supporting structure depreciation. The contribution of all this factors to the exergy input can be defined only when time and space are well defined. For instance the contribution, as exergy input, of the human work evaluated today is different from the one evaluated ten years ago, since the life style of a worker has changed, that is the amount of exergy a man utilize for living; moreover exergy of the labour of a worker in a developed country weights higher than that of one in a developing countries, and this is in turn higher than that of a worker in an underdeveloped countries.

For the evaluation of the exergetic value of labour the following relation has been proposed [6,7]:

$$Ex_w = n \frac{Ex_{in}}{n_{tot}}$$

where n is the flux of work hours into the sector on analysis, n_{tot} is the total amount of work-hours per year and Ex_{in} the exergy influx to the society per year.

For what concern other contributions imputable to material goods, such as for instance machinery, buildings and supporting structure, the exergy evaluation for their construction can be performed as usual. Therefore on the bases of their depreciation, their contribution to the total exergy input can be evaluated.

A short cut method for the evaluation of the exergy of all investments can be evaluated on the basis of the monetary investment, according to the relation:

$$Ex_c = C \frac{Ex_{in}}{C_{ref}}$$

C is the capital depreciation, or the monetary flux, and (Ex/ C_{ref}) is the monetary measurement of the exergy [8]. The evaluation of this term has a certain degree of arbitrariness.

In table 3 EROI analysis for bio ethanol production in Italy, in term of enthalpy and exergy, are compared [9]. While EROI evaluated in terms of enthalpy seems to be favourable for solar energy accumulation in bio ethanol, the exergetic analysis indicates that, at least in Italy, the production of bio ethanol is only a conversion process of various subsidiary energies into ethanol.

For what concerns the production of ethanol from corn, according to US Department of Agriculture [10] the energy balance of ethanol is 1.34:1. This means that ethanol yields 34% more energy than it occurs to produce it, including growing the corn, harvesting it, transporting it and distilling it into ethanol. Other authors reported similar results

[11,12]. In a recent detailed study [13] the energy balance for corn grain ethanol is about 1,25:1, but the 25% gain is attributable to the energy credit for coproducts (as animal feed). Without this contribution the balance of ethanol itself is near zero. Other author state that the energy balance is negative [14,15].

Also the ethanol production from cellulose (all the production plants operating with the old Scholler process were closed in 1950 as no more economic) have had a revamping

Table 3 - EROI of different agricultural production in the Italian system.

BIOETANOL PRODUCTION: ENTHALPIC BALANCE (GJ/Ha)

AGRICULTURAL PRODUCTION	AGRICULT. EXERGY	INDUSTRIAL EXERGY IN	TOTAL EXERGY IN	TOTAL EXERGY OUT	EROI	DISTILLED ETANOL (l/Ha)
MAIS	34 ± 2	27 ± 0,5	76 ± 3	210 ± 8	2,76	3100
WHEAT	29 ± 2	27 ± 0,5	56 ± 2	130 ± 6	2,3	2050
BARLEY	22 ± 2	27 ± 0,5	49 ± 2	130 ± 6	2,6	2050
SUGARBEET	47 ± 3	73 ± 2	120 ± 6	180 ± 10	1,5	4500

BIOETANOL PRODUCTION: EXERGETIC BALANCE (GJ/Ha)

AGRICULTURAL PRODUCTION	AGRIC. EXERGY	INDUSTRIAL EXERGY IN	TOTAL EXERGY IN	TOTAL EXERGY OUT	EROI	DISTILLED ETANOL (l/Ha)
MAIS	28 ± 2	13 ± 0,2	41 ± 3	52 ± 1	1,3	3100
WHEAT	22 ± 2	8 ± 0,2	30 ± 2	31 ± 1	1	2050
BARLEY	15 ± 2	8 ± 0,2	23 ± 2	31 ± 1	1,3	2050
SUGARBEET	28 ± 3	12 ± 0,2	50 ± 2	48 ± 4	0,96	4500

[16,17]; an excess of 60,000 Btu per gallon has been claimed [17]. Actually the exergy balance is similar to ethanol from corn, the only advantage derive from exergy saved in agriculture production if cellulose is obtained from forest and non fm plantations.

For what concerns the biodiesel production, the data are rather contradictory. While Pimentel and Patzek [18] assert a negative balance for all bio fuel production, according to a 1998 study of NREL[19] biodiesel production yields 3.2 units of fuel product energy for every unit of fossil energy consumed. This results agree with that reported in a detailed analysis [20] of bio diesel production in terms of exergy flow analysis (ExFA) based on mass and exergy flow diagram, without considering labour, machinery and building depreciation. ExFa analysis indicates that the efficiency of the industrial process is 98,54% ; actually this analysis is similar to the enthalpic analysis and gives

no additional information. I have made the calculation again, with a short-cut procedure, considering immobilized exergy, labour, etc. the obtained mean yield is in the range 1,7-2,1. This result is still optimistic in comparison with that reported in [13], where a detailed energy balance on soybean biodiesel, considering practically all factors (facility energy use, facility labourer energy use, facilities construction, transportation, household energy use, machinery production, fertilizers and pesticides, fossil fuel use, seeds) provides about 93% more energy than required in its production.

In conclusion it is possible to say that while for starch methanol there is not net gain in the exergy balance, for biodiesel the balance may be positive, it depends from when and where.

Socio-economical considerations

The world oil consumption is about 8,36 barrel/day that is $4,46 \cdot 10^9$ t/a. By assuming a land productivity of 1t /ha of bio-oil (sunflower or canola oil) and an optimistic value of EROI equal to 2, the land surface to get a net added value (NAV) of $4,46 \cdot 10^9$ t/a resulted to be $8,92 \cdot 10^9$ ha. Actually the world productive land is $8,56 \cdot 10^9$ ha. This means that all available land is not sufficient to supply the actual oil needs. Moreover if one considers that all arable lands, now used for food production, amount to $2,8 \cdot 10^8$ ha the net production of bio-oil is limited to $1,4 \cdot 10^8$ t, that is about 3,1 % of total oil consumption, but this amount is alternative to food production.

In Italy the arable land amount to $13 \cdot 10^6$ ha and it would be possible to produce $6,5 \cdot 10^6$ t/a of bio-oil. Since the oil consumption in Italy is about $88 \cdot 10^6$ t/a, if one decide to abandon the food production for fuel production, that is to import foods instead of oil, the total annual production may support the oil consumption for 51 days.

On the bases of these figures it is clear that bio fuel production from renewable energy is not only a dream but, even worse, it is an unsound idea.

To the reported technical analysis one has to add some sociological considerations. The world is evolving quickly, the undeveloped people are rising up, their way of life is improving, and their needs of food are increasing both in quantity and in quality. According to a FAO report the mean world consumptions of cereals is 80% of that of developed countries, proteins about 70% and fats 50%. These data indicate that in the future more land must be devoted to food production, otherwise there will be a dramatic increase of food prices.[21]

Strictly bounded to evolution of underdeveloped country is the phenomenon of migration towards cities, that is how to prevent farm workers abandon their land.

It is my opinion that from an economic point of views the bio ethanol production was not a real business for Brazil, since instead of importing oil it imported energy in others forms like chemicals, farm machinery etc. Nevertheless the bio ethanol project had the great merit to promote an agricultural activity that allowed to keep people in the countryside. To day Brazil has a very strong economy, mainly based on agriculture. Brazil agriculture export amounts to about 27.000 million \$ (4,5% of total world export).

In India the National Planning Commission has integrated the Ministries of Petroleum, Rural Development, Poverty Alleviation and the Environmental Ministry and others industrial groups and National Agencies in a project to cultivate $13,4 \cdot 10^5$ ha of land plus $4 \cdot 10^5$ of wastelands with Jatropha.[4] The aim is to produce 13 Million t of bio-diesel by 2013, that is about 20% of the consumption of mineral diesel by car. The demonstration project (\$300 million) consists of 2 phases, each with 200.000 ha planted

in 8 states of 2 x 25.000 ha "compact area" each. The first results indicate that it is possible to produce 1,82 t/ha of *Jatropha* oil. Each state will have one esterification plant, which is meant to be economical from 80.000 t of bio-diesel onward, expected to come from 50 to 70000 ha each. Expected outputs from 400,000 ha are meant to be 0.5 Million t of bio-diesel, compost from the press cake, and massive generation of employment (16 Mio days/year) for the poor. Looking deep into the program, two great targets seem to stimulate all people involved: to improve degraded land resources, and to give an income to poor families, so that they don't leave the countryside.

These targets are in line with the social results of bio ethanol in Brazil.

There are other problems which need to be solved when such a large amount of land is dedicated for energy production: the use of water and of pesticides.

In all bio energy productions these two aspects have been underestimated.[22,23]

While bio fuel production may have some social justification in developing country, all technical, economical, social and ecological analysis indicate that the bio fuel choice is a losing strategy. Only economical grants from states to the local industries or farmers justify bio fuel production.

I would like to point out to another topic related to renewable energy. A true renewable transformation must be founded on a cycle that restores the starting conditions. This means that, in the balance, exergy consumption in restoring the environment (soil and water) polluted by the agrochemicals, or depleted by industrial plantation must be considered. In the case of corn ethanol the minimum cumulative exergy consumption is 7 times than the maximum shaft work of a car engine burning ethanol! [14]

Probably biomasses are not the right way for fuel production, new ways must be found and this is the main goal for researches.

References

- 1) Gaggioli, R.A. "Thermodynamics: Second Law Analysis" ACS Symposium n°122 American Chemical Society 1988, Washington D.C.
- 2) Göran Wall "Exergy : An Useful Concept" Institute of Theoretical Physics-Report n° 77-42. University of Technology Chalmers and University of Göteborg.
- 3) Göran Wall " Perspective on the energy future using exergy" Statoil-NTNU(Norwegian University of Science and Technology) Global Watch Seminar- Trondheim- August 29-2003.
- 4) Centre for *Jatropha* Promotion & Bio diesel "Biodiesel in India 2004-2008"
- 5) Graf, A. ,T. Koehler "An evaluation of the potential for ethanol production in Oregon using cellulose-based feedstocks" Oregon Cellulose-Ethanol Study June 2000
- 6) Sciubba, E. "Beyond thermoeconomics? The concept of Extended Exergy Accounting and its application to the analysis and design of thermal system" *Exergy Int. J.* **1**(2):68-84(2000).
- 7) Nakićenović, N., Gilli P.V. and Kurz R. (1996) Regional and global exergy and energy efficiencies. *Energy* **21** (3), 223 – 237.
- 8) Reistad, G.M. "Available energy conversion and utilization in the United States" *ASME J.Eng. Power* **97**,29-34(1975)
- 9) Soave G., L. Zanderighi "Enthalpic and Exergetic Analysis of Bio-Ethanol as Energy Vector" *Chemie Ingenieur Technik* **73**(6) 589(2001).

- 10) Wang, M. , H. Shapouri, J. Duffield,USDA: “The Energy Balance of Ethanol: An Update.” National Agricultural Statistics Service, USDA. Aug 2002.
- 11) Kim, S., B. E. Dale “Allocation Procedure in Ethanol Production System from Corn Grain” International Journal Life Cycle Assessments, 2002 OnlineFirst: May 7th, 2002
- 12) Wang, M. , C. Saricks, D. Santini “Effects of Fuel Ethanol Use on Fuel-Cycle Energy and Greenhouse Gas Emissions” Argonne National Laboratory (1999)
- 13) Hill, J. , E. Nelson, D. Tilman, S. Polasky D. Tiffany “Environmental, economic, and energetic costs and benefits of biodiesel and ethanol biofuels” Proc. of the National Academy of Science **103**(30), 11206-11210 (2006)
- 14) Patzek, T,W., “ Thermodynamics of the Corn-Ethanol Biofuel Cycle” Critical Reviews in Plant Science **23**(6)519-567(2004).
- 15) Pimentel, D. “Ethanol Fuels: Energy Balance, Economics, and Environmental Impacts Are Negative” **12**(2)127-134(2003).
- 16) Morton, J., “BIOENERGY: A future for the Australian forest industry”, FOREST, 2001 - fwprdc.org.au
- 17) DiPardo, J. “Outlook for Biomass Ethanol Production and Demand”, Washington, DC: Energy Information Administration, 2004 - eia.doe.gov
- 18) Pimentel, D. , T.W. Patzek “Ethanol Production Using Corn, Switchgrass, and Wood; Biodiesel Production Using Soybean and Sunflower” Natural Resources Research **14**(1) 65-76(2005)
- 19) Sheehan, J.,V. Camobreco, J. Duffield, M. Graboski, H. Shapouri “An Overview of Biodiesel and Petroleum Diesel Life Cycles” NREL/TP-580-24772, National Renewable Energy Laboratori, May 1998
- 20) Talens L., G.Villalba, X.Gabarrell:”Exergy analysis applied to biodiesel production” Resources, Conservation and Recycling **51**(207)397-407(2007).
- 21) Kingsbury, K. “ After the oil crisis a food crisis?” TIME Friday, Nov, 16,2007.
- 22) Ortega, E., F.Günter, S.Hinton “THE ECO-UNIT: an ecomimetic settlement as a basis for sustainable development. Experience in Sweden and Brasil” Biannual International Workshop – Advances in Energy Studies- “Perspective on Energy Future” 12-16 September Porto Venere Italy,2006.
- 23) Coatanéa, E., M.Kuuva, P.E.Makkonnen, T.Saarelainen, M.O.Castillón-Solana “Analysis of the Concept of Sustainability: definition of conditions for using exergy as uniform environmental metric” Proceeding of 13° CIRP International Conference on Life Cycle Engineering- Leuven 31May-2 June 2007.