# EXERGY REPRESENTATIONS IN THERMODYNAMICS

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## ABSTRACT

The paper reviews various representations of exergy and exergy losses in energy systems going from simple heat exchanger (heat transfer, dissipation and embedded exergy) to the exergy of full energy systems from fossil or non fossil resources (including the diffusion exergy). The systems shown include shell in tube heat exchangers, thermal power cycles, cogeneration, heat pump direct heating systems and cryogenic systems. The representations include simple gravitational analogies to extended exergy pinch diagrams and finally to the exergy bowl with the dead states corresponding, for example, to different oxidation products. The transformation from hydrocarbons to $CO_2$ and $H_20$ is shown in particular, highlighting the diffusion exergy of $CO_2$, which is important when dealing with concepts of $CO_2$ capture.

## INTRODUCTION

Exergy is recognized as the best way to analyse energy systems, be it at the component, process, whole site or country levels. It is, however, also often seen as too complex by practitioners, who are used to work around processes and technologies they think to know well. Experience shows that both at the teaching level and the conceptual design level it is often useful to rely on a graphical representation of the concepts. The success of pinch technology [1,2] for example, can also be attributed to having an easier representation of the application of Second Law to the heat transfer in integrated processes. Similar representations can be extended, to more holistically illustrate the other exergy losses like the dissipation exergy losses and the embedded exergy losses [3]. Other only qualitative approaches are cartoon type of representations of energy conversion phenomena [4].

The decomposition of exergy efficiency in the subsystems can help the policy makers to coherently rank technologies like those for heating or air-conditioning [5]. They can also help scholars to better grasp the meaning of concepts, like the need to differentiate between the thermo-mechanical and physico-chemical equilibria or dead states when reactive flows are involved [4]. Other approaches inspired by the van't Hoff box can help in properly identifying the different aspects involved in the calculation of the exergy value of a fuel [4,6]. The objective here is to expose these representations in a comprehensive manner in a single paper.

## NOMENCLATURE

| | | |
|---|---|---|
| $T$ | [K] | Temperature |
| $P$ | [N/m$^2$] | Pressure |
| $P^0$ | [N/m$^2$] | Partial pressure at the thermo-mechanical equilibrium |
| $P^{00}$ | [N/m$^2$] | Partial pressure at the physico-chemical equilibrium |
| $\Delta\tilde{k}^0$ | [J//kmol] | Molar isobaric exergy value of a fuel |
| $\Delta\tilde{g}_f^0$ | [J/kmol] | Molar free enthalpy of formation (Gibbs free energy) |
| $\tilde{e}_d^0$ | [J/kmol] | Molar exergy of diffusion |
| $\dot{N}$ | [kmol/s] | Molar flow |
| $\tilde{r}$ | [J kmol$^{-1}$ K$^{-1}$] | Molar Universal gas constant |
| $\dot{L}$ | [W] | Exergy loss |
| j | [J/kg] | Specific coenthalpy (=u+$P_a$v-$T_a$s)=specific mass exergy |

Special characters

| | | |
|---|---|---|
| Θ | [-] | Carnot factor |

Subscripts

| | |
|---|---|
| $r$ | Dissipation |
| $T$ | Heat transfer |
| $f$ | Fabrication (or embedded) |
| $a$ | Atmospheric |
| $tu$ | Turbine |
| p | Pump |
| 0 | Ambient or reference |
| F | Fuel |
| i | Input or reactant |
| j | Output or product |
| evap | Evaporator |
| cond | Condenser |

## REPRESENTATION OF EXERGY LOSSES IN ENERGY INTEGRATION

From the basic composite representation in a (Temperature - Heat rate) pinch technology diagram a simple step is to convert the surfaces in exergy values by exchanging the temperature scale by a Carnot factor scale (1-Ta/T). In that way the surfaces below the hot and cold composites represent their exergy values and the surface in-between [2,3,5] represent the exergy losses. Staine in [3] further extended these surface representations by adding:

a) a surface on top of the hot composite and below the cold composite representing the exergy losses due the dissipation phenomena (pressure drop) in the streams of the heat exchangers as shown in Figure 1 for a countercurrent heat exchanger
b) Complementary surfaces representing the exergy losses due to exergy used during the fabrication of the heat

exchangers themselves. In that case the fabrication exergy amount (the embedded exergy) is divided by the expected lifetime of the equipment to get an exergy rate that can also be represented by surfaces in the extended composite diagram. In Figure 1 the surface $L_T$ represents the heat transfer exergy loss, the surfaces $L_r$ the dissipation exergy losses in each of the channels and $L_f$ the exergy losses of fabrication.

c) An additional diagram on top of the extended composite diagram, representing vertically the electricity consumed or produced and horizontally a pseudo-Carnot factor. The latter is calculated in such way that we visualize the representative surfaces of the exergy losses occurring in power units like turbines or compressors. Figure 2 shows a representation of a simple Rankine cycle for the conversion from heat or waste heat to electricity. The surfaces horizontally oriented in the lower diagram show the extended exergy losses in the evaporator and in the condenser. The coloured surfaces in the upper diagram illustrate the exergy losses in the turbine $L_{rtu}$, the surface of the fabrication exergy losses of the turbine itself $L_{ftu}$ as well as the similar surfaces corresponding to the feed pump $L_{rp}$ and $L_{fp}$. The electricity balance can be read on the vertical axis showing a net production of electricity as expected.

The advantage of this approach is to provide a visual representation of the sum of the exergy losses and where they occur in the process.

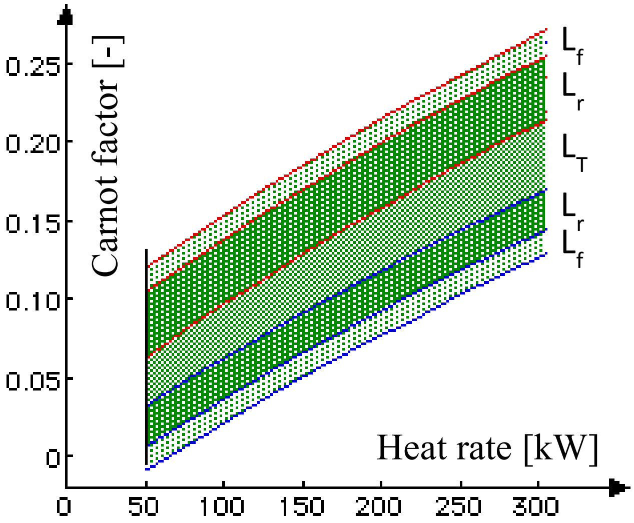

**Figure 1** Extended exergy composites of a countercurrent heat exchanger

Another approach from Marechal [2] and shown in Figure 3 is to extend the concept of grand composite used in pinch technology to include the utilities. In figure 3 we see the grand composite of a given process with one self-satisfied pocket shown in red. The latter indicates a possibility to incorporate an Organic Rankine cycle using process streams themselves and not a utility stream. In this case the utility stream exergy is shown with the surfaces blue, green and yellow, typical of a boiler supply where the blue surface represent the exergy loss of combustion and the green one the heat transfer exergy losses between the combustion gas and the process streams to be heated.

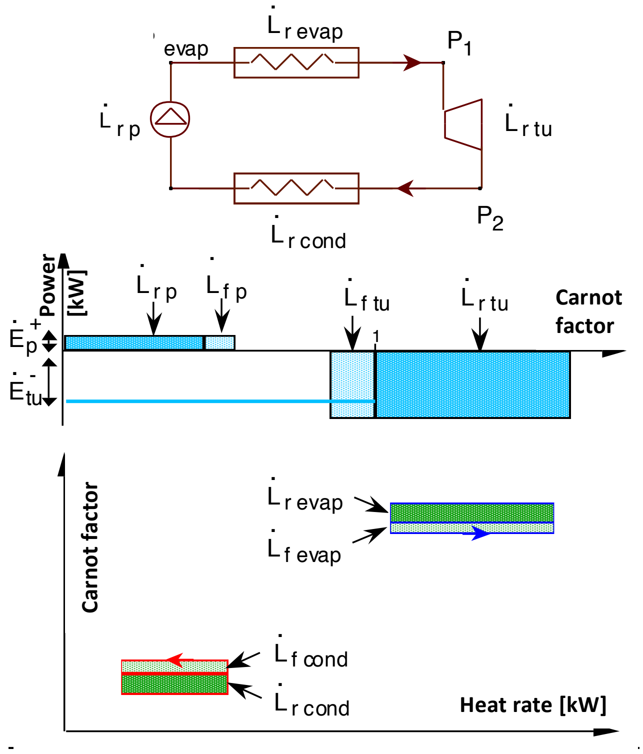

**Figure 2** Extended exergy composites of a Rankine cycle

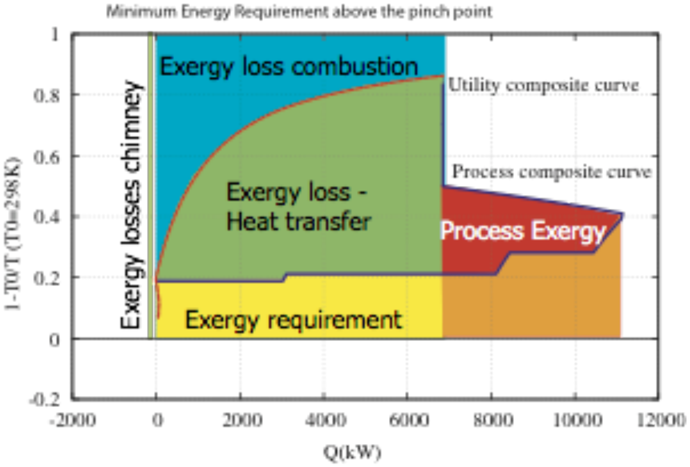

**Figure 3** Grand composite of a process including a boiler as hot utility [2]

Figure 4 shows another representation of the opportunities to introduce heat pumps or ORC in the exergy grand composite diagram of a process [6].

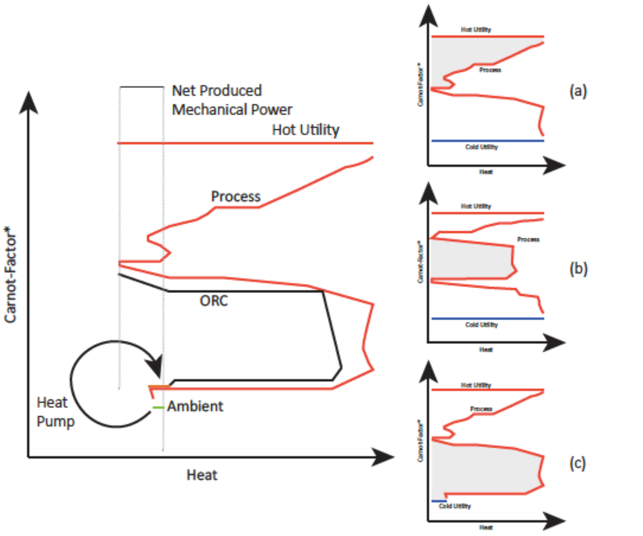

**Figure 4** Exergy that can be accessed only by changing the energy balance: (a) above the pinch point, (b) in between pinch points, (c) in a large exergy pocket.

## REPRESENTATION OF THE EXERGY VALUE OF A FUEL

One subject that is often more difficult to introduce, in particular to students is the determination of the exergy value of a fuel. Many people just use tables of exergy values of the most common fuels, but many modern energy conversion concepts introduce intermediate steps including fuel reforming or fluegas recycling or $CO_2$ separation in fluegas. When analyzing those it is beneficial to have a coherent grasp of how the exergy value of a fuel is effectively calculated and of what it represents. Kotas [7] introduced the van't Hoff box concept to do it and Favrat [5] completed it with clearer system boundaries and additional turbines and compressors required to meet the assumption made in the exergy theory of systems with reactive flows.

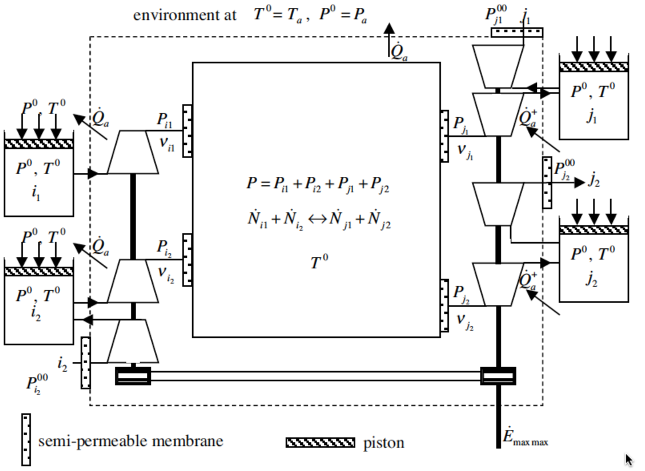

**Figure 5** Van't Hoff's box representation of the exergy value of a fuel [5]

The basic assumption in exergy theory is that the fuel comes in separate from the oxidant and that the fluegas components are released to the atmosphere at the concentration they naturally have in that atmosphere. Since the oxidant $i_2$ is usually taken from the air, the mechanistic model of Figure 5 includes one semi-permeable membrane and a compressor to bring first the oxidant from its partial pressure in the atmosphere to the atmospheric pressure in a dedicated tank upstream of the van't Hoff's box. A second compressor and a semi-permeable membrane then bring the oxidant to the pressure residing in the box where reversible oxidation takes place. The fuel (reactant $i_1$) is first compressed from the atmospheric pressure and temperature to the box through another semipermeable membrane. At the exit the two products of oxidation (typically $CO_2$ and $H_2O$) go through their dedicated semi-permeable membranes and turbines to be delivered to the atmosphere at their natural partial pressure.

The sum of the mechanical work delivered by the isothermal turbines minus the work required by the isothermal compressors gives the maximum theoretical work that can be obtained. When dividing this value by the molar flow we get the molar exergy value of the fuel that corresponds to the following equation:

$$\underline{\Delta\tilde{k}}^0 = \underline{\Delta\tilde{g}}_f^0 + \sum_j \left[\tilde{e}_{dj}^0\right] - \sum_i \left[\tilde{e}_{di}^0\right] \qquad (1)$$

Where the molar exergy of diffusion is:

$$\tilde{e}_{dk}^0 = \frac{\dot{N}_k}{\dot{N}_F} \tilde{\mathbf{r}} T^0 \ln\left(\frac{P^0}{P_k^{00}}\right) \qquad (2)$$

A demonstration of that analogy is given in [5]

## 3D CARTOON REPRESENTATION OF THE EXERGY OF MASS (COENERGY) AND OF ENERGY CONVERSION TECHNOLOGIES.

The coenergy (exergy of mass) can be expressed by:

$$J = U + P_a V - T_a S \qquad (3)$$

Or in specific form by:

$$j = u + P_a v - T_a s \qquad (4)$$

For any substance, the latter can be graphically represented by an exergy bowl (or coenergy bowl) in function of two state properties, for example temperature and entropy as shown in Figure 6. Note that the name coenergy and coenthalpy have been introduced in [5] to clearly differentiate state properties from process dependent entities. Work and heat exergies are process dependent entities while coenergies j or coenthalpies ($k = h - T_a s$) are state properties.

The specific coenergy j (mass exergy) increases away from the center where we have a thermo-mechanical equilibrium or a dead state, as it is expected since any substance at higher or lower temperature than the atmosphere has a higher specific coenergy than at the dead state.

By extrapolation we can superpose the coenergies of different substances to represent energy conversion phenomena of practical interest. In figure 6 we see:

a) Direct electric heating of a house. The electricity exergy level is lowered to the exergy of the rooms in a house (with a comfort temperature of 20°C and an atmospheric temperature of 0°C we get a Carnot factor of 7%, starting from 100% in electric form). Then, the energy is further degraded by leaking through the wall to the dead state.
b) Electrically driven heat pump. The electricity exergy level is lowered to the heat exergy in the rooms but this is done by increasing the exergy level of energy from the environment.
c) Heating with a boiler fed by a hydrocarbon fuel. The high exergy of the fuel is first lowered to the flame exergy of the combustion products and then further degraded by heat transfer between the fluegas and the heating fluid of the house
d) Power plant burning a hydrocarbon fuel. First the exergy level of the fuel is degraded to the flame exergy level and then some of the energy units slide down to the environment (thermo-mechanical dead state) while others are pulled to the top exergy of electricity. Note that in the process of combustion two other dead states appear, one corresponding to the physico-chemical equilibrium of $H_2O$ and the second to the physico-chemical equilibrium of $CO_2$.

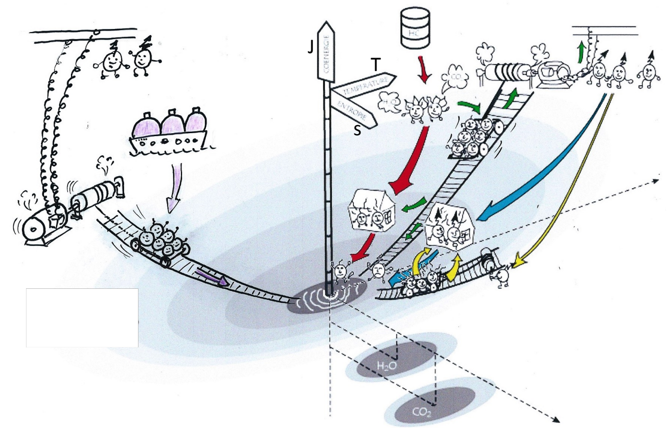

**Figure 6**: Representation of the exergy bowl with different heating and power generation technologies

e) Cogeneration power plant burning a hydrocarbon fuel. If some of the energy units are deviated towards heating a house then one gets a typical situation of cogeneration of heat and power. Since the downgoing path is a bit shorter it means that the electricity efficiency drops slightly in this mode as it is the case for several cogeneration technologies
f) Finally the special case of a Rankine cycle power plant using environmental energy to vaporize a pressurized working fluid. The working fluid then condenses downstream of the turbine, taking advantage of the physical exergy of the evaporation of liquid natural gas. This would be the case at a regasification LNG terminal port.

Note that the exergy of $CO_2$ from the thermo-mechanical dead state to the physico-chemical dead state (equ 2) represents the ideal work that is needed to reseparate $CO_2$ from the environment to the concentration in the tail pipe of the energy conversion device. It can be useful to evaluate the efficiency of new proposed concepts for $CO_2$ separation.

## GRAVITY BASED CARTOON TYPE OF EXERGY REPRESENTATION

To illustrate the concept of exergy and exergy efficiency of energy conversion technologies Borel [5] introduced representations using small characters in an exergy field similar to the gravity field. The representation of simple cycles (thermal power cycle, heat pump cycle and refrigeration cycle) can be found in [5]. Figure 7 illustrates the case of direct electric heating together with electricity generation in a thermal power plant. It schematically shows the exergy losses in the power plant and the much more significant exergy drop associated with direct electric heating. Even with a very efficient combined cycle power plant the multiplication of the exergy efficiency of both technologies result in a heating exergy of less than 4%. The vertical scale T can be linked to a Carnot factor $\theta = 1 - \frac{Ta}{T}$.

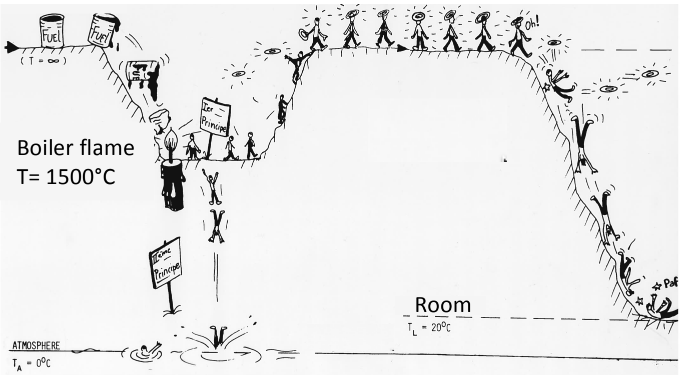

**Figure 7** Gravity cartoon of a thermal plant and direct electric heating (courtesy of L.Borel)

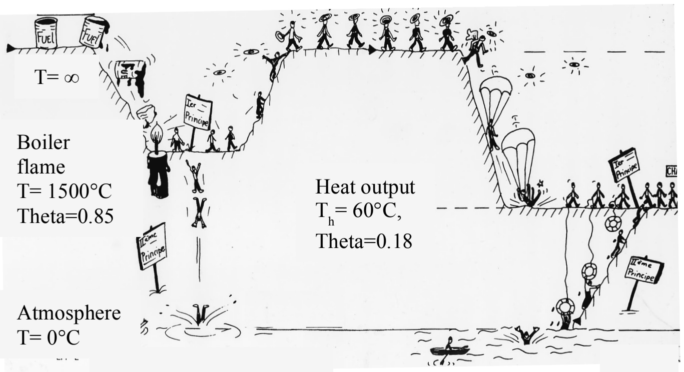

**Figure 8** Gravity cartoon of a thermal power plant and electrical heat pump (courtesy of L.Borel)

Figure 8 illustrates heating using an electrical heat pump. If the power plant and the heat pump have exergy efficiencies of 56% and 45% respectively, the exergy efficiency to the hydronic heating system is about 25%. As shown in [6] one would have to add the exergy efficiency of the radiator themselves to get the complete picture.

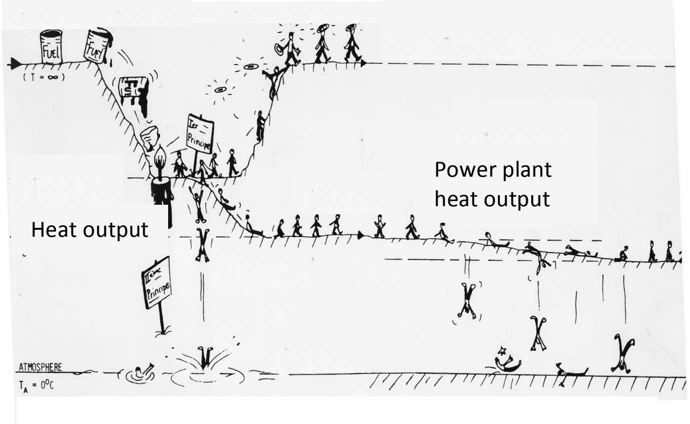

**Figure 9** Cogeneration power plant and District heating network (courtesy of L.Borel)

Figure 9 illustrates the situation at a cogeneration power plant delivering heat to a District heating network, which has its own thermal losses.

## EXERGY EFFICIENCY RANKING OF HEATING AND AIR-CONDITIONING SYSTEMS

The above examples show only a partial representation of the components to be considered when assessing heating or cooling systems. In fact and as shown in [6] it is advisable to decompose the global system into at least 4 subsystems as shown in Figure 10. Then specific tables of exergy efficiency can be established in order to be able at the end to obtain the global exergy efficiency by just multiplying the different sub-systems exergy efficiency. Such tables are given in [6]. That was done in Geneva to allow practitioners to determine the exergy efficiency of the active systems that they propose.

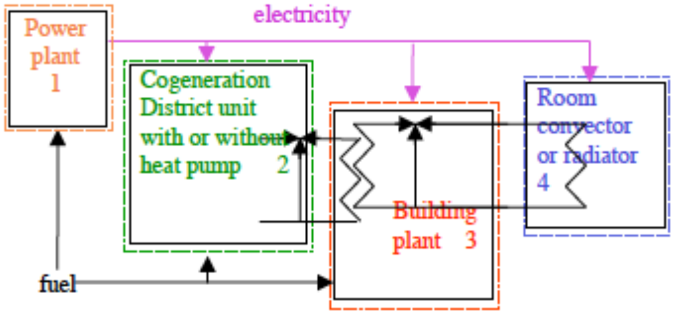

**Figure 10** Decomposition of the calculation of the exergy efficiency of heating or air-conditioning

Figure 11 shows the results of global heating efficiencies for various technology combinations and for two different house heating network temperatures (supply/return). A first observation to be made is that the exergy efficiencies are rather low, particularly for those used to analyse only with First Law indicators. The second observation is that for the lowest efficiency combinations is that the combinations with the lowest efficiency are not affected by the change of temperature level of the house heating network. This is not surprizing due to the fact that they do not count on either gas condensation or heat pumping. As a reminder condensing boilers start to be effective when the fluegas temperature drops below the due point that is around 59°C for gas boilers and lower for heating oil. Some technologies including a District heating network (DH) are also not affected since the hypothesis was made in this particular calculations that the DH network requires a supply temperature of 80°C.

The top technologies are those using heat pump and hydropower since the exergy efficiency of hydropower conversion is known to be high.

Note that the nuclear power exergy efficiency is taken here with the commonly accepted efficiencies based only on the heat delivered by the nuclear fuel bars of present day technology (either pressurized or boiling water reactors). In fact those efficiencies would be much lower if the true exergy potential of uranium would be considered as shown in [8].

The combination giving the highest values could increase in the future as heat pumps and power conversion technologies further improve. Furthermore the trend is to lower the DH temperatures so better efficiencies could be obtained in the future with DH fed by heat pumps

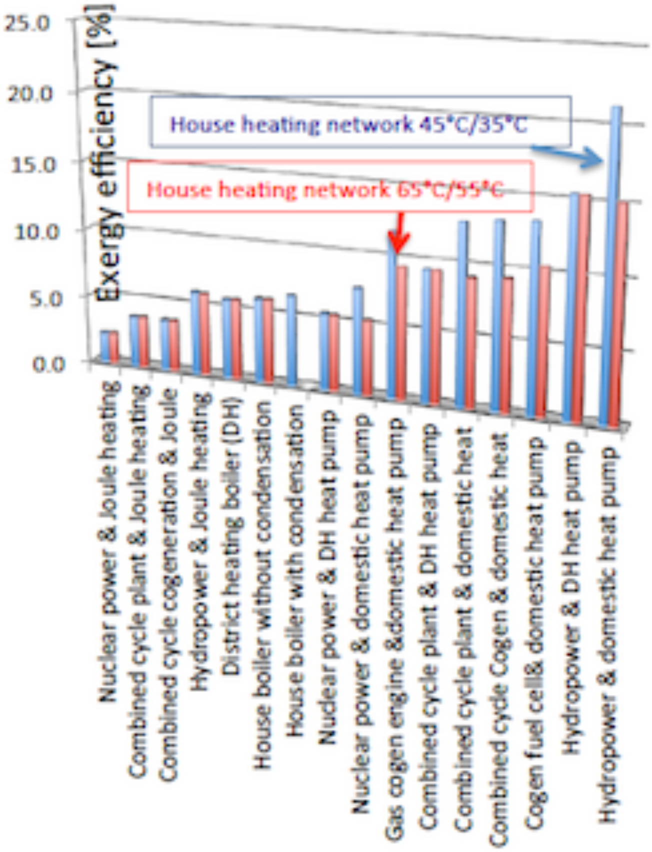

**Figure 11** Ranking of the heating exergy efficiency of various technology combinations

## CONCLUSIONS

Various representations have been proposed to illustrate the concept of exergy, both in industrial processes and in building or city energy systems. They go from extended exergy composites curves with or without Life cycle elements to cartoon types of representations to help grasp the concepts in a humoristic way. Finally we show that exergy efficiency is a coherent way to rank technologies as shown with the example of heating technologies. In many problems decompositions in subsystems can facilitate the calculation of the global exergy efficiency by using simple multiplications of sub-systems exergy efficiencies.

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