**The Carbon Cycle. Methanisation and Iron Oxide Nanoparticles.**
**(extract from: Starting Up under RRI principles, by Marti Busquets-Fité, Eudald Casals, Ignasi Gispert, Josep Saldaña and Victor Puntes. Applied Nanoparticles S.L. Barcelona Spain)**

The majority of the energy around us comes directly or indirectly from the sun. The small remaining extra portion comes from heat at the centre of the planet that is slowly cooling, from the gravitational pendulum of the moon and the seas, and from splitting heavy atoms in nuclear reactors. The rest, like the wind, is produced by the sun, which heats air masses that expand and become lighter displacing cooler ones. The wind also moves the waves. There is also the sun energy stored in chemical bonds by biology. This is why wood burns. And coal is fossilized wood. Photosynthesis is a very interesting way to store energy. Trees are made of condensed air by converting $CO_2$ into organic molecules and carbon based materials. Only a part of the water and little amounts of essential minerals are taken by the roots and come up to the leaves by capillarity. The roots are also made of air, from the $CO_2$ in air that is reduced by the sun via the photosynthesis. Thus, when the tree and the trunk are burned, the heat generated is a portion of the energy they took from the sun to build themselves. A portion, because there is always a loss of energy in any transformation, dissipated in form of entropy.

A chemical reduction reaction that begins with $CO_2$ in the atmosphere, accumulates it in the form of hydrocarbons and, progressively, in a multistep manner, evolves towards carbon, petroleum and shale gas. $CO_2$ is taken from the atmosphere, digested, transformed into more complex molecules and oxygen released. Ironically, the end of life in the planet will occur when no more $CO_2$ is available, when all the Carbon has been buried in solid and liquid forms into the rocks and the ocean depths. "Ironically", because today the massive extraction of fossil fuels that is taking place is subtly altering the chemical composition of the atmosphere by releasing vast amounts of $CO_2$ that was previously reduced by photosynthesis, thus going back on geochemical time, with very apparent consequences for climate change[1].

All organic matter, the biosphere, in its natural reduced state, is immersed in an atmosphere rich in oxygen, and has stored energy. As such, organic waste, pig manure and excrements also store energy. When something stops living, it decomposes. Being alive prevents us from decaying in a few hours. This decomposition ends up returning humidity in the form of water vapour, degraded organic matter, ultimately in the form of $CO_2$, small parts of other gases, and ashes with nitrates, phosphates and small amounts of other inorganic matter. Interestingly, if this process occurs in conditions where there is a low oxygen concentration, such as the naturally occurring underwater, underground or in man-made closed recipients; the organic matter is degraded into methane, $CH_4$. This is because a fraction of this organic matter, in the form of *archaea* bacteria, can breathe the oxygen bound in organic molecules and release

[1] At the beginning, when the Earth was very young, the atmospheric concentration of $CO_2$ was 98%. Now it is only 0.03%. Of course the temperature before was 240-340 ºC on the surface of the planet while it is 13ºC now. Similarly, the concentration of free oxygen was almost non-existent and today it is at 21%.

methane. This molecule can easily be stored and transported for its posterior burning into $CO_2$, releasing thus all the energy contained in its four chemical bonds.

This process of transformation of organic matter into methane, or methanization, is not a spontaneous chemical process.[2] It is produced by consortiums of specialized archaic bacteria. These bacteria were among the first inhabitants of our planet. It is said that in that free-oxygen-less world then, life forms incorporated carbon into their organic matter by capturing $CO_2$ through photosynthesis. In the process they released 2 atoms of oxygen that progressively accumulated as a toxic waste in the atmosphere. Oxygen is of course very reactive, and it was very toxic back then. This is why we can still use hydrogen peroxide, $H_2O_2$, as a disinfectant. It burns things. And it was this waste from life, from initial metabolism, that caused the first massive extinction 2.400 million years ago in the Precambrian era[3]. Not all Precambrian forms of life disappeared. Some stayed alive in places without a good oxygen supply, at the bottom of wells, between rocks, inside of living things (the concentration of free oxygen inside the body is very low; it's all transported by haemoglobin), and they produce methane. This is why sewers explode when there is an accidental spark. These bacteria are everywhere, proliferating whenever they have the opportunity to access organic matter in the absence of oxygen – excrement, under skin or corpse. When exposed to oxygen, many die while some form spores to wait for more optimal conditions for their biochemical living.

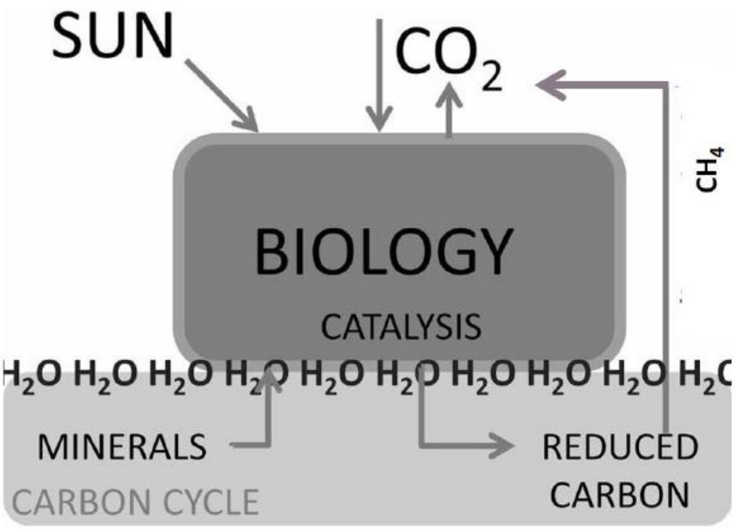


*Fig.1 Carbon Cycle. Note that part of the reduced carbon is transformed into $CH_4$ which is constantly emitted to the atmosphere where it will be slowly oxydized to $CO_2$. Before that, in the form of $CH_4$, it produces about 20 times more green house effect than $CO_2$.*

Both anaerobic and aerobic bacteria need iron for their functioning, like animals, plants and fungi. In fact, all life forms base part of their metabolism on the oxidative reduction of iron ions between valence states +2 and +3. In physiological conditions, iron can easily afford to donate or take an electron. Taking and giving away electrons is the essence of (bio) chemistry. Normally, bacteria does not store iron, as mammals do with ferritin, therefore, they need to

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[2] A steak lost in space will be around forever. Putrefaction is not a physicochemical degradation like the one that molded cliffs and valleys, but rather a biological process.

[3] Apparently, we needed four more to get ready to produce the sixth.

take it from the environment. In the environment, there is a great abundance of iron in its inorganic form. The planet's core is made of iron and it is the fourth most abundant element in the crust. But it takes an important biochemical effort to transform the iron found in rocks into biologically available, like in blood. For us, eating screws or red soil will never cure anaemia, but microbes can do it, even if they also prefer to take iron already inserted in the biological units. Thus, when bacteria infect an organism, the largest and most immediate genetic expression alteration they experiment has to do with the finding, trapping and use of iron for their proliferation. And it is for this reason that when bacteria are detected by the immune system, one of the first defence actions is to remove iron and sugar available in blood[4].

Interestingly, in this context, in conditions of anaerobic breakdown, in the absence of oxygen, small doses of mixed iron oxide nanoparticles (NPs) serve as a *catalyst* that stimulates bacteria metabolism and accelerates the production of biogas (a mixture of different gases produced by the breakdown of organic matter in the absence of oxygen, mainly $CO_2$ and $CH_4$) up to three times with cellulose as feedstock in laboratory conditions (DIN-38414)[5]. Thus, the process that converts organic waste into raw matter for energy production is optimized by simply adding a small dose of iron NPs either to a large waste treatment reactor, a septic tank or a homemade biodigester.

This is based on the effects of the presence of essential trace elements in the methanogenesis process, and the optimized dosing when using small unstable NPs that corrode and dissolve as ions provider. In fact, a challenging area of anaerobic digestion research remains largely unchartered with respect to understanding the role of trace metals in enabling biogas production. This major knowledge gap and scientific challenge is a multifaceted problem involving metal chemistry, physical interactions of metal and solids, microbiology and technology optimisation.

## Climate Change and transition to renewable energy systems

Due to the fact that every molecule of $CH_4$ ends up being oxidized to $CO_2$ and that a molecule of $CH_4$ causes up to 20 times more greenhouse effect than a molecule of $CO_2$, it is the responsibility of everyone, in order to create a cleaner planet with a more stable atmosphere, to prevent $CH_4$ from entering the atmosphere and rather to introduce it into our stoves, vehicles and heaters. When this $CH_4$ comes from $CO_2$ in the atmosphere that was trapped by recent photosynthesis, returning it to the atmosphere will assure the maintenance of a constant concentration of gases in the atmosphere, while combustion of fossil fuels is altering it.

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[4] This is a classic example of burning a city and its reserves before it falls in the hands of the enemy. The infected person is thus weakened so as not to provide nutrients to the bacteria that have invaded the organism. Ironically, many years ago, someone thought it was a good idea to combat the symptoms of an infection, like apathy, tiredness and anemia with iron supplements, which exacerbated the virulence of the infection at once.

[5] E Casals, R Barrena, A García, E González, L Delgado, M Busquets-Fité et al. Programmed iron oxide nanoparticles disintegration in anaerobic digesters boosts biogas production. Small 10, 2801-2808, 2014

In this sense, the urgency in tackling climate change and promoting renewable sources of energy has been universally agreed and it is the responsibility of all citizens, including the scientific and business communities[6]. The UN General Assembly adopted unanimously on 25 September 2015 the New Sustainable Development Agenda (*Transforming our world: the 2030 Agenda for Sustainable Development*) with 17 global goals at its core, being Goal 7 "*Ensure Access to affordable, reliable, sustainable and modern energy for all* and Goal 13 *Take urgent action to combat climate change and its impacts"*. Interestingly, unlike their predecessor (the Millennium Development Goals) the Sustainable Development Goals (SGSs) explicitly call on all business and scientific communities to apply their creativity and innovation to solve sustainable development challenges: *"We the peoples"* are the celebrated opening words of the Charter of the United Nations. It is *"we the peoples"* who are embarking today on the road to 2030: *The journey should involve Governments as well as parliaments, the United Nations system and other international institutions, local authorities, indigenous peoples, civil society, business and the private sector, the scientific and academic community – and all people. Millions have already engaged with, and will own, this Agenda. It is an Agenda of the people, by the people and for the people – and this, we believe, will ensure its success.*

Aligned with this broad framework, the EU is building a regulatory framework favouring the development of energy from renewable sources that, ideally, should be closely linked to increased energy efficiency and decentralized energy production. In this sense, one of the most promising renewable energy sources is the Biogas produced during anaerobic digestion of organic substrates. Biogas production represents a non-polluting, carbon neutral energy source from local raw materials. Also, methane is rising as an alternative to store energy from other renewable sources. Furthermore, biogas production is aligned with the EU strategy and current regulation on waste management.

There is not a biogas sectorial regulation, but the biogas sector is being directly affected by divers EU directives in a wide variety of fields (among others): Directive 2003/55/EC (Injection of biogas into the natural gas network. Aims to open the existing gas network from other inputs than natural gas); Directive 1999/31/EC (Gradual reduction of the filling of biodegradable municipal waste on landfills, by 2016 to 35% of the level of 1995); Directive 2009/28/EC (Promotion of the use of energy from renewable sources); Directive 91/676/EEC (The Nitrate Directive setting limits to the quantity of nitrates that can be spread on agricultural land); Directive 86/178/EEC (The sewage sludge directive); Directive 96/61/EEC (IPPC directive); Directive 98/70/CE; (Quality of petrol and diesel fuels with specific rules for biofuels).

Recently, after Germany, transition to renewable energy was designed by the France's government in 2015, and -in line with the experiences in north of Italy, Sweden and Denmark- a new ideal is being created for the development of biogas and renewable energy. At the same time, untreated waste from organic matter continues to pollute the planet and sends uncontrolled amounts of $CH_4$ into the atmosphere.

[6] www.un.org/ga/search/view_doc.asp?symbol=A/RES/70/1&Lang=E