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## Innovative Chemistry is required to fight Climate Change

Measures taken until now to fight climate change are insufficient according to the IPCC. Innovative sustainable solutions are urgently needed, also from the chemical industry, which requires intensive R&D and investments. Examples are cited of recently developed chemical solutions applied to energy storage, CO<sub>2</sub> Capture and Sequestration, and biofuels production.

Keywords

IPCC, Greenhouse gases, R&D, Energy storage, CCS, Biofuels

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IN NOVEMBER 2014 the Intergovernmental Panel on Climate Change (IPCC) finished his Fifth Assessment Report (AR5) [1], which provides the state of knowledge on climate change. It states that "Human influence on the climate system is clear, and recent anthropogenic emissions of green-house gases are the highest in history... Limiting climate change would require substantial and sustained reductions in greenhouse gas emissions..."

AR5 warns that "without additional mitigation efforts beyond those in place today, and even with adaptation, warming by the end of the 21st century will lead to high to very high risk of severe, wide-spread and irreversible impacts globally."

About the multiple pathways available to mitigate climate change and warming AR5 says: "Adaptation and mitigation responses are underpinned by common enabling factors. These include effective institutions and governance, innovation and investments in environmentally sound technologies and infrastructure... Adaptation options exist in all sectors."

Important climate change mitigation measures and solutions have already been developed and adopted during the last years, such as important investments and the increased use at big scale of renewable energies, especially wind and solar, but to a much lesser extent biofuels, biomass and waste to energy, small hydro, geothermal and marine energy.

The latest report of the United Nations Environment Programme (UNEP), "Global Trends in Renewable Energy Investment 2015" [2], based on data from Bloomberg New Energy Finance, informs about the deals, issues and policy moves that lay behind the 17% rebound in world renewable energy investment, the first increase in three years, thanks to the expansion of solar en wind energies, and also of geothermal energy. However biofuels fell 8%, - probably because of lower crude oil prices -. Biomass and wasteto-energy also went 10% down (Figure 1). According to Report AR5, all efforts and achievements up to now have been clearly insufficient.

Another recent study of Bloomberg New Energy Finance [3] reveals that since 2013 more capacity for renewable power is added each year than coal, natural gas, and oil combined, and that it will continue. It foresees also that the shift will accelerate. But on the other side, because of the financial crisis investments have fallen short of the target and many fossil fuel power plants will still be needed.

The chemical industry sector must be an essential player in fighting climate change because it can bring by several innovative, environmentally sound and cost-efficient technologies urgently needed, which require intensive R&D and investments, as well as adequate economic support from institutions and from private companies.

### DISCUSSION

The following is a synopsis of some relevant and promising recent breakthrough chemical developments.

The first and far most important sustainable solutions are energy efficiency and energy savings, because the least sustainable energy is the one that is being lost. The UNEP report contains a special chapter entitled "Structural challenges in the electricity system", which examines new barriers facing renewable energies but also energy smart technologies such as smart grid, efficiency, advanced transportation and power storage. The following are two examples of chemical power storage developments.

### MOLTEN SALTS ENERGY STORAGE

The only big scale power storage known until recently was the pumped-storage hydropower system. (Batteries are normally used for smaller storage). But now a new power storage using molten salts has become commercially available, since the first thermal solar plant in the world went on stream in Seville in 2011, owned by Gemasolar [4]. The plant uses a technology



developed by Sener with the collaboration of CIEMAT. Thermal storage capacity is 670 MWh. The molten salt system stores the excess thermal energy produced during daylight time and provides the energy required to ensure the plant can remain operational for up to 15 hours without sunlight. Energy is recovered from the molten salts by heat exchange, producing steam to feed a steam turbine. According to Sener, the process reduces by more than 30,000 tons per year the CO<sub>2</sub> emissions. Sener received the European Business Award 2011, category of innovation, for the Gemasolar project.

### SCALING DOWN OF MOLTEN SALTS ENERGY STORAGE

Halotechnics [5,6] is a company based in Emeryville, California, and founded in 2009 in order to commercialize the molten salts technology. It is a spinoff of Symyx Technologies, where research on molten salts was started at the end of 2007. The company is now developing a factory assembled modular thermal energy storage system for utility procurement in the range of 30-50 MW, which the company claims to be as low as half the cost of batteries.

Other solutions will be necessary such as carbon capture and sequestration (CCS) in facilities with high  $CO_2$  emissions, but are mostly still in the development stage.

### Carbon Capture and Sequestration – CCS

Some aspects of CCS, in particular  $CO_2$  absorption, sequestration and storage, raise technical and/or environmental and/or economic issues. Recent developments of innovative technologies are signs that creative efforts are being made. Several of these technologies were born in university research labs supported by and in collaboration with industry. Hereafter are some examples.

### CO<sub>2</sub> CAPTURE BY CHEMICAL STRUCTURES

The classical method of  $CO_2$  capture from combustion effluent gases is by absorption in aqueous amines, such

as MEA. But these compounds suffer progressive oxidative and thermal degradation. A promising method to solve the problem is the direct removal  $CO_2$  from the flue gas, for example from coal-fired power plants, using metalorganic frameworks (MOFs) (Figure 2) based on magnesium, which are synthesized and developed by researchers of the University of California, Berkeley, hopefully with a significant reduction in cost [7]. The chemists from the University used a modified metal-organic framework (MOF) compound with diamines, enabling the material to be tuned to absorb  $CO_2$ at different temperatures.

Another solution of the same problem: A team, led by scientists from Harvard University and Lawrence Livermore National Laboratory, used a microfluidic assembly technique to produce microcapsules that contain liquid sorbents, or absorbing materials, encased in highly permeable polymer shells. According to the authors, they have significant performance advantages over the carbon-absorbing materials used in current capture and sequestration technology. For instance they have a practically unlimited life as compared to amines. The researchers are working on the improvement of the  $CO_2$  capturing process in order to apply the technology at a bigger scale.

### CHEMICAL CO, SEQUESTRATION

The preferred sequestration method of captured  $CO_2$  is transforming it into useful products, such as polymers or fuels. Examples are:

### CO, TRANSFORMATION INTO POLYMERS

For the first time a polymer produced by combining  $CO_2$  with epoxides is being commercialized. The most common epoxides used are ethylene oxide and propylene oxide. The final product, the polymer, is a polyol of polypropylene carbonate, which is the basis for the manufacturing of polyurethanes and then into foam used for thermal

**Figure 2.** Metal-Organic Frameworks (MOFs) for CO<sub>2</sub> Capture (Courtesy: Jarad Mason, Long Group, University of California Berkeley)



insulation. The polymer, containing about 50% of  $CO_2$ , is produced by Novomer, a company especially founded in 2004 for its commercialization. The process uses a cobalt based catalyst first developed at the Cornell University of Itaca, New York, by Prof. Geoffrey Coates, scientific cofounder of Novomer, and which has been successively improved [8]. The polymer is produced in a batch process whose capacity has been increased considerably during last year from less than 100 tons in 2013 till several thousands of tons at the facility in Houston.  $CO_2$  is provided by nearby factories, methanol fermentation and thermal power plants.

Novomer claims that the process has serious advantages such as the low cost of the prime material,  $CO_2$ , and the unique yields of polymer having a precise structure and produced almost without by products as compared to polymers obtained from oil or biological sources. Novomer is now investigating, together with the Dutch company DSM, the production of polymers for resins used for paints and coatings which would be commercialized within the next years [9].

### CO, TO BOOST FARMING OF CROPS

Petroleum companies are converting themselves into energy companies to become more sustainable. Repsol is one of these and has several projects going on or completed with successful results [10]. One completed project is carbon fertilization, called ' $CO_2$  Funnels', developed at Repsol's Technology Centre and tested in several greenhouses installed in the Industrial Complex of Puertollano (near Ciudad Real). The project has shown that carbon fertilization improves the yield of non-food plant species, which will then be used as biomass to produce bioenergy, because these plants grow faster thanks to higher doses of  $CO_2$ .

## SUSTAINABLE BIOFUELS CRITERIA

A debate is going on about the environmental and social problems associated with some prime materials used for

the production of biofuels [11, 12]: competition with food such as crops, or land use for energy agriculture instead of for food. The European Commission's Directorate-General of Energy states that for biofuels to reduce greenhouse gas emissions without adversely affecting the environment or social sustainability, they must be produced in a sustainable way. The EU therefore sets rigorous sustainability criteria for biofuels and bioliquids which are:

•To be considered sustainable, biofuels must achieve greenhouse gas savings of at least 35% in comparison to fossil fuels. This savings requirement rises to 50% in 2017. In 2018, it rises again to 60% but only for new production plants. All life cycle emissions are taken into account when calculating greenhouse gas savings. This includes emissions from cultivation, processing, and transport.

• Biofuels cannot be grown in areas converted from land with previously high carbon stock such as wetlands or forests.

• Biofuels cannot be produced from raw materials obtained from land with high biodiversity such as primary forests or highly biodiverse grasslands.

Following are two examples of innovative solutions in agreement with the EU criterion of sustainable production. The first one is the direct conversion of a greenhouse gas,  $CO_2$ , into fuel. The second example is the conversion of a waste byproduct of an alcoholic beverage production into biofuel.

### CO<sub>2</sub> CONVERSION TO FUELS

Joule, a company based at Bedford, Massachusetts, pioneered the development of a CO<sub>2</sub>-to-fuel production platform using only solar energy, called Joule Sunflow® [13]. Using proprietary catalysts, waste CO<sub>2</sub> is continuously converted directly into renewable fuels, including ethanol





or hydrocarbons for diesel, jet fuel and gasoline. Joule's platform was awarded the 2015 Technology Innovation Award by Frost & Sullivan for its ability to recycle waste carbon dioxide  $(CO_2)$  into drop-in liquid fuels using sunlight.

Joule was founded in VentureLabs®, a business accelerator program delivered by Simon Fraser University (SFU), the University of Victoria (UVic), the British Columbia Institute of Technology (BCIT) and the Emily Carr University of Art+Design (ECUA+D), in partnership with the British Columbia Innovation Council (BCIC), government and industry partners.

### **BIOFUEL FROM WHISKY BYPRODUCTS**

Celtic Renewables Ltd is developing a technology (Figure 3) to convert the byproducts of the whisky distillation into biofuel [14]. Only about ten percent of the distillation process produces whisky while as the rest are byproducts called "draff", a distillation residue used as a prime material for the production of animal food, and "pot ale", a liquid similar to beer. The whisky industry produces every year about 1,600 million liters of pot ale and 500 thousand tons of draff. Both byproducts can be converted into biofuel, using an innovative process by hydrolysis and fermentation of draff and pot ale in the presence of microorganisms (bacteria) and specific enzymes, selective for the production of acetone, butanol and ethanol, in a weak acidic medium (pH about 5). The process has been developed during two years at the Biofuel Research Centre at the Sighthill Campus of the Edinburgh Napier University, which filed a patent for the new biofuel. The Biofuel Research Centre was the UK's first research centre dedicated to the development of renewable and

sustainable biofuels and where Celtic Renewables Ltd. has been created as a spinoff in January 2012. The samples of the whisky byproducts were supplied by the nearby Glenkinchie Distillery. In 2014 the patent was granted to Celtics Renewables. The owners and developers of the process received several awards: IChemE Innovation award, "Best Innovation" award at the Scottish Green Energy Awards, GlaxoSmithKlein Innovation Award.

## CONCLUSIONS

The foregoing is only a small sample of the possibilities and the variety of innovative solutions that chemistry can and could offer to fight climate change as a consequence of original R&D with adequate industry and government funding.

But climate change is a global problem and consequently requires also a strong and sustained effort of collaboration between countries, between and within each continent, involving universities, private companies and governments.

### Bibliography

[1] Intergovernmental Panel on Climate Change (IPCC), November 2014, "Fifth Assessment Report (AR5)", IPCC website. (http://www.ipcc.ch/report/ ar5/index.shtml)

[2] Frankfurt School – UNEP Collaborating Centre for Climate and Sustainable Energy Finance, 2015, "Global Trends in Renewable Energy Investment 2015". Pdf document UNEP website. (http://fs-unep-centre.org/ sites/default/files/attachments/key\_messages.pdf)

[3] Randall, T., Bloomberg Business website, April 14, 2015, "Fossil Fuels Just Lost the Race Against Renewables" (http://www.bloomberg.com/news/ articles/2015-04-14/fossil-fuels-just-lost-the-race-against-renewables)

[4] Gemasolar, a Torresol Energy Company, "Gemasolar: how it works", pdf document Torresol Energy website.. (http://www.torresolenergy. com/EPORTAL\_DOCS/GENERAL/SENERV2/DOC-cw4cb709fe34477/ GEMASOLARPLANT.pdf)

[5] Jonemann, M., Halotechnics Inc. Emeryville, California, December 8, 2011 - April 30, 2013, "Advanced Thermal Storage System with Novel Molten Salt". Pdf Document National Renewable Energy Laboratory website. (http://www.nrel.gov/docs/fy13osti/58595.pdf)

[6] Bullis K., February 27, 2014, "Molten Salts Might Provide Half-Price Grid Energy Storage", MIT Technology Review. (http://www.technologyreview. com/news/525121/molten-salts-might-provide-half-price-grid-energystorage/)

[7] Prof. Jeffrey R. Long Group (Several authors of the inorganic chemistry group, of articles at different dates), Department of Chemistry, UC Berkeley, "Metal-Organic Frameworks". Long Group website. (http://alchemy.cchem. berkeley.edu/metal-organic-frameworks.html)

[8] Ju. A, Cornell Chronicle, November 21, 2014, "Cornell-developed polymer has commercial debut", Phys.org. (http://phys.org/news/2014-11-cornell-developed-polymer-commercial-debut.html)

[9] Catalano J., March 29, 2015, "Novomer turns CO2 into highperformance plastics", Ithacajournal. (http://www.ithacajournal.com/story/ money/2015/03/29/novomer-carbon-dioxide/70337192/)

[10] J.M Daganzo, 9 October 2013, "Repsol demuestra los beneficios del CO2 en cultivos", Repsol blog. (http://blogs.repsol.com/web/innovacion/ inicio/blogs/1379571/)

[11] European Commission Directorate-General of Energy, "Sustainability Criteria", European Commission Directorate-General of Energy website. (http://ec.europa.eu/energy/en/topics/renewable-energy/biofuels/ sustainability-criteria)

[12] Stevens B., University of North Dakota Energy & Environmental Research Center, "Biofuels Sustainability: A Nonfood Feedstock Primer", Biomass Magazine. (http://biomassmagazine.com/articles/2411/biofuelssustainability-a-nonfood-feedstock-primer)

[13] Jenkins S., April 1, 2015, "End-to-end demonstration of CO2to-ethanol process achieved", Chemical Engineering. (http://www. chemengonline.com/end-end-demonstration-co2-ethanol-processachieved/)

[14] Lane I., March 2, 2015, "Celtic Renewables to build whisky-based biobutanol production facility in Scotland", BiofuelsDigest. (http://www.biofuelsdigest.com/bdigest/2015/03/02/celtic-renewables-to-build-whisky-based-biobutanol-production-facility-in-scotland/