

## Ernst Hammel<sup>1</sup>, Klaus Mauthner<sup>1</sup> and Walter Brichta<sup>2</sup>

## Nanotechnology as a useful contribution to the reduction Carbon Dioxide Emissions

The Intergovernmental Panel on Climate Change (IPCC) shared the 2007 Nobel Peace Prize with former Vice President of the United States Al Gore for their fundamental work for and commitment to the protection of the world climate. This is a hot issue in science and politics and causes a lot of arguments for and against specific measures to be taken by governments, industries and individuals.

The problem is generally known and can be summarized in a few graphs [1].



Fig.1 (by courtesy of IPCC)

Figure 1 indicates the exponential increase of greenhouse gases since the industrial revolution within the last 150 years. In contrast we find no significant change over the last 10,000 years before.

<sup>1</sup> ELECTROVAC AG, Klosterneuburg/Austria

<sup>2</sup> HEAT Wärmetechnische Anlagen GmbH, Biedermannsdorf/Austria



Fig. 2 (by courtesy of IPCC)

Within the timescale of 150 years the average global surface and ocean temperatures started to drift (figure 2), indicating global warming and reduced coverage by snow and ice [2,3].



Fig. 3 (by courtesy of NSIDC)

In 2007 the National Snow and Ice Data Center (NSIDC) measured the lowest ice coverage in the northern hemisphere since the existence of direct measurement (figure 3) and found strong deviations from standard global warming climate models. This corresponds well with the fact that the gobal land surface temperature from January to September showed a record high since systematic measuring has been taking place.



Fig. 4 (by courtesy of NOAA)

Figure 4 indicates a +1.04 °C increase of the average land surface temperature in 2007. Modelling of the global temperatures allows to determine mini-max scenarios, as shown in figure 5.



Fig. 5 (by courtesy of IPCC)

These graphs show that the global temperature increase could be up to +4 °C in 2100 unless we interrupt the emission cycle of greenhouse gases. No reduction of  $CO_2$  emissions are observed on a global scale although many countries have signed agreements to limit their emissions. The worldwide carbon dioxide emissions are observed by IRS observatories worldwide. Mauna Loa station in Hawaii is usually taken as a reference and figure 6 shows actual data from this observatory.



Fig. 6 (by courtesy of NOAA)

Warnings have even been issued over the last months that carbon emission has considerably increased compared to the past.

Polar icecore analysis has been considered as a valuable probe for testing the relationship of atmospheric carbon dioxide contents versus local temperatures.



Fig. 7 (by courtesy of NGRIP)

Figure 7 shows such an icecore from the North Greenland Icecore Project. Systematic data have been obtained from the icecore drilling at Vostok station [4] in the Antarctica.

Figure 8 was published by the UN Environment Programme (UNEP) to demonstrate the longtime effect of carbon dioxide on the world climate. This graph indicates maximum atmospheric  $CO_2$  levels of 280 ppm compared to currently measured 385 ppm! Using these data, we can simply extrapolate what will happen to the polar regions within the next few years.



Fig. 8 (by courtesy of UNEP)



Fig. 9: Linear model for polar climate change

The extrapolation in figure 9 shows alarming temperature values for current  $CO_2$  levels far beyond the global climate change models. Actual reports on the accessibility of the North-West Passage last summer and measurements of temperature anomalies in the polar regions could well correspond to the predictions above.



Fig. 10 (by courtesy of NOAA)

If we continue to use our fossile resources for caloric power generation by oxidation processes we might expect far higher levels of  $CO_2$  in the atmosphere and even stronger effects on the world climate.

	Stocks [10 <sup>15</sup> kg]	CO <sub>2</sub> [10 <sup>15</sup> kg]	∆ air conc. [ppm]	ΔT [°C]
Oil	0.21	0.49	+ 71	+ 5.6
Gas	0.24	0.66	+ 96	+ 7.6
Coal	0.67	2.46	+357	+28.5

In order to avoid a complete breakdown of the world climate, it is generally assumed that hydrogen shall be used as a future energy source for mobile devices from cars to laptops. Hydrogen is the lightest element, escapes from atmosphere into space and is difficult to store. It must be kept either in form of (1) pressurized gas tanks, (2) cryogenic containers or (3) chemically adsorbed or bound in metal hydrides.

According to the IEA 95 % of the worldwide hydrogen production [7] is based on reforming of natural gas. The conventional processes convert the contained carbon into  $CO_2$  which is then released into the atmosphere. This means that cars could be fuelled with "green" hydrogen and the emissions are moved from the consumer to the producer. Carbon sequestration has been introduced to store  $CO_2$  in abandoned oil and gas fields or coal mines. This concept needs to be critically studied also in context of the true  $CO_2$  prevention costs.

The Steam Reforming (SR) Technology is based on the reaction of methane with water vapour using a catalyst at temperatures around 850 °C and at pressures around 20 bar. Methane first reacts with water vapour to form CO and hydrogen. Thereafter CO and water vapour react to form  $CO_2$  and more hydrogen (shiftreaction).



Fig. 11: Steam Reforming

The resulting  $CO_2$  is then split off using a Pressure-Swing Adsorption (PSA) process or membrane filtering.

Direct cracking [5] of methane with nanoscaled catalysts into hydrogen and nanoscaled carbons, e.g. in form of nanofibers, is our answer to the emission of 7 kg  $CO_2$  per kg hydrogen produced by SR processes.



Fig. 12: Nanocatalytic Direct Cracking

Catalysts are chosen from the family of cementite forming metals like Fe, Ni and Co. The scale of the grain size determines the fiber diameters. Carbide forming diffusion velocities determine the fiber growth rate. This number is strongly dependent on the temperature and the flow rates of the gas supply. The process works best at ambient pressure or slightly above.

The reduced yield on hydrogen and the slightly increased costs of the catalyst materials could be compensated by industrial application of the so produced nanofibers or other forms of nanocarbon. For further applications the fibers have to be cleaned from foreign substances.





ELECTROVAC and HEAT have engineered processing techniques [6] and systems for hydrogen production in industrial applications with very little or no carbon dioxide emissions.

This process can also be combined with current SR systems and contribute significantly to "cleaning" them from  $CO_2$  emissions. This might be a useful concept for upgrading existing hydrogen plants in refineries.



Fig. 14: Basic scheme for hydrogen plant



Fig. 15: Upgrading scheme for SR plants

The CO<sub>2</sub> prevention costs depend critically on the world market prices for hydrogen when considering the actual carbon emission certificates and the achievable market prices for nanocarbons.

The annual production of hydrogen is more than 50 million tons expecting a strong increase over the next years. Steam Reforming of natural gas balances each ton of produced hydrogen with seven tons of emitted carbon dioxide, or worldwide 350 million tons of carbon dioxide. The total amount of carbon dioxide emitted from the use of natural gas as energy carrier is 5 billion tons per annum. The contribution to the atmospheric concentration is 0.7 ppm per annum and the effect on the world climate is +0.1 °C per annum. There seems to be a window of opportunity for this nanocatalytic direct cracking process which can reduce carbon emission up to 90 %.

## Conclusion

Carbon dioxide emission has reached a critical level and threatens the socio-economic progress of human civilization by strong climate change effects. Some sources of the carbon emissions are well known and understood, so that alternative technologies with significantly reduced carbon emissions can be used to substitute them without major changes in the infrastructure. We present a new concept of nanocatalytic direct methane cracking, where higher costs of hydrogen productions can potentially be absorbed by the industrial application of the by-products in form of carbon nanofibers. This is a first step of preventing carbon dioxide emission by modifications in the reaction mechanisms of fossile fuels. It also shows the potential of catalytic additions into well known conversion reactions.

## References

- [1] IPCC Report at the GMEF and UNEP GC-24 Nairobi, 6 February 2007
- [2] "Shrinking Arctic Sea ice opens Northwest Passage", Environment News Service, 1 October 2007
- [3] "The North Pole is melting", Scientific American, 21 September 2007
- [4] J. R. Petit et al.: "Climate and atmospheric history of the past 420,000 years from the Vostok icecore, Antarctica", Nature 399: 429-436, 1999
- [5] E. Hammel et al.: "Thermocatalytic cracking of Methane", WHTC 2005, Singapore
- [6] Patent Publications WO07051213, WO06084295
- [7] IEA World Energy Outlook 2006

[27.11.07]

Anschrift der Autoren:

Ernst Hammel ELECTROVAC AG Aufeldgasse 37-39 A – 3400 Klosterneuburg