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Nanotech Biofuels and Fuel Additives

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1. Introduction

This chapter was inspired by an invited presentation of the author at the Chemindix conference in Bahrain in October 2010. This was the 8th. International Conference & Exhibition on Chemistry in Industry, promoted by the Saudi Chapter of the American Chemical Society and Aramco. The focus is on reviewing the application of nanotechnology to biofuels production and to the utilization of fuel additives, some of which are derived from renewable materials.

To introduce the topic, the broader context of petroleum fuels and biofuels is presented. A smart future of oil refining would be to increasingly utilize margins to finance a transition away from oil towards future alternative providers of mobility, in particular biofuels.

Future scenarios of liquid biofuels involve the market penetration of second and further generations of technologies and the continuous improvement of first generation processes. On the other hand, nanotechnologies are among the candidate technologies for the biofuels of the future. The nanotechnology field is vast and its applications unbound.

This is followed by a brief review of nanotechnology developments, especially as they apply to liquid particles, beyond the more common solid particle applications.

Algae growth, harvesting and conversion are presented and discussed, given the immense potential of their contribution towards an energy future where biofuels play a significant role.

Most of the current effort in second generation conversion to liquid biofuels is based on biomass cellulosics to ethanol and biodiesel. Nano processes are being pursued and will be reviewed in the chapter.

Likewise, the presently used processes to convert oils and animal fat into biodiesel are based on trans-esterification with methanol or ethanol, which inevitably generates glycerol, which must find a market or get disposed properly. Nano processes may be useful in addressing this issue.

Speculative considerations are made about the role of liquid nanoparticles of fuel additives in enhancing the performance of additized biofuel/fuel blends, in connection with surface and combustion effects.

Public concerns over the impacts of nanotechnologies on security, health and the environment are also mentioned and discussed. But, a cautionary optimistic view is presented on the huge benefits of a careful penetration of nanotechnologies in the realm of biofuels and fuel additives, and in many more applications, especially those dealing with human health.

2. The future of oil refining [1] and the oil transition to alternatives [2]

Crucial challenges to the oil industry are evolving, as the demand for energy services (mobility, lighting, rotary movement, heating and cooling) increases, which with the current technology setup, is translated into expanding demand for liquid fossil fuels. Oil producers and refiners face difficulties finding sufficient good quality crude oil in adequate amounts and reasonable costs to meet growing demand over the long run, while users and the public at large are pushing for environmental improvements, such as better air quality in the immediate future. Moreover, concerns about the impacts of climate change caused by increased greenhouse gases emissions from the production and use of liquid hydrocarbons may eventually force a transition to climate friendly energy services providing systems. This offers biofuels a market penetration opportunity in the transition towards a yet undefined new energy future.

Under this background, the oil refining industry in the USA and the European Union has been stagnant. It has been immobilized by environmental obstacles posed by an articulated public, augmented by a “not in my backyard” attitude that makes it difficult to build new refineries. In addition, declining margins for refined products may have led major players to focus more on the upstream.

On the other hand, refining is expanding in other parts of the world, such as India, China, Brazil and the Middle East, as these countries develop and the oil producers attempt to add more value to their resources. An evidence of the shift of refining towards developing economies is the fact that the largest refinery in the world is in India and belongs to Reliance.

But, all over the world, the increase in the long-term marginal cost of oil combined with environmental pressures and stricter government regulations and mandates are likely to lead to the decline of the centrality of oil in the global energy mix in favor of natural gas. This shift in dominance happened to wood and coal over the past two centuries and is now happening to oil. Oil companies are increasingly calling themselves energy companies. Some of them will leverage their current oil production margins to make a smooth transition to alternatives over time. A profitable transition to alternatives in the oil economy would require a gradual transfer of oil profits into green investments and the stretching of current oil supplies.

3. Liquid biofuels issues [3]

The enormous global daily consumption of liquid fuels is of the order of 80 million barrels/day (equivalent of 12.7 million m³/day). The sugar cane area required to produce the same volume of ethanol is about 700 million hectares, assuming a yield of 6.5 m³/ha/year of ethanol. This area is equivalent to 100 times the sugar cane cultivated area in Brazil, the second largest bio-ethanol producer in the world. Biofuels definitely face an issue of scale. In 2010, fuel ethanol and biodiesel combined displaced a mere 3% of oil in the world.

Figure 1[4] below illustrates the scale issue by showing how much land it would take for the USA to grow its own fuel.

It appears that algae require the least area to meet the large scale demand of liquid fuels in the USA, whereas the area required by soybeans is larger than the USA's 48 continental states. The area required by corn is substantial. This suggests that the current biofuels production base of the USA would not be able to meet demand, and imports would be required to meet the colossal American energy appetite.



Fig. 1. How much land would it take for the USA to grow its own fuel?

The scale challenge posed to biofuels relates to the labour, management, land, water and sunshine required to produce the biomass and the processing that originates them. These are scarce resources that are also needed to grow food, feed and fibre to ultimately meet various human demands. These are resources that have an opportunity cost from competing markets. To develop biofuels in the scale of commercial liquid fuels require massive financing, a resource that may have alternative uses as well. The mobilization of private capital under a perception of market and other uncertainties is another issue that biofuels have to resolve in order to thrive.

The production of biofuels is accompanied by local environmental issues that need addressing. For instance, in the case of sugar cane ethanol, stillage the liquid residue of distillation, has a high chemical and biological oxygen demand and requires appropriate processing before final disposal. From a global climate change perspective, designed and managed properly, a biofuels production system would add minimally to greenhouse gas emissions. But, in practice, many biofuel production systems in the world are contributing net GHG emissions.

A bone of contention in the development of the biofuels industry is the present competition for feedstocks between the food and fuel industries. In the case of biodiesel, all commercial

vegetable oils that are used in preparing food are also convertible to biodiesel. A similar situation exists with respect to fuel ethanol, especially for the starch-based feedstocks (corn and wheat). However, the hike in food prices that happened globally in 2007/8 and is happening in 2010/1 derive mostly from other causes such as droughts and other climate related phenomena, higher oil prices and market speculation.

Since the cost of biofuels is dominated by feedstocks cost, access to feedstocks in the required amounts, timing and at adequate prices is key to the success of the biofuels economy. The combination of the food versus fuel conundrum with the need to have reliable and economic access to feedstocks is shifting the industry towards non-food feedstocks and to the market penetration of second generation technologies to convert cellulosic biomass into liquid biofuels.

Concern in important consuming markets about the sustainability of biofuels producing systems is putting pressure on suppliers to abide by sustainability protocols subject to certification. The sustainability of biofuels is actually linked to freer international trade, which would tend to phase out unsustainably produced biofuels in favour of regions of the world that can meet sustainable production requirements. A valuable discussion on this matter was hosted by the Rockefeller Foundation in 2008 at its Bellagio Centre and produced a sustainable biofuels consensus. The objective was to understand the many drivers for sustainable trade, consumption and production of biofuels, and the comparative advantage of supplying regions combined with demand and technology from consuming regions [5].

However, much remains to be done to achieve free international trade of biofuels. The World Trade Organization Doha rounds have reached an impasse. Currently, biodiesel is considered an industrial product, whereas fuel ethanol is categorized as an agricultural product, which allows more protectionism. What is needed is a unified treatment of biofuels, where they are classified under environmental goods and services. But, irrespective of these drawbacks, a sign pointing to a larger role for biofuels in the future are the new biofuels technology initiatives by large oil companies, such as BP, Chevron, Exxon and Shell. The development of the international trade in biofuels is likely to distribute more evenly the production and consumption of biofuels in the world. For the time being, biofuels production is overwhelmingly concentrated in the USA, Brazil and the European Union, as shown in Fig. 2 below[6].

4. The vastness of nanotechnology

Nanotechnology can be simply defined as the discipline of building machines/devices on the scale of molecules, a few Nanometers (10^{-9}m) wide, way smaller than a cell. Table 1 below show some practical applications of nanotechnologies and confirms the vastness of their domain [7]:

In the practically important area of polymers, nanotechnologies originate nano-structured polymers, where applications can be found in support structures; manufacturing processes; diagnostics and therapy; pharmaceuticals; medical and dental prosthesis; and thin films for surface treatment. The main chemicals involved in nano-structured polymers are: poly-oxides; poly-acrylates; poly-vinyls; poly-saccharides; and poly-ethylenes. The main materials incorporated into polymer nano-matrices are silicon, chromium and carbon[8]

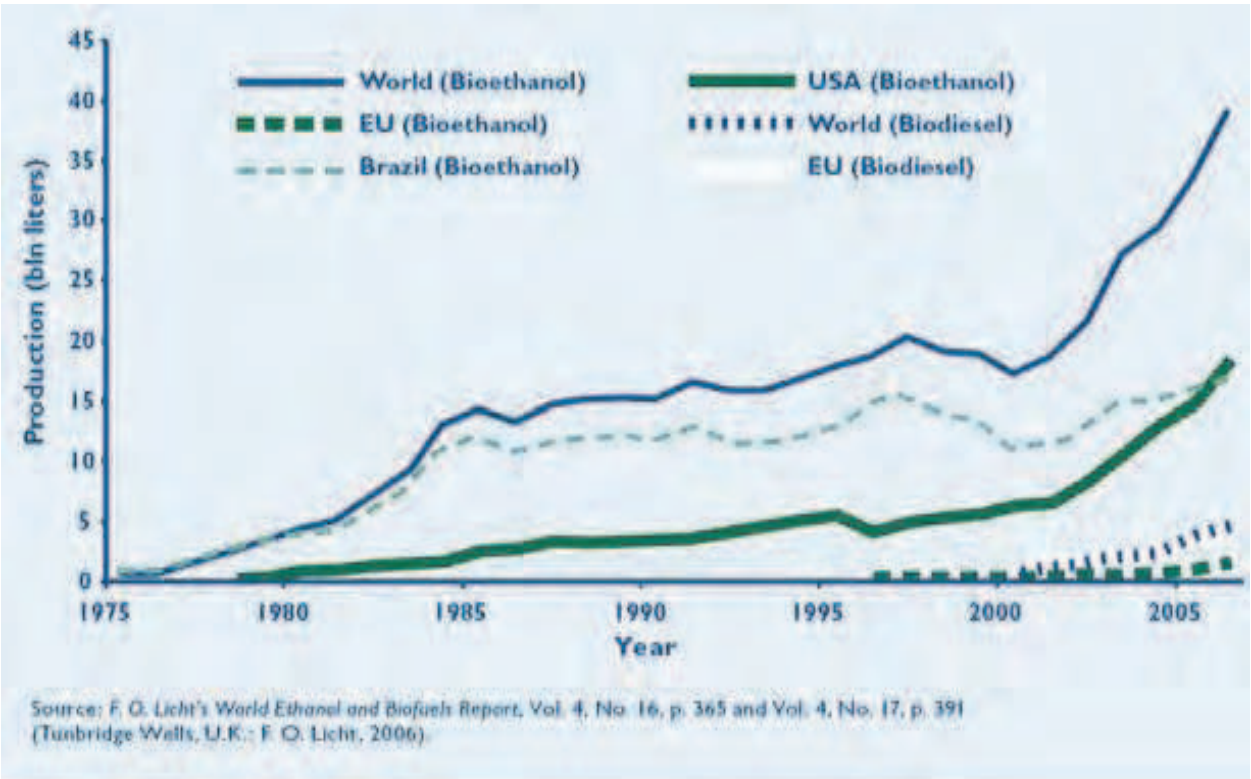


Fig. 2. World’s biofuels production is concentrated in the US, Brazil and the EU

Nanocrystalline Drugs	Oxide Nanoparticles
Nanofilm Coatings	Carbon Nanotubes
Cosmetics	Silicon Nanomaterials
Nanocatalysts	Metal nanoparticles
Ceramics	Polymer Nanocomposites
Rubbers	Inorganic Nanocrystals

Table 1. Some applications of nanotechnology

5. Turning algae into biofuels

As shown in Fig. 1, biofuels derived from algae offer a great potential in view of the possible high yields and smaller area requirements. In addition, algae can play a role in carbon mitigation, as one way of growing algae is to feed them carbon-dioxide (CO₂), besides water and sunlight. Algae can be fed other substrates as well, because to grow, cost-effectively, on carbon dioxide there would be a need of concentrated sources of the gas, such as found in combustion off-gases from fossil fueled power plants.

Oil can form up to 50% of the algae mass, in contrast with the best oil-bearing plants – oil palm trees – where less than 20% of the biomass is made out of foil. Algae carbohydrates can also be made into ethanol or gasified into bio-gas, or methane or hydrogen [9].

But, algae development into biofuels must overcome a number of challenges before algae can become significant sources of commercial biofuels. Since algae also need water to grow,

expansion of algae production may create a dilemma of water versus fuel, similar to food versus fuel dilemma discussed previously. Another challenge is the low natural carbon dioxide concentration in the atmosphere, hence the consideration of additional sources of carbon for algal growth in a commercial biofuels system. One response to these challenges may include the use of nanotechnology to turn algae into biofuels.

As way of examples, in 2009, the company QuantumSphere received a grant from the California Energy Commission to develop a nano-catalyzed algae biogasification. Also in California, the Salton Sea receives large amounts of agricultural runoff, which sometimes create large algae blooms. These algae and similar biomass have been turned experimentally into methane, hydrogen and other gases [10].

One nanotechnology relevant to algae development is the use of nanoparticles as no-harm harvesters of biofuel oils from algae, as illustrated in Fig. 3 [11]. The nano particles are shown on the left hand side of the photograph before the oil pregnant algae are added. The right hand side shows the contacting between the algae and the nano particles, which results in extracting the oil without harming the algae. Maintaining the algae alive can dramatically reduce production costs and the generation cycle.

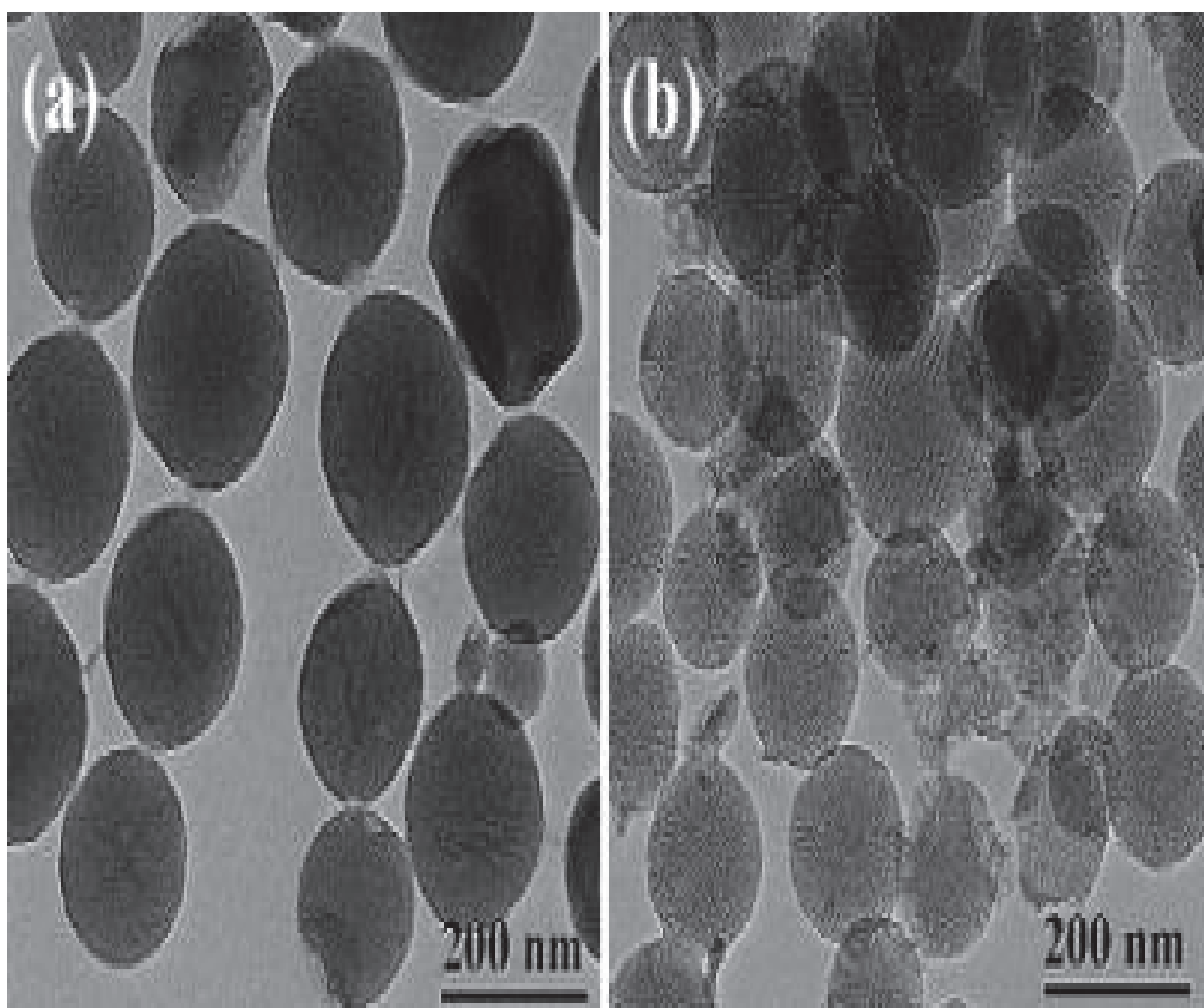


Fig. 3. Nano-particles harvesting oil from algae without harming the organism

One possible downside of the nano-harvesters is the risk that they may be released into the environment, although the spherical nano-particles are made of calcium compounds and sand [12]. The pores of the spheres are lined with chemicals, which extract algal oil without breaking the cell membrane. Nevertheless, prior to commercial market penetration of nano-harvesting, there would be a need to carry out due diligence to ensure the safety of these processes.

6. Nanotechnology applied to landfill facilities[13]

The organic matter in landfills tend to undergo anaerobic fermentation yielding methane and CO₂ [14], which if naturally vented into the atmosphere would add to the greenhouse emissions that warm the climate. And the climate change impact of methane is 25 times larger than that of carbon dioxide for a time horizon of 100 years [15]. Thus, there is a need to sequester the carbon present in landfill methane. Nano-catalysts can crack methane into elemental carbon and hydrogen. The carbon can be produced in high-purity nano-graphite for use in aerospace, automobile, batteries, etc. This approach to handling methane can considerably improve the economics of landfills as well as of anaerobic digester plants that generate electricity from biogas fueled electricity.

7. Nanotechnology to convert biomass into biofuels

Delinking biofuels production from food crops is a necessary condition to expand the scale of the market penetration of biofuels globally. Among the challenges this strategy faces is the inherent resistance of cellulosic feedstocks to conversion to simpler sugars that can be fermented into ethanol. Here, the promise lies in nano-particles used as immobilizing beds for expensive enzymes that can be used over and over again to breakdown the long chain cellulose polymers into simpler fermentable sugars [16].

The Louisiana Tech University is one among many organizations worldwide engaged in this endeavour, through the work of Dr. James Palmer, in collaborating with fellow professors Dr. Yuri Lvov, Dr. Dale Snow, and Dr. Hisham Hegab [17]. The focus is on non-edible cellulosic biomass, such as wood, grass, stalks, etc, to be converted into ethanol. This approach to produce ethanol can reduce GHG emissions by some 86% over fossils fuels.

The broader field of nanotechnology research into converting biomass into biofuels is growing fast. For example, in 2007 the oil company BP has granted a research fund of \$500 million to the University of California, at Berkeley, and the University of Illinois, to explore the conversion of corn, plant material, algae and switch grass into fuel [18].

In the past, Berkeley had used nanotechnology in research for cost-effective solar panels [19]. But, the new Energy Biosciences Institute – EBI created at Berkeley will focus on fuel production with minimum environmental impacts and carbon emissions. A three pronged approach is being employed that begins with technologies for better crop production, improved feedstocks processing and development of new biofuels. The application of this approach aims at developing better feedstocks, breaking down plant material into sugars and their conversion to ethanol. Success along this pathway is expected to lead EBI to investigate the use of nanotechnology to develop other alternative fuels, such as butanol and renewable hydrocarbon fuels.

Another relevant application of nanotechnology is the use of nano-catalysts for the transesterification of fatty esters from vegetable oils or animal fats into biodiesel and glycerol

[20]. The nano-catalyst spheres replace the commonly used sodium methoxide. The spheres are loaded with acidic catalysts to react with the free fatty acids and basic catalysts to react with the oils. This approach eliminates several production steps of the conventional process, including acid neutralization, water washes and separations. All those steps dissolve the sodium methoxide catalyst so it can't be used again. In contrast, the catalytic nanospheres can be recovered and recycled. The overall result is a cheaper, simpler and leaner process. In summary, the process claims to be economical, recyclable, to react at mild temperatures and pressures, with both low and high FFA (free fatty acid) feedstock, producing cleaner biodiesel and cleaner glycerol, greatly reducing water consumption and environmental contaminants, and can be used in existing facilities.

8. Nanotech liquid additives

All previous presentation and discussion referred to solid nano-particles playing a catalytic role in the obtaining biofuels from algae, landfill methane and biomass. The following segments will examine the practical opportunities that exist for liquid nano-particles or droplets [21]. Consider multifunctional surface active liquid additives, whose lubricity enhancement is achieved via the formation of a monolayer over the surfaces in contact with additized fuel. [22] The treat rate for lubricity is determined by the adsorption saturation concentration. Speculate that the improved detergency and water co-solvency is obtained by the formation of nano emulsions. Also, postulate that the more complete combustion and consequent fuel efficiency increase is the result of the behaviour of nano droplets. These nano droplets result from the surfactant action of the additive in the fuel formulation and the presence of some water in all commercial fuel systems, usually due to evening condensation. Research by Wulff and colleagues [23] has shown that nano emulsions, which the authors call micro emulsions, with fuel (biofuel included most likely), water and surfactant are:

- Thermodynamically stable and
- Microscopically isotropic, and
- Nano-structured (thus, nano emulsions).

Their research concluded that:

- The use of these nano structures with fuel, water and surfactant is able to break the usual trade off between reduction of soot and NO_x emissions, by achieving them simultaneously, and
- For the same fuel consumption, higher efficiency is obtained.

Strey and collaborators filed patent applications for what they call micro-emulsions used as fuel [24]. The interpretation offered for the behaviour of stable diesel (and most likely biodiesel)-water-surfactant nano emulsions is as follows:

- The surfactant components –oleic acid and nitrogen containing compounds (amines) – dissolve readily in diesel (and possibly in biodiesel) fuel and bind water to it without stirring;
- The water droplets are as small as a nanometer across, helping stabilize the emulsion
- The result is a “liquid sponge”, can be stored indefinitely, like ordinary diesel fuel, without risk of phase separation
- This fuel formulation, when burned, results in the near-complete elimination of soot, and a reduction of up to 80% in nitrogen-oxide emissions
- The surfactant in the formulation also burns without creating emissions beyond water, carbon dioxide and nitrogen

9. Public concerns over nanotechnology: security, health and the environment

As with all new technologies, there may be cause to concern about impacts, such as on security, health and the environment. Nanotechnologies have been the subject of many assessments seeking to anticipate possible consequences of their deployment, to humans and to the environment. For instance, the Woodrow Wilson Center carried out a Nanotechnology project [25] from 2005. The project managers said that “manipulating materials at the atomic level can have astronomic repercussions, both positive and negative. The problem is no one really knows exactly what these effects may be.” This was the motivation for the Project on Emerging Nanotechnology at the Woodrow Wilson Center. Another initiative came from the International Risk Governance Council – IRGC’s Nanotechnology project [26]. Two expert workshops were held. The first in May 2005 focused on how to frame nanotechnology, its risks and its benefits. A distinction was made between the nanotechnologies of the so-called Frame One (passive or classical technology assessment) and Frame Two (active or the social desirability of innovation). The second, in January 2006, concentrated on identifying gaps in nanotechnology risk governance and developing recommendations for improved risk governance. A symposium on the subject took place in Zurich in July 2006. A presentation by Ortwin Renn[27] discussed the policy implications of Frame One, referred to in Fig. 4. The fact is that “most people have no clear associations when it comes to nanotech. They expect economic benefits but no revolutionary technological breakthroughs. Risks are often not explicitly mentioned but there is a concern for unforeseen side effects. There is a latent concern about industry, science and politics building a coalition against public interest. And one negative incident could have a major negative impact on public attitudes.”

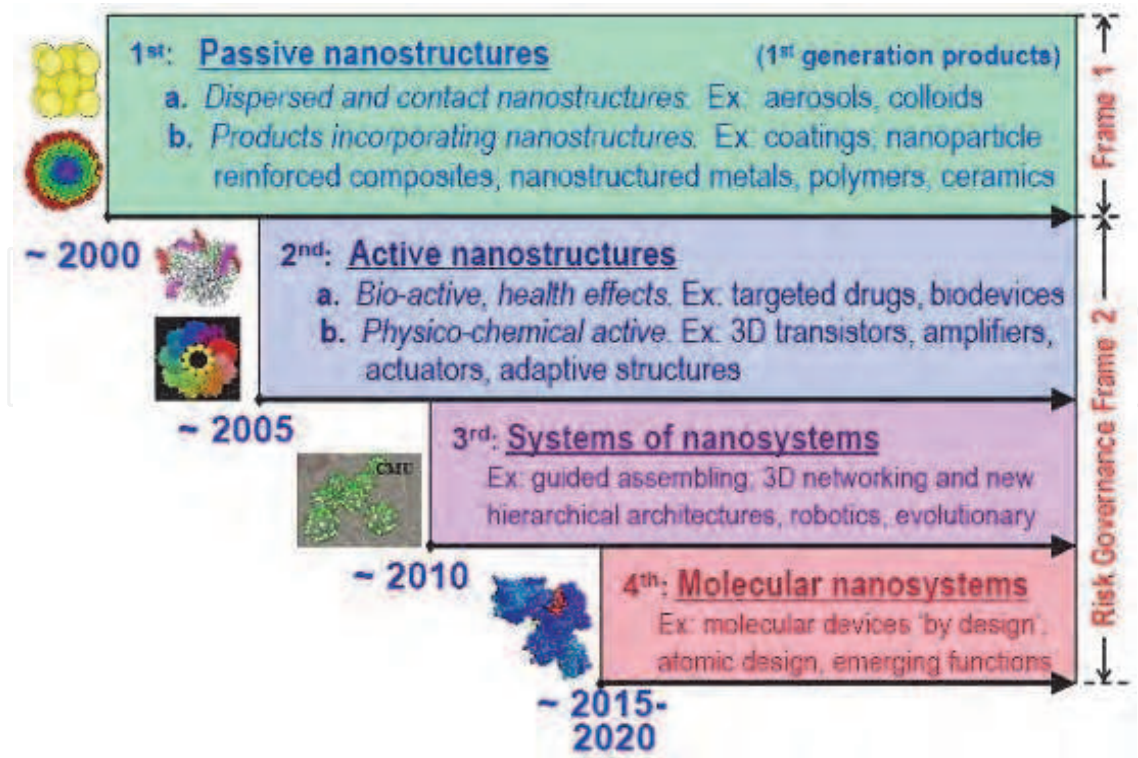


Fig. 4. Frames of reference of nanotechnology generations

The IRGC's Nanotechnology project concluded[28], among other things, that "communication about nanotechnology's benefits and risks should reflect the distinction between passive and active nano-materials and products, stressing that different approaches to managing risks are required for each. Care should also be taken to ensure that potential societal concerns about the possible impacts of Frame Two active nano-materials do not have the effect of unnecessarily increasing anxiety regarding Frame One products using only passive nanostructures." This is further expounded by Renn [29] as follows: "Frame One passive nanostructures are found, for example, in easy-to-clean surfaces, paints or in cosmetics. Frame Two refers to active nanostructures and molecular systems which could be able to interact actively or could be understood as evolutionary biosystems which change their properties in an autonomous process."

In reality, nanotechnologies are already facing challenges. Man-made nano-materials have been banned by the UK Soil Association from all its certified organic products. The 2008 annual report of the Soil Association of the UK contains the following statement [30]: "The Soil Association published the world's first standards banning nanotechnology. The risks of nanotechnology are still largely unknown, untested and unpredictable. Initial scientific studies show negative effects on living organisms, and three years ago scientists warned the Government that the release of nanoparticles should be 'avoided as far as possible'. There are many parallels with GM in the way nanotechnology is developing, particularly because commercial opportunities have run ahead of scientific understanding and regulatory control. What's more, while nano-substances are being rapidly introduced to the market, there is no official assessment process or labeling of the products - which is even worse than GM.

Health and beauty products that use nanoparticles are of concern for their potential toxicity if they get under the skin. Similar concerns exist regarding food and textiles. Definitely, more studies about health and environmental impacts are needed, to alleviate public concerns.

On the other hand, there is so much potential for nanotechnologies to do good, that Frame One and Two assessments should proceed as new applications evolve, including for instance more effective delivery of drugs to fight human and animal disease.

Fig. 5 showing a RNA nano-particle created by Peixuan Guo of Purdue University, illustrates the point. Strands are spliced together from two kinds of RNA - a scaffold and a hunter to find cancer cells. This nano-structure has proven effective against cancer growth in living mice as well as lab-grown human nasopharyngeal carcinoma and breast cancer cells.

10. Conclusions

Increasing demand for energy services in the decades ahead will require an expanding supply of liquid fuels, despite efforts at improving energy efficiency and diversification of energy systems, including growing use of electricity in transportation. Biofuels have a key role to play in this scenario. However, the future supply of biofuels must be of such a scale that non-food feedstocks and new technologies are intensively employed. Nanotechnologies are primary candidates to play a prominent role in this energy future. They will help bring to markets liquid biofuels, including renewable hydrocarbons, from algae, carbohydrates, fatty esters and biogas. Nanotechnologies will also play a role in augmenting the efficiency of using current and future liquid fuels, especially biofuels, by providing improved

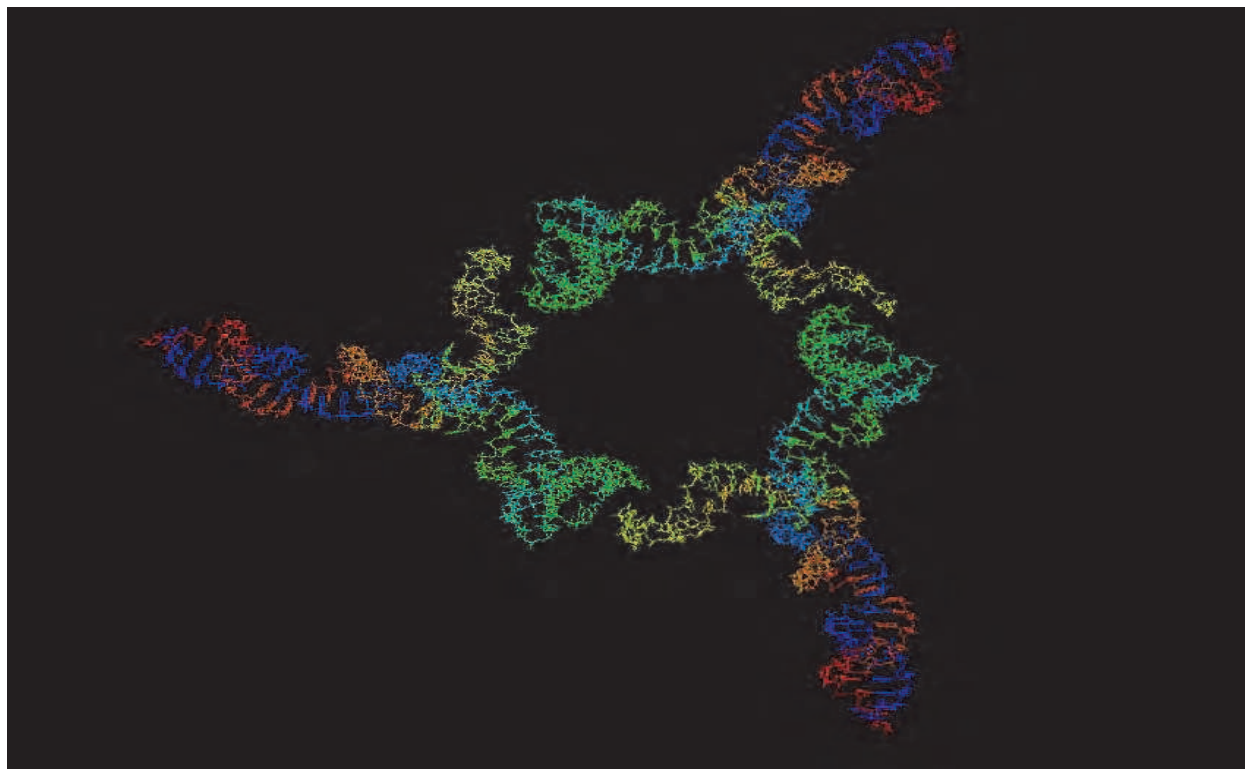


Fig. 5. RNA nano-particle created by Peixuan Guo, Purdue University [31]

combustion of nanodroplets. While there are risks in each and every new technology, the world today is much better equipped to assess risks and act accordingly, that it seems possible to advance nanotechnologies applied to biofuels, without jeopardizing security, public health or the environment. But, the reach of nanotechnologies is vast and goes much beyond biofuels and offer hopes in so many areas, including importantly, human health.

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Biofuel's Engineering Process Technology

Edited by Dr. Marco Aurelio Dos Santos Bernardes

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This book aspires to be a comprehensive summary of current biofuels issues and thereby contribute to the understanding of this important topic. Readers will find themes including biofuels development efforts, their implications for the food industry, current and future biofuels crops, the successful Brazilian ethanol program, insights of the first, second, third and fourth biofuel generations, advanced biofuel production techniques, related waste treatment, emissions and environmental impacts, water consumption, produced allergens and toxins. Additionally, the biofuel policy discussion is expected to be continuing in the foreseeable future and the reading of the biofuels features dealt with in this book, are recommended for anyone interested in understanding this diverse and developing theme.

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