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From conventional to more sustainable fuels Trends and needs in research in the thermodynamics area

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ABSTRACT

To provide the world's population with energy for mobility is a major challenge for the 21st century because of global warming and depletion of fossil fuels. Combustion engines will remain the most used propulsion mode during several decades; therefore both cleaner conventional fuels and alternative resources are required calling in turn for the development of new transformation and process pathways. IFPEN is strongly involved in this challenge, with R&D activities aiming at the improvement of catalysts performance or dealing with the process design for biofuels production. Simulation work in the field of thermodynamics is a key technology in this undertaking, like e.g. the "in silico" description of mechanisms at the atomic scale, or the development and use of predictive methods that allow to limit the experimental work. The present paper illustrates this ambition of providing more sustainable fuels through examples of IFPEN ongoing research activities dealing with thermodynamics.

1. Introduction

New global challenges have emerged since the end of the last century and most of them are going to reach an unprecedented importance in the decades to come. Amongst these challenges, climate and energy issues are very critical and so, they have given rise to many efforts for limiting their impacts and for providing new solutions in terms of renewable and low-carbon energies. Air pollution is another environmental concern that becomes increasingly critical, although it has been identified and addressed from an even longer time.

Demographic projections, combined with the rising standard of living in emerging countries, lead to predict a large increase in energy demand over the next decades, and most climate scenarios anticipate increasing CO_2 emissions with alarming effects on global warming and its consequences (AIE World Energy Outlook 2010).

Indeed, fossil fuels which enabled the development of the industrial civilization are largely responsible for CO_2 emissions. While carbon dioxide capture and storage (CCS) technologies have been developed and can be used for large emitting sources, mainly power plants and energy intensive industries, this technology is not adequate to combat the diffuse emissions from the transport sector. Moreover, fossil fuels are not renewable, so that they are undoubtedly going to their end (peak oil) with various but not too far time horizons, depending on their nature (oil < gas < coal). On the other hand, hydrocarbon fuels have very attractive properties, like their energy density and their relative ease of use and transportation, which make them well adapted for many applications.

2. The energy challenge for mobility

In the field of renewable energies, many improvements have been achieved, allowing the actual deployment of infrastructures in many countries, by taking advantage of their natural assets: wind, solar, geothermal, bio-resources, etc.

Moreover, the intrinsic performance of these energy production systems encountered a significant increase during the last decade, thanks to research and development, and more especially in highly developed countries, where ambitious goals had been defined by public authorities for environmental and for economic reasons (new green economy).

Nonetheless, renewable sources provide energy in two forms, electricity and heat, that are not (yet) easily usable for the purpose of mobility. Actually, even if fully-electric vehicles are already available for customers, their adoption on a large scale will take time for cost reasons and because charging infrastructures will need to be deployed. Moreover, historically, the demand for individual mobility has been correlated to the GDP (Fig. 1, from Schäfer [1]) and it is expected that this correlation persists, thus leading to an important increase of demand of mobility in emerging countries. However, for

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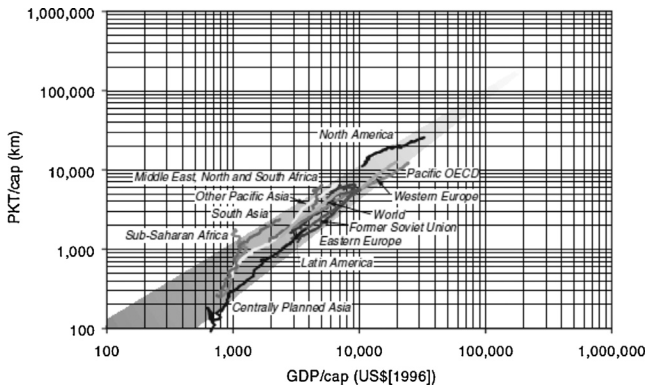

Fig. 1. Relationship between mobility (passenger-km per capita) and per capita GDP (Growth Domestic Product) for 11 world regions and the entire world from 1950 to 2000 [1].

most countries, conditions for alternative vehicle propulsion systems to reach a significant level will not be met in short to medium term, and more especially in the case of long-distance domestic travels.

As a consequence, for the requirements of individual mobility, thermal vehicles are going to remain the "global standard" for still a long time (at least until 2050), even in the case of strongly targeted policies for introducing alternative propulsion modes (Fig. 2). So, considering the constraints arising from the need for lowering CO_2 emissions and from the future decreasing availability of fossil fuels, a great deal of R&D efforts is needed to provide sustainable fuels for "conventional" combustion engines.

This challenge can be met through the use of innovative and efficient production routes and by using a greater range of available resources, including industrial and household wastes. Chemistry and process engineering are key-disciplines to achieve this, and important work is also required in the field of thermodynamics to provide relevant data, methods and tools that encompass the multiplicity of raw materials and transformation pathways, as illustrated in Fig. 2.

Focusing on thermodynamics, current research activities of IFPEN concerning innovative fuels for internal combustion engines are exposed hereafter. They illustrate complementary approaches to accelerate the development of cleaner and more sustainable fuels.

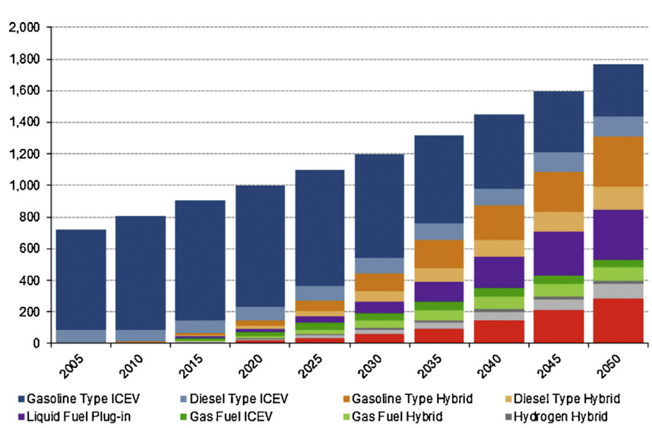

Fig. 2. Anticipated repartition of propulsion modes for road vehicles – regulated scenario (Global Transport Scenarios 2050 – World Energy Council 2011).

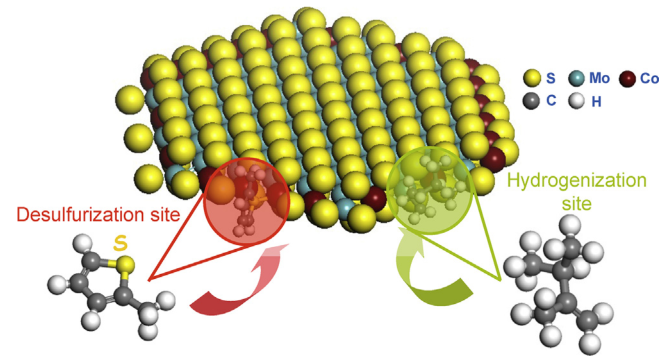

Fig. 3. Modelling at the atomic scale of a versatile catalyzer based on hexagonal nano-cristallites of CoMoS – depicting active sites.

3. Improving cleanliness of conventional fuels

Cleaner fuels are required to fulfil environmental regulations that aim at limiting polluting emissions by combustion engines. This requirement, which concerns both gasoline and diesel fuel, leads to improve refining processes and comes along with the need for cost reduction.

The hydrotreatment (HDT) process is the one involved for removing sulfur, one of the major pollutants under constraint, and its efficiency in that field greatly depends on the performance of catalysts. The activity and the selectivity of the latter are key properties that must be improved in that respect.

To achieve this, computer chemistry has become an essential tool which allows a huge acceleration of development through the use of in silico pre-screening. As depicted in Fig. 3 (from Krebs et al. [2]), molecular modelling allows to simulate the mechanisms involved in the catalytic activity at the atomic scale. It helps to understand and quantify the interaction of some sites with the feedstock components. The given example of a catalyst cristallite, illustrates the fact that different active sites co-exist on it, with different functionalities according to the local atomic neighbourhood. Some edges are desulfurization sites (desired reaction) while others host the reaction of hydrogenization (reaction to avoid).

These computer calculations allow to anticipate the performance of catalytic materials, for instance their versatility, as a consequence of their composition and nano-structure. They thus allow us to focus more quickly on promising materials and to limit accordingly the amount of experimental testing. By doing so, molecular modelling has a full part to play for the design of catalysts, with a great ability for reducing the time of development. Beyond the interest for considering more innovative solutions with limited expenses and delays, the replacement of experimental screening tests by computer simulations is also advantageous when experimental conditions are hazardous or difficult to achieve.

4. Developing biofuels

The use of biofuels for transportation of persons and goods is a means for reducing the carbon footprint of mobility. Indeed, these fuels are considered neutral according to the complete carbon cycle since the growth of biomass consumes CO_2 from the atmosphere. This is the reason why they gain interest in many countries, especially those disposing of suitable resources. The 1st generation is already in use for gasoline and diesel engines, with fuel solutions respectively based on ethanol from sugar and on fatty acid esters. However, even used as a mix with conventional fossil fuels, sufficient amounts of these bio-products cannot be produced due to the limited amount of available biomass. Last but not least, competition with food markets is still an open question.