FAST CARD Newsletter

FASTCARD - FAST industrialisation by CAtalysts Research and Development

No. 4 – September 2015

FASTCARD

FASTCARD Project Meeting 25-26 June 2015 in Brussels, Belgium

The EU FP7-funded project FASTCARD had its 18M Project Review and its fourth General Assembly with the Project Officer and the Project Technical Advisor present. 42 delegates from 9 different countries participated in the meeting which took place in Brussels on 25-26 June 2015. Further results were reported and discussed on the first day in different working group sessions.

On the second day, the official Project Review took place. Representatives from Johnson Matthey and REPSOL presented a status of the gas and liquid value chains relative to the overall goals of the project, as introductions to the presentations from the work package leaders. In the following, a few significant results from the work packages are reported.

Above: Group photo

Right:
Coordinator Duncan Akporiaye (left) and Project Technical Advisor Joginder Fagura (right)

Within **WP1** (hydrocarbon reforming), further progress in catalyst development was possible. Fig. 1 shows a bimetallic Fe-Ni/$MgAl_2O_4$ catalyst, where an Fe-Ni alloy is formed at higher temperatures. The Fe-Ni alloy is the active phase while Fe partially segregates from the alloy forming FeO_x. This is beneficial as it reduces the surface carbon accumulation through interaction with FeO_x lattice oxygen, producing CO.

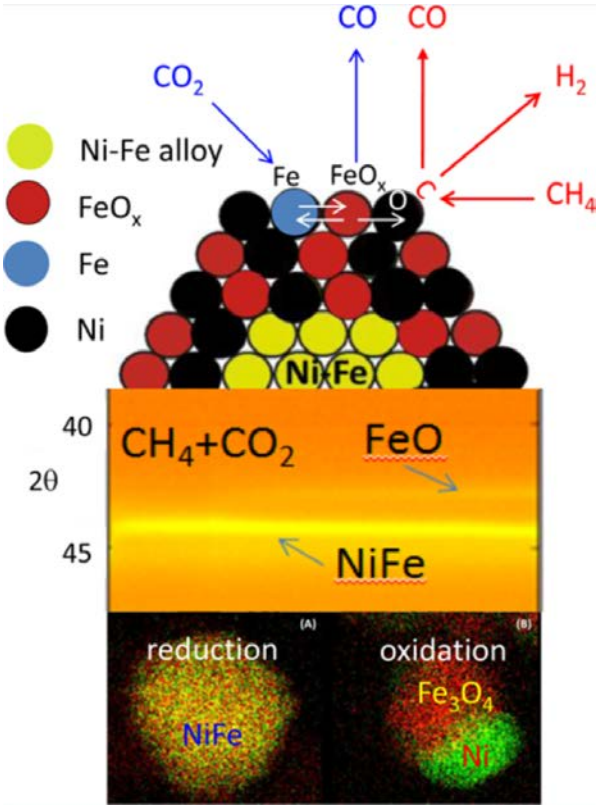

Figure 1: Fe-Ni/MgAl2O4 catalyst for methane dry reforming (S.A. Theofanidis, V.V. Galvita, H. Poelman, G.B. Marin, ACS Catal. 5 (2015) 3028).

Within **WP2** (Fischer Tropsch synthesis), DFT calculations have been performed for molecular adsorption energies for the most stable configuration of Fe_3C (001). Further understanding of the deactivation mechanisms of the State of the Art catalyst has been achieved using TEM, STEM-EDX and pyrolysis GC-MS. Modifications to the "wet" synthesis method of the iron carbide phase Fe_5C_2 have resulted in a material with comparable FT activity to the State of the Art catalyst, despite a significantly lower Fe content (4.9wt% vs. 78wt%). The selectivity towards CO_2 was also much improved.

Within **WP3** (hydrotreating of pyrolysis oils), it could be shown that Mo-modification resulted in a higher stability of the Picula catalyst. By leaving out the Co from CoMo catalysts, the removal of oxygen from phenolics could be improved and more (hydrogen) efficient.

Within **WP4** (co-FCC of conventional feeds and biooil), a phenomenological model for the co-processing of HDO bio-oil (low oxygen content) was built. For the microkinetic model construction, the phenol molecule was considered as first model compound and the Reaction Network Generation Program is running. MCM-22 was found to be a very promising catalyst with regard to hydrothermal stability and acidity retention during deactivation. Hydrotreated pyrolysis oils have been characterized in detail by 2D gas chromatography. In addition, ^{31}P NMR allows for the quantification of oxygenates by using an internal standard.

Within the important cross-linking work packages **WP5** (nanoscale probing and modelling) and **WP6** (conceptual process design and energy efficiency), a lot of alignment work has been done in several joint working sessions together with the other work packages. Within WP5, a template for information exchange was created. For bio-feed modelling and reconstruction, an evident correlation between overall oxygen content and concentration of sugar/lignin-derived compounds was found. Comprehensive reaction and reactor modelling going from the microkinetic model via the pellet scale to the reactor model has started. Within WP6, modelling of a base case for each value chain and economic evaluations were performed.

The following pages introduce 4 more partners in greater detail.

ENI

Brief description of the organisation and of the department contributing to the execution of the project

Eni is an integrated energy company employing more than 84,000 people in 83 Countries in the world. It operates in oil and gas exploration, production, transportation and marketing, in petrochemicals, oilfield service and engineering.
Istituto eni-Donegani will be involved in this project. It is one of the most prestigious industrial chemistry research centres in Italy. Owned by eni since 1992, its historical background is related to industrial chemistry research. Today hires about 100 researchers.

Role in project and previous experience relevant to the task

Fischer Tropsch (FT) section process design including separation/recycle/upgrading +CAPEX/OPEX.
Eni has developed a proprietary FT technology, based on Cobalt catalyst.
Eni is interested in participating at the Fischer Tropsch work package, in terms of engineering approach, as process assessment, and in particular in the FT synthesis section with iron catalyst.

Person assigned to the project

Alessandra d'Arminio Monforte is a process engineer. She has been at the Eni - Process technologies Department -Research Center for Non-Conventional Energy Istituto eni Donegani since 1980. With more than 30 years of experience, her main activities concerns the modelling, simulation and optimization of processes. In the last years about Biomass to Liquids they have simulated the whole process from gasification to Fischer Tropsch synthesis, and they have calculated the economic evaluation to build an industrial BtL plant. She took part of Chrisgas, an European project with the objective to study the production for synthetic vehicle fuels.

Letizia Bua is a process engineer. She has been at the Eni - Process technologies Department -Research Center for Non-Conventional Energy Istituto Eni Donegani since 2000. Her main recent research interests refer to biomass gasification and conversion to fuels. Project manager of the research project Biomass to Liquids (BTL) since 2007. Scientific person in charge of the CHRISGAS project.

Irene Rapone is industrial chemist. She has been at the Eni - Process technologies Department -Research Center for Non-Conventional Energy Istituto eni Donegani since 2008. In these years of work, she has been focused on simulation and economic evaluation of Biomass to Liquids (BtL) process. The principal steps of this process have been simulated and evaluated: biomass gasification, water gas shift (WGS) and reformer section, Rectisol® Unit and Fischer Tropsch synthesis.

Special Equipment available for the project

The process simulator CheOpe (Chemical Operation), eni's proprietary software, and the commercial software, Aspen Process Economic Analyzer V7.3.1, for economic evaluation.

References (publications) and patents related to the project

1. Co-authors, d'Arminio Monforte A. and Bua L., in the 2nd chapter of:"Greener Fischer-Tropsch Process for Fuels and Feedstocks-Fundamental Chemical, Industrial, Economic and Environmental Aspects- Edited by P.M.Maitlis and Arno de Klerk. Wiley Vch Verlag Gmbh (feb 2013)
2. Rapone I., d'Arminio Monforte A., Chiodini A., Bua L., Carnelli L. "Acid gas removal from syngas with Rectisol process in a BtL plant". Proceedings of ANQUE´s International Congress of Chemical Engineering, Seville, June 2012.
3. Bua L., Chiodini A., Rapone I, Carnelli L., La Palombara A. "Gasification: an Integrated Approach". Proceedings of the European Combustion Meeting, Cardiff, June 2011
4. Rapone I., Bagatin R., Bua L., d'Arminio Monforte A., Carnelli L. "Kinetic modeling of biomass gasification process". Proceedings of the 19th European Biomass Conference and Exhibition, Berlin, June 2011.

Patents: Bua L., Chiodini A., Carnelli L. MI2010A001244 (06.07.2010); WO 2012/004001 A2 (12.01.2012).

REPSOL

Brief description of the organisation and of the department contributing to the execution of the project

REPSOL is an international integrated energy company, operating in more than 30 countries, with more than 24,000 employees all over the World. REPSOL leads the Spanish oil market and is one of the largest private oil companies of the world. The company explores, develops and produces crude oil and natural gas, and performs other oil related activities as refining, production and retail of oil products, oil derivatives, petrochemicals, etc. Besides the oil exploration and production, REPSOL's technology activities include both the research and development of new products and production processes. REPSOL has been working in the field of biofuels production during the last ten years, in different routes for biofuel production (etherification, vegetable oil transesterification, co-processing of renewable feedstock in conventional petroleum refineries, biomass pyrolysis, among others). REPSOL is fully equipped with the necessary bench scale and pilot plant equipment to simulate the main biofuels production processes and laboratory.

Role in project and previous experience relevant to the task

REPSOL will participate in the WP's 4 and 7, mainly involved in the validation and demonstration of the upscale development of the most promising catalyst at pilot plant scale.

Person assigned to the project

Pedro Gómez Martín, Degree in Chemistry (1981) and PhD in Chemical Engineering (1986) at the University of Málaga. He has been working as Researcher and Consultant in Catalytic Process for 20 years. Managed research and development projects on refining processes: hydrogenation, catalytic reforming, Hydrocraking, biofuels, Methane conversion, catalyst development, and also specialized technical support and optimization studies to industrial units.

Rubén Miravalles Gutiérrez, Degree in Chemistry and Master Degree in Refining, Marketing an Gas, Senior Technologist and FCC Project Leader. He has been as Researcher in REPSOL's R&D Refining Department for 10 years, mainly involved in FCC and Biofuels production processes.

Rebeca Yuste Pilar, Degree in Chemical Engineering (2003) at University Rey Juan Carlos, Madrid. She joined Repsol in 2006 as Reseacher in R&D Refining Department. She has worked as Refining Technologist in FCC and biofuels production processes, and also specialized in technical support and optimization studies to industrial units.

Previous participation in other projects related to this project

Repsol has participated in ACENET-HECABIO project, which objective was to explore new developments in heterogeneous catalysis to be applied in catalytic pyrolysis of biomass to improve bio-oil quality for further upgrading into existing refining processes.
Repsol has also participated in CENIT-BIODIESEL project, which objective was to explore new routes of biofuel production through co-processing of triglyceride-based materials in existing refinery units

Special Equipment available for the project

REPSOL is equipped with the necessary bench scale and pilot plants to simulate the upgrading of bio-oil to biofuels through co-processing in a FCC unit. REPSOL R&D facilities include laboratories for complete characterization of catalysts, feedstock and products.

References (publications) and patents related to the project

Melero, J. A.; Clavero, M. M.; Calleja, G.; García, A.; Miravalles, R.; Galindo, T., Production of Biofuels via the Catalytic Cracking of Mixtures of Crude Vegetable Oils and Nonedible Animal Fats with Vacuum Gas Oil. Energy and Fuels 2010, 24, 707-717.

Process Design Center BV

Brief description of the organisation and of the department contributing to the execution of the project

Process Design Center (PDC) is a leading technology provider in structured conceptual design methodologies. PDC´s proprietary expert system PROSYN and process synthesis technology has been used in numerous industrial projects reaching capital & operating cost savings up to 50 % compared to existing state-of-the-art designs.

Role in project and previous experience relevant to the task

PDC's task encompasses the conceptual design aspects, techno-economic evaluation and an environmental assessment focussing on the overall energy efficiency. PDC provides such services to the (petro)chemical and bio-based process industries.

Person assigned to the project

Raf Roelant, Dr. ir., is a consultant working at PDC since 2011. He holds a PhD from Ghent University. He has participated in the EU projects EUROBIOREF and CARENA, where he performed conceptual process design.

Wei Zhao, Dr. ir. , is a consultant working at PDC since 2011. He holds a PhD from the Institute of Process Engineering, Chinese Academy of Sciences, Beijing. He performed post-doctoral research at the University of Twente in Lignocellulose biomass conversion for fuel production. He has performed conceptual design and techno-economic evaluation in the EU project EUROBIOREF.

Hans Keuken, Ir. , is managing director at PDC since 1987. He studied at the University of Amsterdam and Delft University of Technology. Conceptual design and Energy Efficiency. He is a member of the fuel standardization committee. He has participated to the following EU projects CACHET, EUROBIOREF, CARENA.

Previous participation in other projects related to this project

INSERT (FP6) reactive distillation 2004 – 2007
NEPUMUC (FP6) microreactors 2005 – 2008
CACHET (FP6) CO2 precombustion capture 2006 – 2009
F3 Factory (FP7) flexible, fast and future production processes 2009 – 2013
EuroBioRef (FP7) integrated biorefinery 2010 – 2014
CAPSOL CO2 post-combustion capture 2011 – 2014
CARENA (FP7) catalytic membrane reactors 2011 – 2015

Special Equipment available for the project

PDC uses computer aided process engineering tools.

References (publications) and patents related to the project

1. Hans Keuken and Hendrik Cornelis de Jager, "Environmentally improved motor fuels", WO 2009/096788 A1, 06-08-2009.
2. Herman De Meyer and Johannes Sijben, "Catalyst and Method for Preparing Aromatic Carboxylic Acids", WO 2006/068471 A1, 20-12-2005.
3. Johannes Sijben and Herman De Meyer, "Process for Preparing Aromatic Carboxylic Acids", WO 2006/068472 A1, 20-12-2005.
4. Johannes Sijben, "Motor fuel based on ethanol and gasoline", WO 2006/137725 A1, 28-12-2006

University of Stuttgart (USTUTT)

Brief description of the organisation and of the department contributing to the execution of the project

The University of Stuttgart is a member of the so called TU9, which is the network of leading Institutes of Technology in Germany. The Institute of Chemical Technology has a staff of about 30 people, including about 15 PhD students. Its research is devoted to porous materials and reaction engineering. Over many decades the institute has been leading in tailoring and optimizing micro- and mesoporous materials such as zeolites or metal-organic frameworks for applications in industrial adsorption and catalysis.

Role in project and previous experience relevant to the task

USTUTT will mainly be involved in downscaling, zeolite preparation and testing as well as in situ characterization for Co-FCC (WP5). The Institute of Chemical Technology has a long-term expertise in the design, characterization and use of nanoporous materials (especially zeolites). With Elias Klemm being CEO of the European Network ENMIX, USTUTT will also be responsible for dissemination and exploitation (WP9).

Person assigned to the project

Elias Klemm, Prof. Dr.-Ing., was appointed full professor of Heterogeneous Catalysis and Chemical Technology at the University of Stuttgart in 2009. Prior, he was 5 years full professor of Chemical Technology at the University of Chemnitz. He worked for 2 years as Process Engineer at Degussa AG in Hanau in the field of Chemical Micro Process Engineering. From 1995 to 2001 he was leader of a research group at the University of Erlangen-Nuremberg. Elias Klemm studied chemical engineering at the University of Erlangen-Nuremberg and received his Pd.D. in the field of heterogeneous catalysis in 1995. He received the Jochen-Block-Award of the Dechema Subject Division Catalysis and the Carl-Zerbe-Award of the German Society for Petroleum and Coal Science and Technology (DGMK).

Michael Hunger, Prof. Dr., received his PhD degree in Experimental Physics in 1984 at the University of Leipzig. In 1992, he changed to the University of Stuttgart, Institute of Chemical Technology, where he became the leader of the solid-state NMR group. Since 1999, Michael Hunger is professor for Chemical Technology. His research topics include solid-state NMR studies on solid catalysts, spectroscopic investigations of the mechanisms of heterogeneously catalyzed reactions, and of transport processes in porous solids as well as the development and application of novel in situ techniques utilized for solid-state NMR spectroscopic studies in the field of heterogeneous catalysis.

Yvonne Traa, PD Dr., received both her chemistry degree and PhD under Prof. J. Weitkamp at the University of Stuttgart. She also conducted research at the Universities of Cape Town (C.T. O´Connor) and Cardiff (G.J. Hutchings) and at Worcester Polytechnic Institute (R.W. Thompson). In 2008, she completed her Habilitation at the University of Stuttgart. Her research interests focus on heterogeneous catalysis, main interests being direct coal liquefaction and zeolite catalysis.

Moritz Heuchel, Ph.D. student, holds a master degree of chemistry of the University of Stuttgart.

Swen Lang, Ph.D. student, holds a master degree of chemistry of the University of Stuttgart.

Previous participation in other projects related to this project

USTUTT was a partner in the EU projects TROCAT, INSIDEPORES, ToKCata, NEXT-GTL and COPIRIDE.

Special Equipment available for the project

Various in-situ characterization methods are available like solid state NMR, XRD, IR (ATR or transmission).

References (publications) and patents related to the project

1. “Successive steps of hydration and dehydration of silicoaluminophosphates H-SAPO-34 and H-SAPO-37 investigated by in situ CF MAS NMR spectroscopy”, A. Buchholz, W. Wang, A. Arnold, M. Xu, M. Hunger, Micropor. Mesopor. Mater. 57 (2003) 157-168.
2. “Deactivation Behavior of Alkali-Metal Zeolites in the Dehydration of Lactic Acid to Acrylic Acid”, G. Näfe, M.-A. López-Martínez, M. Dyballa, M. Hunger, Y. Traa, Th. Hirth, E. Klemm, J. Catal. 329 (2015) 413-424.