

**International Symposium on
Hydrocarbon Catalysis and Catalytic Engineering:
Present Status and Perspectives**

in honor of Professor Iacovos A. Vasalos



June 28-30, 2007

Sifnos, Greece

Photo: Sifnos Kastro, Church of Eptamartiros

**International Symposium on
Hydrocarbon Catalysis and Catalytic Engineering:
Present Status and Perspectives**

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**Cultural Center Artemonas
Sifnos, Greece**

Organizing Committee

A.A. Lemonidou, AUTH

A.A. Lappas, CERTH/CPERI

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Under the auspices of

***General Secretariat of Research and Technology (GSRT) and
Sifnos' island Major***

Symposium Programme

Thursday June 28

21.00- Welcome Reception

Friday, June 29

8.00-8.45 Registration

8.45-9.00 Symposium opening

9.00-9.30 **A. A. Lemonidou** and **A. A. Lappas**
Prof. I.A.Vasalos' career and achievements

Chairman: Prof. Michael Stoukides, Aristotle University of Thessaloniki, GR

9.30-10.15 Plenary: Prof. **Adel Sarofim**, University of Utah, USA
"Multiscalar Simulation of the Combustion of Real Fuels:
Application to Fires and Explosions"

10.15 -10.30 Coffee Break

Session I Hydrogen and Fuel Cells

Chairman: Prof. Johannes Lercher, Technical University of Munich, DE

10.30-11.00 Dr. **Claude Mirodatos**, IRCELYON, FR
"New Trends in Catalytic Processes for Methane Conversion"

11.00-11.30 Prof. **Hubert Veringa**, University of Twente, NL
"Hydrogen Production out of Biomass"

11.30-12.00 Prof. **Costas Vayenas**, University of Patras, GR
"Syngas and Hydrogen: Fuel Cell Opportunities and Challenges"

12.00-12.30 Discussion

12.30-13.30 Lunch

Session II Environmental Catalysis

Chairman: Prof. Xenophon Verykios, University of Patras, GR

- 13.30-14.00 Prof. **Michael Amiridis**, University of South Carolina, USA
"Atomic Scale Design and Construction of Supported Bimetallic Catalysts by the Use of etal- dendrimer Nanocomposites"
- 14.00-14.30 Prof. **Maria Flytzani-Stephanopoulos**, Tufts University, USA
"Tailoring Gold and Silver Catalysts for some Environmental Catalysis Applications"
- 14.30-15.00 Prof. **Gabriele Centi**, University of Messina, IT
"Behavior of SO_x-traps derived from ternary Cu/Mg/Al hydrotalcite materials"
- 15.00-15.30 Discussion
- 15.30-16.00 Coffee Break

Session III Hydrocarbon Conversion

Chairman: Prof. Manfred Baerns, Leibniz Insitute for Catalysis, DE

- 16.00-16.30 Prof. **Enrique Iglesia**, University of California, Berkeley, USA
"Structural Requirements and Pathways in Methane Reactions Catalyzed by Supported Metal Clusters"
- 16.30-17.00 Prof. **Fabrizio Cavani**, University of Bologna, IT
"Oxidative Dehydrogenation of Ethane and Propane: How Far from Commercial Implementation?"
- 17.00-17.30 Dr. **Carel Pouwels**, Albemarle, NL
"Catalyst Accessibility Effects on the Conversion of Heavy Hydrocarbons"
- 17.30-18.0 Discussion
- 21.00 - Dinner by the sea (Vathi)

Saturday, June 30

Chairman Prof. Nikos Papayannakos, National Technical University of Athens, GR

9.15-10.00 Plenary: Dr. **Jan Campbell**, BP, UK
"Biofuels – A Manufacturing Perspective"

Session IV Future Fuels

Chairman Dr. George Hoekstra, BP, USA

10.00-10.30 Dr. **Cheryl Joyal**, BP, USA
"Pilot Plant Evaluation of FCCU Catalyst Technology
and Use of Data for Commercial Catalyst Applications"

10.30-11.00 Prof. **Julian Ross**, University of Limerick, IE
"Has Biomass a Place in the Energy Spectrum?"

11.00-11.30 Coffee Break

11.30-12.00 Dr. **Paul O' Connor**, BIOeCON, NL
"Sustainable Fuels, Chemicals and Energy from Biomass
Recent Developments"

12.00-12.30 Prof. **Athanasios Konstandopoulos**, CPERI/AUTh, GR
"Hydrogen Production in Solar Reactors"

12.30-13.00 Prof. **Emanuel Kakaras**, National Technical University of Athens, GR
"CO₂ Emissions Strategy for Cleaner Environment-
Zero Emissions Power Plants"

13.00-13.30 Discussion

13.30-14.00 Prof. **I.A. Vasalos**, Closing Remarks

21.00 - Dinner by the sea (Kamares)

Abstracts of Presentations

Multiscalar Simulation of the Combustion of Real Fuels: Application to Fires and Explosions

Adel F. Sarofim and Hongzhi Zhang
Department of Chemical Engineering
University of Utah, Salt Lake City, UT

Research at the University of Utah on the simulation of accidental fires and explosions for the past ten years has been motivated by the U.S. Department of Energy's nuclear stockpile stewardship program. The ultimate goal of the program is to integrate large computer models from various disciplines into single, comprehensive models necessary to solve critical problems. The test problem selected by the University of Utah is the simulation of the explosion of containers filled with high energy materials immersed in a pool fire. Progress of the team in predicting the heat transfer to pulsating fires, the heat transfer to an immersed container filled with explosives, the time to explosion, and the intensity of the explosion will be summarized. One practical spin off of the program has been in determining ways of configuring the explosive to reduce the threat of detonation during transport, based on both experimental and theoretical studies. But the current program has an empirical formulation for soot formation. Progress being made to replace this empirical formulation with more rigorous calculations will be summarized, following the sequence:

- use of ^{13}C NMR to characterize jet fuels,
- development of surrogate fuels composed of a mixture of components with known kinetics that match the major functional groups in the JP fuel,
- construction of reaction mechanisms for the mixture of components consisting of hundreds of species and thousands of elementary reactions,
- estimation of reaction pathways and kinetics of elementary reaction steps using quantum mechanical calculations coupled to transition state theory,
- reduction of the mechanisms for use in CFD codes,
- implementation of the solution to real problems.

Impressive progress has been made towards developing the multiscalar models from the atomistic sub-nanometer scale to the systems of tens of meters and predictive simulation is finding increasing applications to-day. However, uncertainties in the predictions are such that simulation remains a complement rather than a replacement of experiment. Furthermore, experiments are needed, if for no other reason, because discovery and invention are often their serendipitous spin-offs.

New trends in catalytic processes for methane conversion

C. Mirodatos

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Further developments in catalytic processes for methane conversion are boosted by new potential applications such as hydrogen production for feeding fuel cells, needs for process intensification and miniaturization adapted to remote and/or domestic uses, perspective to produce higher hydrocarbons for chemicals syntheses. Some of these trends will be surveyed such as the non stationary methane cracking and the partial oxidation over various noble metal/CeO₂ doped catalysts.

The two-step cracking/regeneration of methane is investigated by DRIFT spectroscopy and a kinetic model is proposed. The production of H₂ is improved by the capacity of the cerium oxide to store carbonaceous surface species thanks to the tight interaction between the noble metal and the support. Doping the ceria with lanthanide oxides and replacing Pt by more efficient and eventually better dispersed metals like Rh and Ir lead also to significant improvements in the process performance.

The partial oxidation of methane under transient conditions is also investigated over doped ceria-zirconia mixed oxides and a kinetic model presented.

Finally, new reactor concepts such as micro-structured or membrane systems adapted to high temperature methane activation are briefly described, underlining their advantages and drawbacks.

Hydrogen production out of biomass

H.J. Veringa

University of Twente, The Netherlands

Advanced uses of Biomass as a renewable fuel comprise co-firing in large scale utility boilers, either by direct injection along with the coal, or by applying pre-gasification to inject the product gas into the boiler, combustion to add heat to the steam raising units in large scale power plants, stand alone gasification for direct electricity production to more advanced use of the biomass as a source for fuels.

In this latter respect, the present emphasis is on second-generation syngas derived fuels like FT oil, SNG, methanol and, possibly in the more distant future, also hydrogen. Obviously there is no preferred technology choice as the quality and availability of the biomass determines to a large extent the best way to produce fuels along with local conditions. As an example in Netherlands, the high availability of biogenic waste results in large potential for co-firing whereas the dense natural gas grid stimulates input of biomass for SNG. In Finland there is no extensive gas infrastructure but a high availability of pulp and paper waste that makes production of liquid fuels more appropriate. Contrary to fossil fuels the disperse availability is one of the main concerns of implementation of biomass. When using biomass with only little pre-treatment like drying and chipping, use of it will preferentially be at disperse locations in plants of moderate sizes. When a pre-treatment leads to significant reduction of duties connected to transportation, more centralized final conversion can be considered. Pyrolysis is in this respect an attractive pre-treatment technology as it results in a liquid product with substantially enhanced energy density compared to raw biomass. This pre-treatment technology opens also the way to decentralized collection and pretreatment of biomass combined with centralized secondary conversion to for instance hydrogen. In such a way the pyrolysis oil replaces crude oil inputs at refinery sites, but can also be used as a feedstock for syngas production in large-scale production of bulk chemicals.

The TCCB group at Twente University started some three years ago new research lines to hydrogen production out of biomass, one based on supercritical gasification with wet biomass a feedstock, and two based on high temperature conversion, on the one hand using a reforming catalysts and on the other hand cheap iron oxide with the pyrolysis oil as feedstock.

In this presentation these three techniques will be explained and results obtained this far will be reported. Also the application areas for such techniques and shortcomings or further R&D directions will be outlined.

Syngas and Hydrogen: Fuel Cell Opportunities and Challenges

F.M. Sapountzi, M.N. Tsampas and **C.G. Vayenas**

Department of Chemical Engineering, University of Patras, GR-26504 Patras, Greece

PEM fuel cells are promising key elements of the H₂ economy but CO poisoning of the anode remains an important technological obstacle. In this work the treatment of methanol reformat, containing up to 2500 ppm CO, by the anode of a PEM fuel cell, operating as a preferential oxidation (PROX) reactor, was investigated in order to examine the possibility of electrochemically promoting the water-gas-shift (WGS) reaction and thus making the gas mixture suitable for anodic oxidation. It was found that the electrochemical promotion effect plays a significant role in a normal fuel cell operation (air at the cathode) but not in a hydrogen pumping operation (H₂ at the cathode). This implies that the role of oxygen crossover in the electropromotion (EP) of the WGS reaction and in the CO oxidation is vital. During fuel cell operation, the increase in the rate of CO consumption over a Pt/C anode is 2.5 times larger than the electrochemical rate, 1/2F of CO consumption, while for oxygen bleeding conditions (fuel mixture + 1%O₂ at the anode) the increase is up to 5 times larger than 1/2F, i.e. the Faradaic efficiency is up to 5. This shows that the catalytic properties of the Pt anode are significantly modified by varying catalyst potential and by the extent of O₂ crossover.

The effect of temperature, gas composition, membrane thickness and Pt anode alloying with Cu was studied. It was found that the rate of CO consumption is significantly enhanced by increasing T, p_{H₂} and increasing O₂ crossover rate. Also the Faradaic efficiency reaches even higher values (up to 9) when using PtCu/C anodes. However, the Faradaic efficiency drops in general below 100% at high current densities and CO conversion levels.

Atomic Scale Design and Construction of Supported Bimetallic Catalysts by the Use of etal- dendrimer Nanocomposites

Michael Amiridis

University of South Carolina, USA

Conventional methods used for the preparation of supported catalysts involve the deposition of the metal precursors from solutions and often provide limited control over the structure and composition of the resulting materials. In recent years, alternative synthetic routes based on the use of templating polymers capable of stabilizing nanoparticles of various metals in solutions have been proposed. Among such templates, poly (amidoamine) (PAMAM) dendrimers have attracted growing interest due to the potential for >a tight control of the average metal particle size and distribution in the resulting catalysts.

The preparation of metal-dendrimer nanocomposites bares similarities to the synthesis of colloids and involves the complexation of metal cations with interior tertiary amine or amide groups of the dendrimers, followed by a reduction step during which the formation of metal nanoparticles, encapsulated within the dendrimer structure, is anticipated. However, the absence in the literature of any direct structural evidence showing the formation of such dendrimer-encapsulated nanoparticles, raises questions about the proposed templating mechanism. Furthermore, little is known about the delivery of metal-dendrimer nanocomposited onto inorganic oxide surfaces, a necessary step for the synthesis of heterogeneous catalysts.

Our goal is to develop a better molecular-level understanding of the processes taking place during the synthesis of (Pt, Rh)-PAMAM catalysts. EXAFS results indicate that the hydrolysis of H_2PtCl_6 and RhCl_3 precursors leads to the formation of $[\text{PtCl}_3(\text{H}_2\text{O})_3]^+$ and $[\text{RhCl}_3(\text{H}_2\text{O})_3]$ species, respectively. These species can strongly interact with amine/amide groups of the dendrimer as evidenced by the replacement of chlorine ligands from the first coordination shell of each metal by nitrogen atoms from the dendrimer interior. The formation of small Pt clusters incorporating on average no more than 4 atoms was observed when the Pt^{4+} -G4OH complex was treated with H_2 for several hours. Similarly, the formation of small Rh clusters with a nuclearity of 3 was observed following treatment of the Rh^{3+} -G4OH complex with NaBH_4 . The formation of larger Pt nanoparticles, with an average diameter of approximately 1nm, was finally observed after the deposition and drying of the H_2 -treated Pt^{4+} -G4OH nanocomposites on a $\gamma\text{-Al}_2\text{O}_3$ surface, suggesting that the formation of such nanoparticles may be related to the collapse of the dendrimer structure. In contrast, deposition of the NaBH_4 -treated Rh^{3+} -G4OH nanocomposites on a ZrO_2 surface does not lead to any substantial modifications of the Rh coordination environment. Some sintering of the metal particles was observed with both systems following thermal treatments in O_2/H_2 , indicating that the metal nanoparticles have relatively high mobility on the catalyst surface. However, the degree of such sintering in the case of Rh was minimal, leading to highly dispersed Rh/ ZrO_2 catalysts with extremely narrow distributions of Rh particles. These results provide for the first time evidence that highly dispersed catalysts with very narrow distribution of metal particles can be successfully prepared via the dendrimer root. Finally, catalytic results obtained >with the supported Rh catalysts for probe reactions (i.e., ethane hydrogenolysis and CO oxidation) are consistent with the presence of sub-nanometer Rh particles and further indicate the stability of such particles in the reactive environments examined.

Tailoring Gold and Silver Catalysts for Some Environmental Catalysis Applications

Maria Flytzani-Stephanopoulos

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Tufts University
Medford, Massachusetts, USA

Atomically dispersed metals and metal clusters on oxide supports are being investigated as new heterogeneous catalysts for some reactions of interest to energy and environment. It is envisioned that synthetic approaches, which have proved so successful for homogeneous catalysts, will also become available to heterogeneous catalysis, making possible the design, control, and fabrication of certain structures with an unprecedented degree of precision. Probing single-site functionalities is mechanistically exciting, while designing a catalyst “to do more with less” is practically important as it can reduce dramatically the amount of a noble metal required for applications as diverse as exhaust gas treatment, fuel processing, fuel cells, and electrocatalyst design.

In our work, we investigate silver, gold, platinum, and copper clusters stabilized in various oxide matrices. One of the preparation methods we use involves leaching of the metal particles and all weakly bound metal species from a traditionally prepared (by impregnation, deposition/precipitation, etc.) supported metal catalyst. The leached structures contain embedded metal atoms and strongly bound metal clusters of distinct activity and stability from that of the metal nanoparticles. We have investigated [Ag_n-O-Al] structures as catalysts for the selective catalytic reduction of NO by CH₄ in exhaust gas streams laden with high (1000 ppm) SO₂ concentrations and found them to be stable and active at temperatures as high as 650 °C. In extensive studies of the activity and stability of gold clusters prepared on ceria and iron oxide, [Au_n-O-Ce] and [Au_n-O-Fe], we have found them very active for the water-gas shift reaction, but not for the low-temperature CO oxidation reaction. Metallic nanoparticles of gold on the same supports have the reverse properties. Various spectroscopies were used to complement the catalytic studies and improve our mechanistic understanding of the function of these novel catalysts. Results from our recent investigations will be shown and common features identified among the different materials will be pointed out in the presentation.

References

1. X. She, M. Flytzani-Stephanopoulos, *Catal. Today* Festschrift, in press.
2. X. She, M. Flytzani-Stephanopoulos, *J. Catal.* 237 (2006) 79-93
3. F.C. Meunier, D. Reid, A. Goguet, S. Shekhtman, C. Hardacre, R. Burch, W. Deng, M. Flytzani-Stephanopoulos, *J. Catal.* 247 (2007) 269-79
4. M. Manzoli, F. Boccuzzi, A. Chiorino, F. Vindigni, W. Deng, M. Flytzani-Stephanopoulos, *J. Catal.* 245 (2007) 308
5. Q. Fu, H. Saltsburg, M. Flytzani-Stephanopoulos, *Science* 301 (2003) 935
6. Q. Fu, W. Deng, H. Saltsburg, M. Flytzani-Stephanopoulos, *Appl. Catal. B* 56 (2005) 57
7. W. Deng, M. Flytzani-Stephanopoulos, *Angew. Chem. Int. Ed.* 45 (2006) 2285

Behavior of SO_x-Traps Derived from Ternary Cu/Mg/Al Hydrotalcite Materials

Gabriele Centi and Siglinda Perathoner

Dept. of Industrial Chemistry and Engineering of Materials of the University of Messina and ELCASS (European Lab. for Catalysis and Surface Science)¹

Cu/Mg/Al ternary HT-like materials show significantly better SO_x trap performances with respect to binary Cu/Al HT-like materials and represent an interesting type of materials either to protect NO_x traps from the deactivation by sulphur or as SO_x additives in FCC applications. The kinetics of SO₂ uptake was studied both at low (10 ppm) and higher (1000 ppm) SO₂ concentration in a thermobalance (TG) apparatus, and compared with the results obtained by measuring the SO₂ breakthrough curves in a flow reactor apparatus under reaction conditions simulating those of autoexhaust gases, in particular regarding the use of high space-velocities and presence of CO₂ in the feed. The feed composition and type of experiments and/or experimental apparatus influence the SO_x trap performances, but in general it was noted that the order of reactivity and the ranking of the SO_x trap performances were similar in the different configurations. Better performances were obtained using the Cu/Mg/Al = 1:1:2 ternary sample which was demonstrated to have also improved hydrothermal stability with respect to Cu/Al binary samples.

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Structural Requirements and Pathways in Methane Reactions Catalyzed by Supported Metal Clusters

Enrique Iglesia

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Kinetic and isotopic evidence for elementary steps is provided for CH₄ reactions on Rh, Pt, Ir, Ru, Pd, and Ni clusters. Turnover rates for CH₄ reforming with CO₂ or H₂O depend only on C-H activation rates on essentially uncovered surfaces. The elementary steps include rigorously those required for water-gas shift and Boudouard reactions. Reforming turnover rates increased with decreasing cluster size, because of the reactivity of low-coordination atoms prevalent in small clusters. With O₂ co-reactants, C-H bonds react on Rh, Ru, and Pt clusters covered partially with oxygen (O*) using O*-O* or O*-vacancy active pairs. O*-vacancy sites form as O₂ is depleted and activate C-H bonds much faster than bare metal surfaces. Cluster size effects in CH₄-O₂ reactions reflect changes in surface coordination and in reactivity and binding of chemisorbed oxygen. H₂ and CO were not detected when O₂ was present; thus direct partial oxidation does not occur and H₂-CO mixtures form via combustion-reforming pathways.

Oxidative dehydrogenation of ethane and propane: How far from commercial implementation?

Fabrizio Cavani

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The demand for olefins, especially ethylene and propylene, is expected to increase significantly in the near future. At the present time, the main sources of olefins are steam-cracking, fluid-catalytic-cracking, and catalytic dehydrogenation. Although these processes are widely used, an intense research activity is taking place to develop catalysts for the *oxidative dehydrogenation* (ODH) of alkanes.

In this review, the recent literature on the ODH of ethane and propane is examined. The following aspects are discussed: (a) the main features affecting the catalytic properties of systems based on supported vanadium oxide and molybdenum oxide; (b) the characteristics of catalysts producing outstanding olefin yields; (c) advantages in selectivity gained by means of either special reactor configurations or non-conventional conduction of the reaction; (d) the contribution of other reactions to the formation of olefins during the ODH of alkanes.

"Catalyst accessibility effects on the Conversion of Heavy Hydrocarbons"

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Iron, nickel, vanadium and sodium are the most common contaminants in FCC. For Ni, V and Na the deleterious effects on zeolite destruction, activity decline and dehydrogenation have been studied extensively. The effects of these poisons on FCC performance can be predicted reasonably well. Today, iron is often a problem too. One of its deleterious effects is the change in morphology of the catalyst particle, thereby enhancing the diffusional limitations of the hydrocarbon flow in and out of the catalyst particle.

Important to withstand that iron effect is the use of catalyst systems with a high accessibility, which remain highly active and selective, even when high amounts of iron are deposited. Simulating the effects of vanadium, nickel and sodium in the laboratory is well understood. However the effect of iron and particularly the effect of catalyst accessibility is more complex though.

In this presentation we will have a look at the effects of the poisoning metals, what they do to the catalyst, and how they influence the deactivation and impact the activity and selectivity. A particular focus will be given to catalysts of low and high accessibility, which are compared and studied in different test units.

Biofuels – A Manufacturing Perspective

Jan Campbell,
British Petroleum, UK

There are significant challenges being set by legislation to worldwide refiners for implementation of biofuels in road transportation fuels to reduce greenhouse gas (GHG) emissions and improve energy security. The manufacturing challenge is to deliver competitive fuel components to a quality that is compatible for blending with existing refining based hydrocarbon fuels.

The current situation is that manufacture of ethanol is a well proven technology and growth of biodiesel by transesterification of vegetable oils has been significant in a highly dieselised European market.

In the future, new feedstocks and manufacturing processes are required, which may be standalone or integrated into the existing refining environment. Particular focus is on lignocellulose, in the form of crop residue or dedicated energy crops, as a feedstock. The big prize is to develop cost competitive manufacturing processes, which have the potential to provide a high proportion of the transportation fuels requirements.

BP is working in all areas of the biofuels arena. BP has recently announced a collaborative partnership with the University of California Berkeley and its partners the University of Illinois, Urbana-Champaign and the Lawrence Berkeley National Laboratory over the next ten years to establish a dedicated biosciences energy research laboratory. BP is also in a Joint Venture with Dupont to develop, produce and market next generation biofuels, the first product being biobutanol which will provide benefits in the transportation of fuels of the future.

This presentation will expand on the challenges for Refiners.

Pilot Plant Evaluation of FCCU Catalyst Technology and Use of Data for Commercial Catalyst Applications

Cheryl Joyal¹, Matthew Westby¹ and Angelos Lappas²

¹BP Refining Technology, Naperville, IL, USA

²CERTH/CPERI, Thessaloniki Greece

The application of best-fit catalyst technology to commercial Fluid Catalytic Cracking Units (FCCU's) delivers additional yield value to the refinery and most importantly, provides additional high-value products such as gasoline and/or diesel for our customers and communities. By using laboratory deactivation protocols and pilot plant evaluation of new FCCU catalyst technologies, the catalyst yield performance, operational fit, and value for a commercial unit can be projected. An example of how continuous improvements in catalyst evaluation techniques were applied to one BP European unit to deliver year-on-year value delivery and product yield improvements is described. The success of this program is the result of a dedicated technical focus as well as strong working relationships between the BP global FCCU team, BP Refining Technology, CPERI, and the catalyst suppliers. This program has delivered over 30 successful commercial FCCU catalyst technology changes during the past 6 years that have delivered significant value to the refineries and additional consumer products to our customers.

Has biomass a Place in the Energy Spectrum?

Julian R.H. Ross¹, Daniel J. Hayes¹, A. Ersson, Michael H. B. Hayes¹ and Stephen W. Fitzpatrick²

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With diminishing reserves of hydrocarbon feedstocks, there has recently been an increased interest in the conversion of biomass to useful chemical products. Cellulose is much more abundant in nature than is starch, and its annual production is estimated at 100×10^9 tonnes. Furthermore, cellulosic feedstocks tend to be more productive and require less energy to produce than starch crops. Several so-called "Second Generation" processes have been developed to convert cellulosic feedstocks to usable products. One such is the Biofine Process (1) which hydrolyses the biomass in a two-stage process, the main products from cellulose being levulinic acid, formic acid and a high quality char. The levulinic acid produced can be converted catalytically to a number of high-value products, for example methyl tetrahydrofuran. Some of these conversions and the catalysts used for them will be reviewed. We have recently examined a series of catalysts for the "steam reforming" of formic acid, i.e. decomposition in the presence of water vapour, and some of these results will also be summarized.

References

1. Daniel J. Hayes, Julian Ross, M. H. B. Hayes and Steve Fitzpatrick, The Biofine Process: Production of Levulinic Acid, Furfural and Formic Acid from Lignocellulosic Feedstocks, in *Biorefineries – Industrial Processes and Products*, Eds. B. Kamm, B.R. Gruber, and M. Kamm, Wiley-VCH Verlag GmbH and Co., Weinheim, Germany, 1, 139-164 (2006).
2. Bozell, J. J., Moens, L., Elliott, D. C., Wang, Y., Neuenschwander, G. G., Fitzpatrick, S. W., Bilski, R. J. and Jarnefeld, J. L., Production of levulinic acid and use as a platform chemical for derived products. *Resources, Conservation and Recycling* 28 (2000) 227–39.
3. A. Ersson and J.R.H. Ross, unpublished results

Sustainable Fuels, Chemicals and Energy from Biomass Recent Developments

Paul O'Connor
BIOeCON, The Netherlands.

The first generation of biofuels (Bio-diesel and Ethanol from sugar and starch) are rather limited in supply and it is questionable if it really makes sense to 'downgrade' these valuable edible feed stocks to transportation fuels. The story is different for the second generation of biofuels which is based on using abundantly available lingo-cellulosic biomass wastes.

Cellulosic Ethanol can be produced via enzymatic conversion. Unfortunately the conversion and separation of ethanol remains difficult and costly, while eventually ethanol volatility may limit the quantity which can be blended into the fuel pool. An alternative route is to gasify the solid biomass and reform this into synthesis gas ($\text{CO} + \text{H}_2$), which can then be converted into a liquid fuel via the Fischer-Tropsch process. This route requires several complex process steps and is rather expensive in investment as well as energy consumption.

A simpler and more robust approach is to convert the solid biomass into a bio-crude by direct thermal liquefaction. The bio-crude can then be transported (by pipe-line) to existing refineries for further upgrading. Unfortunately the quality of the bio crude produced is poor and extensive hydro treatment is required in order to produce the right components for transportation fuels.

Interesting new developments have emerged from the field of heterogeneous catalysis which enables the effective and economical conversion of the solid biomass into sustainable fuels, chemicals & energy.

Hydrogen Production in Solar Reactors

C. Agrafiotis, C. Pagkoura, S. Lorentzou, M. Kostoglou and **A.G. Konstandopoulos***
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The present work summarizes the recent activities of our Laboratory in the field of solar-aided hydrogen production with structured monolithic solar reactors. This reactor concept, “transferred” from the well-known automobile exhaust catalytic aftertreatment systems, employs ceramic supports optimized to absorb effectively solar radiation and develop sufficiently high temperatures, that are coated with active materials capable to perform/catalyze a variety of “solar-aided” reactions for the production of Hydrogen such as water splitting or natural gas reforming. Our work evolves in an integrated approach starting from the synthesis of active powders tailored to particular Hydrogen production reactions, their deposition upon porous absorbers, testing of relevant properties of merit such as thermomechanical stability and hydrogen yield and finally to the design, operation simulation and performance optimization of structured monolithic solar hydrogen production reactors. This approach, among other things, has culminated to the world's first closed, solar-thermochemical cycle in operation that is capable of continuous hydrogen production employing entirely renewable and abundant energy sources and raw materials - solar energy and water respectively – without any CO₂ emissions and holds, thus, a significant potential for large-scale, emissions-free hydrogen production, particularly for regions of the world that lack indigenous resources but are endowed with ample solar energy.

CO₂ Emissions Strategy for Cleaner Environment - Zero Emissions Power Plants

E. Kakaras, A. Doukelis

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The purpose of the presented work is to examine and evaluate the state of the art in technological concepts for capture and sequestration of CO₂ from power plants, aiming at the formulation of the Zero Emission Power Plant concept. The discussion is based on the evaluation of the most promising identified options for clean utilisation of coal, oil and natural gas and is focused on the pre-combustion, post-combustion and oxyfuel technological options. The basic technological issues related to the different CO₂ sequestration options are discussed and thermodynamic simulation results, based on studies conducted within the framework of European projects, demonstrate the operational characteristics and efficiency penalty for CO₂ capture. The CO₂ capture cost and electricity cost for the different technological options is assessed, in comparison with a conventional power plant, against the economic penalties related to the CO₂ tax for non-application of CO₂ sequestration technologies.

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