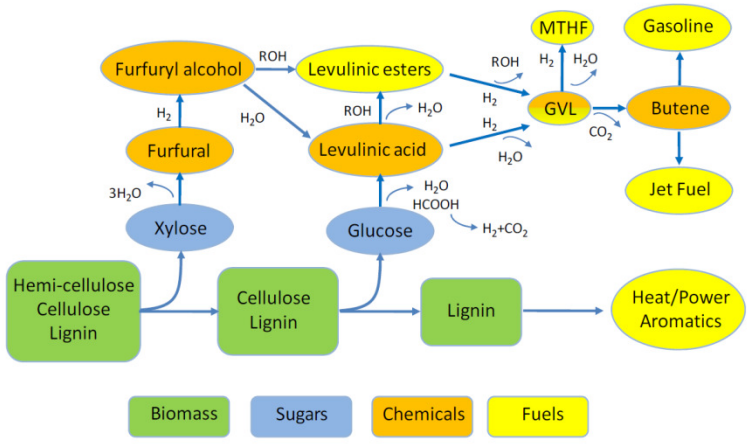
Conference Report – ISCRE 2012 – MECC Maastricht, Netherlands
Sam Wilkinson

Highlight Presentations:

'Catalytic conversion of hemicelluloses and cellulose to fuels and chemicals' – James Dumesic, University of Wisconsin, Madison, USA

Abstract: We will address how the hemicellulose fraction of lignocellulosic biomass can be converted to furfural and levulinic acid using biphasic reactors with alkylphenol solvents, and we will address the conversion of levulinic acid to gamma-valerolactone (GVL) in these solvents. In addition, we will show how various biomass-derived solvents can be used to extract levulinic acid produced by deconstruction of the cellulose in aqueous solutions of mineral acids.
Finally, we will address the decarboxylation of GVL to produce butene over solid acid catalysts, combined with the oligomerization of butene to produce liquid transportation fuels.

Discussion: James Dumesic's plenary gave insight into the roadmap of conversion of lignocellulosic biomass to fuels and chemicals (see diagram below). As mentioned in the abstract above, key conversion steps, such as furfural and levulinic acid formation were discussed as well as downstream processing of gamma-valerolactone. See further reading for more information on specific processes:



Further reading:

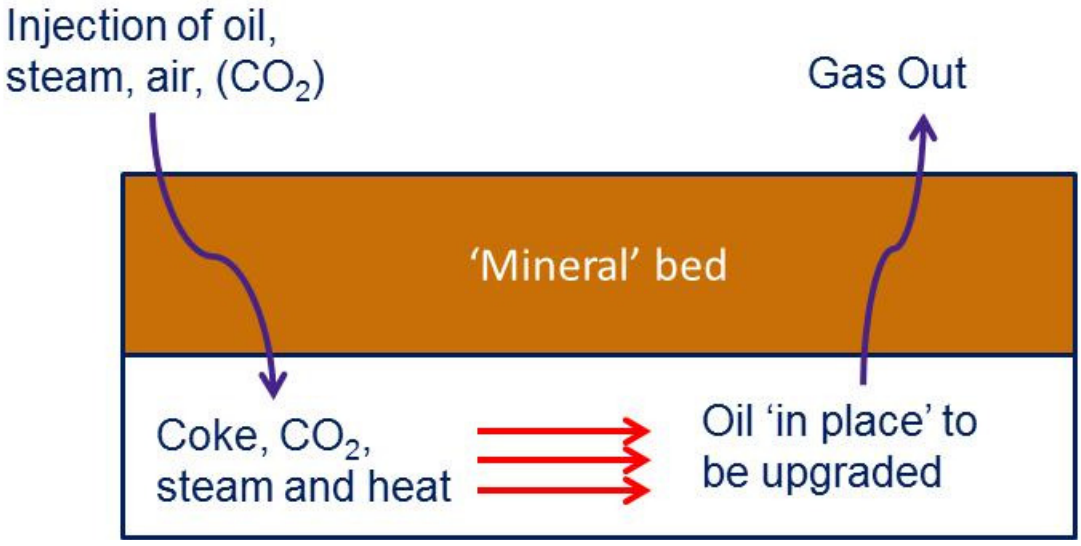
1. J.J. Bozell, Petersen G.R., 'Technology development for the production of biobased products from biorefinery carbo-hydrates – the US Department of Energy's 'Top 10' revisited', Green Chemistry. 12 (2010) 539-554
2. Garbuz E.I., Alonso D.M., Bond J.Q., Dumesic J.A., 'Reactive extraction of levulinate esters and conversion to gamm-vaerolactone for production of liquid fuels', ChemSusChem 4 (2011) 357-361
3. Bond J.Q., Alonso D.M., Wang D., West R.M., Dumesic J.A., 'Integrated catalytic conversion of gamma valerolactone to liquid alkenes for transportation fuels', Science 327 (2010), 1110-1114

4. Dumesic Research Group: http://jamesadumesic.che.wisc.edu/

***'Oil production by in-situ combustion: A large scale multi-phase, heterogeneous reactor'* – Theodore Tsotsis, University of Southern California, USA**

Abstract: In-situ Combustion (ISC) is an enhanced oil recovery process that can be described as a large, field-scale multifunctional and multiphase heterogeneous reactor. In ISC, air is injected into a reservoir, where it mixes with water and oil. Various inorganic minerals in the subsurface catalyze a number of reactions, including oxidation and upgrading of the oil in place. This paper studies both standard ISC operation as well as a novel CO2-recycle ISC operation, whereby the produced CO2 is re-injected. It is shown that the recycle operation produces significantly less CO2 for the same level of oil recovery.

Discussion: Reduction of CO_2 emissions from the ISC process is the key target for this work due to ever tightening emissions legislation in California. ISC, in principle, aims to achieve two key goals: a) to use heat and gaseous products (CO_2 and steam) to reduce the viscosity of oil (thus enhancing transport through the substrate and to production wells and b) carry out in-situ upgrading to improve oil quality. This is achieved by initial injection of air, oil and water which react (in the presence of inorganic minerals as catalysts) to form coke, CO_2, heat and steam to drive the aforementioned goals for the oil in place downstream in the 'reactor'.



The principle of operation is shown above (with CO_2 addition). Theodore Tsotsis gave a good overview of the complex control requirements for such as reaction system. This was followed by applying the CO_2 recycle methods to two existing ISC processes (the 9-spot pattern and line-drive) to show applicability. In both scenarios, by replacing some injected air with CO_2, it was demonstrated that emissions could be decreased by up to 30% for both operational modes.

Further reading:

1. Ramney H.J.Jr, Stamp V.W., Pebdani F.N., Mallinson J.E., 'Case History of South Belridge, California, In-situ combustion oil recovery., Proceedings, Tulsa OK, 1992, Paper SPE 24200

2. Turta, A.T., Pantazi I.G., Development of the In-Situ Combustion process on an industrial scale at Videle Field, Romania, SPE Reservoir Engineering, November 1986, pp. 556-564, Paper SPE 10709

***'Role of hydrodynamics on chemical reactor performance'* - Sankaran Sundaresan, Princeton School of Engineering and Applied Science, USA**

Abstract: Our understanding of the transport characteristics of multiphase reactors has expanded rapidly in recent years as a result of detailed experiments and large scale computations. This, in turn, is driving both new innovations and new approaches to modelling industrial scale reactors. This talk will highlight several examples, where, a the flow behaviour is being manipulated to improve or intensify reactor operation, and, b detailed understanding of the flow behaviour is being used to construct simpler and more practical models to interrogate reactor performance.

Discussion: Sankar Sundaresan's talk probed the role of hydrodynamics in reactors on a variety of levels. The body of the talk was largely focussed around a trickle bed and fluidised bed reactor study. In each case, a range of techniques were used to better understand reactor hydrodynamics with clear messages around understanding these phenomena on a multi-scale but also the consolidation of the key link with reactor performance analysis. The work carried out in this field and its application is very far reaching – whether on plant scale or for screening rigs within the lab.
Techniques such as tomography (electrical capacitance, acoustic, X-ray), PEPT, NMR imaging, particle image velocimetry (PIV) as well as multiphase flow simulations (eg CFD) have all had their role in better understanding flow hydrodynamics in reactors.

Key flow effects for trickle beds discussed in the presentation were centred on initial liquid distribution, extrudate effects and hot spots. The merit of using imposed feed modulation was also highlighted. For fluidised beds, particle behaviour was discussed on a micro, meso and macro scale.

Further reading: See actual presentation posted at:
http://www.princeton.edu/cbe/people/faculty/sundaresan/group/presentations/Sundaresan_ISCRE_22.pdf

A large number of references are posted within the presentation for further reading on the areas discussed.

***'Behind the industrialisation of higher-temperature slurry Fischer-Tropsch process'* - Yong-Wang Li, Synfuels China**

Abstract; Recent operation records reached by two Fischer-Tropsch (F-T) plants using the HTSFTP technology have greatly promoted the industrial interests for developing large scale coal to liquid (CTL) projects, and behind this the fundamental R&D efforts connecting all the aspects of chemical (reaction) engineering sciences have greatly been enhanced in the past and will continue being so by combining all the fundamental tools covering fundamental understanding of mechanism of F-T catalysis, reaction engineering for better reactor design, and process integration for improving the conversion efficiencies of both material and energy.

Discussion: To date, two demonstration scale projects for high-temperature slurry FT have been carried out, each achieving ~4000b/d liquid products. Capacity, following modifications, has increased for these plants over the past three years. Yong-Wang Li's talk looked at the key aspects of fundamental research and process development that have helped develop these projects. Three key areas were addressed:

Firstly, existing data were discussed but caution was advised due to the often contradictory nature of existing literature and data, chiefly due to the complexity of FT catalysis phenomena. Fundamental models, such as those produced through DFT were highlighted to aid in providing direction in this area and understand the nature of the catalytic processes.

The second area was based around the need to link FT catalyst development to chemical reactor engineering developments for this system. Neither can develop properly without understanding and provision of operating constraints from the other.

The third area followed on from this and addressed the use of kinetics in reactor and process development. Intrinsic kinetics for FT is largely a 'holy grail' but it is essential to know where current kinetics development is at and guide reactor design and development appropriately.

Further reading: http://www.synfuelschina.com.cn/

'The need for fundamental insight in the development of new technology solution for the refining and petrochemical industries' **– Kurt Vanden Bussche, UOP, USA**

Abstract: Ever tightening and more broadly implemented environmental specifications, the continuously growing importance of energy efficiency and the diversifying feed slate are continuing to drive the processing industries to come up with novel technology solutions. Given the maturity of the refinery and petrochemicals industries, the development of these solutions can no longer rely on the use of Edisonian methods. Instead, it increasingly calls for a thorough understanding of the fundamentals behind the existing technology and the creative use of computational tools. The current paper will briefly describe the macro-trends observed in the processing industries and will then go over two case studies, illustrating the judicious use of surface science and advanced modelling techniques in the development of next generation technology solutions, for the upgrading of naphtha range feeds.

Discussion: Against a backdrop of talks on emergent industries such as biofuels, Kurt Vanden Bussche's talk critically emphasised the fact that there is still great need for greater fundamental understanding and innovation in refining and petrochemicals. In the face of tightening fuel specification legislation (eg. Diesel sulphur) and a shift in feedstocks (such as the systematic increase in use of shale gas in the past 3-5 years) the need for increased fundamental understanding is valued even further.

Two case studies were given: the catalytic reforming of naphthas and sulphate zirconia paraffin isomerisation. In the former, metal:acid catalysis is key, particularly around selectivity of ring closure vs. cracking reactions. Addition of chloride was discussed and their role in stabilising Pt3 surface clusters. The importance of appropriate characterisation was also discussed, in this case centred around EXAFS and STEM. In the latter case study, the shift from using zeolites to Tm/Pt/Zirconia catalysts was discussed → analysis of catalyst stability was given, particularly around the role of dopants.

Further reading: http://www.uop.com/processing-solutions/petrochemicals/

Other presentations to investigate:

1. Marc-Olivier Coppens, Rensselaer Polytechnic Institute, USA, **'Nature-inspired routes to guide innovation in chemical reaction engineering'** http://nice.che.rpi.edu/
2. Joris Thybaut, Ghent University, BE, **'Relumped single-event micro-kinetic model for aromatics hydrogenation on a Pt Catalyst'**
3. Ming-Lei Yang, China University of Science and Technology, **'First-principles calculations of propane dehydrogenation over Pt/Sn catalysts'**
4. Dmitry Murzin, Abo Akademi University, FI, **'Kinetic modelling of propene hydroformylation'**
5. Mahsa Motegh, Michiel T. Kreutzer, Delft University of Technology, NL **Guidelines for the design of two-phase slurry photcatalytic reactors'**
6. Jose Santamaria, University of Zaragoza, **'Reaction engineering for the production of nanomaterials'**
7. Nazita Sedaie Bonab, University of Birmingham, **'Effect of scale up and mass transfer limitations on selectivity of three phase hydrogenation reactions'**