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THE HIGH-THROUGHPUT RESEARCH APPROACH TO BIOREFINERIES – A POWERFUL TOOL FOR STUDYING THE COMPLEXITY OF CATALYTIC PROCESSES

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The integration of complex catalytic reactions in biorefineries will require a considerable research effort. Up-front new catalysts will have to be developed and the ever changing feed composition and impurity profiles of biomass will require fast constant adjustments of the process. The capabilities of High-throughput methodologies to simultaneously perform several reactions will offer advantages for the development of the new processes required and in the daily operation of the new biorefinery concepts.

Keywords: High-throughput experimentation, integrated biorefinery, sugar dehydration, furanics hydrogenation, syngas conversion

INTRODUCTION

It is a widely accepted idea that, in the future, the so-called biorefineries will provide large amounts of fuel and chemicals, which are currently obtained from petrochemical sources. Like present-day oil-refineries, it is expected that the biorefineries will provide complex facilities, which will rely heavily on the integration of various (bio-)catalytic processes, such as gasification of syngas or H_2 production, pyrolysis of wood or lignin feeds, followed by hydro-deoxy/desulfo and denitrogenation reactions for fuel production,[1] sugar dehydration to furanics,[2] furfural and levulinate,[3,4] as platform chemicals for fine chemicals, or sugar fermentation to bio-ethanol and bio-butanol. High-throughput catalysis research is beneficial in facilitating an optimal integration of these various processes, and can also be used to address the changing feedstock compositions typically encountered with natural product feed streams. Recently, several excellent reviews have appeared, addressing the potential of (bio-)catalytic processes of producing chemical building blocks and fuels.[5-8]

A high-level concept of the connection of various complex chemical conversions in a wood/sugar-based biorefinery is illustrated in Figure 1. On the feedstock side, sugars can be derived from relatively pure but expensive forms, such as sucrose, glucose and starch, or from cheaper but very impure sources – such as lignocellulosic biomass. The latter contain not only a complex mixture of sugars, but also significant amounts of lignin and inorganic ashes as unwanted constituents. To complicate things even further, the amount and type of sugars and impurities in all feed changes depend on local origin, time of harvest and crop type. Within a biorefinery concept, these feeds will need to be coupled with the various process steps with as little purification in-between processes as possible. It is thus quite obvious that robust catalytic processes need to be developed, allowing the necessary adjustments of the process conditions, depending on the variability between the used feedstock(s). The frequently available possibility of variable product compositions depending on market demands is further adding to the complexity of the entire catalytic process in a biorefinery.

Although refined sugars (sucrose, starch) can be used in a carbohydrate-based biorefinery, especially for biofuel applications, the preferred feeds would typically include wood, side and waste streams, such as hemicellulose streams, beet pulp, citrus peel or new carbohydrate rich crops, such as Switchgrass and Sweet Sorghum, which can grow better on marginal and dry lands, or algae with optimized compositions. All these feedstocks are characterized by non-uniform composition and various levels and types of impurities, as depending on seasonal, annual and geographical variations. Understanding the influence of the compositional changes and major impurities on the catalytic processes is important for maintaining optimal process conditions. Therefore, robust processes need to be developed. Nevertheless, each time a new feed is used, more experiments will be needed to fine-tune the process conditions for optimal performance.

Clearly, a huge catalysis research effort is needed to understand the complex inter-process relations and how to steer the biorefinery to its optimum productivity on such widely varying feeds. High-throughput research offers an answer to this problem by providing the required vast amount of catalytic data needed for this knowledge. Although it is most commonly applied for rapidly screening catalysts and, as such, it is highly valuable in the development of the process, it can also be very advantageous for determining the process envelope for an existing catalytic process, when a change in feed composition occurs. A quick screening of a new feed over the expected process window will allow a better selection of the process conditions to be applied for optimal performance.

In this paper, the key benefits of using High-throughput technologies, *e.g.* costs, speed and safety, will be presented by studying several of the key processes within biorefineries. Examples that will be used to show the benefits of High-throughput methodology are the dehydration of sugar feed streams into Avantium furan-based YXY building blocks;[5] hydrogenation of furanic molecules to a new class of bio-fuels[6,7] and syngas chemistry as a function of feed and impurities, for relevant processes – such as the Fischer-Tropsch one.[8]

EXPERIMENTAL

Each of the three chemistries here discussed had their specific High-throughput experimentation platform, set up to best deal with the requirements of the catalytic reaction.

In the dehydration of hexose and aldose feeds, the reaction mixtures were prepared from stock solutions. To an 800 μL aqueous sugar solution containing 81.25 mg/mL, appropriate amounts of aqueous 1.64 M H_2SO_4 and of water were added, to fill up to a total 1.00 mL reaction volume. Three variables were studied: acid concentration, temperature and reaction time. Experiments were performed at 33, 100 and 300 mM H_2SO_4 concentrations, for 30, 45 and 60 min. Ketose dehydration was performed at 100, 120 and 140 °C, and aldose dehydration at 120, 140 and 160 °C. Experiments were performed on Avantium's QCS High-throughput batch platform. The analysis of both substrates and furan products was performed on a Waters Acquity™ UPLC system equipped with an X-Bridge C-18 column (1.8 μm, 50 mm x 20 mm). The sugars were analysed with an evaporative light scattering detector (ELSD) and the furan compounds – with a diode array detector (DAD). The analysis of levulinic acid was performed on an Interscience TRACE™ GC equipped with a Varian VF-WAXms column (0.25 μm, 30 m x 0.25 mm) and a FID detector.

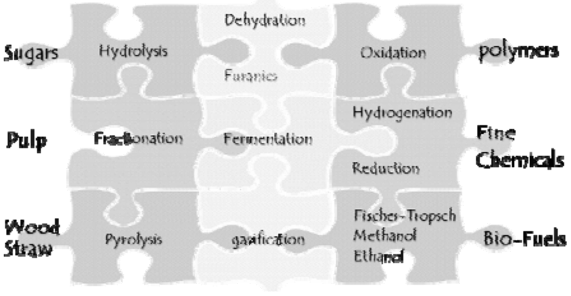

Figure 1: A sugar-based biorefinery concept. Several different type of bio-feeds are processed through an interlinked cascade of (bio-)chemical conversions into higher value products

High-throughput experiments for syngas conversion processes were performed on 64 fixed-bed tubular reactors operated in parallel and in co-current downstream mode. The so-called 3rd generation Nanoflow consisted of four reactor blocks containing 16 reactors each. The tubular reactors had internal diameters of 1.0, 1.5 or 2.0 mm, and were typically used for testing catalyst masses between 25 and 200 mg. The reactors can operate at a maximum temperature of 550 ºC, maximum pressure of 100 bar and gas hourly space velocities of up to 100000 h^{-1}. To enable the investigation and optimization of the process conditions, pressure, temperature and flow rates may be systematically varied during a run. The reactor holder is of special design and the reactor effluent can be diluted with liquid or gas, thus preventing the condensation of products, so that up to C-15 products can be measured on-line using GC.

Ruthenium catalysts (1 wt% Ru) were prepared by incipient wettness impregnation of the appropriate support using aqueous solutions of $RuNO(NO_3)_3$, $Ni(NO_3)2$-x H_2O and $Pd(NO_3)_2$ (Hereaus). Materials were dried at 120 °C for 16 h after impregnation, and calcined for 3 h at 450 °C. Prior to catalytic testing, the materials were reduced *in-situ*, using 5% H_2 in N_2 at 200 °C for 1 h, at GHSV 6000 h^{-1}.

All catalysts involved in the hydrogenation of furanic molecules were synthesized using a wet impregnation procedure. The liquid volume was chosen so that all catalysts could be prepared using identical precursor mass concentrations. This gives a rather dilute impregnation slurry, where the volume is determined by the metal precursor with the lowest solubility. In all cases, impregnation time was of 24 h. Drying of catalysts was performed at 105 °C, followed by calcination in air, at 320 °C. All experiments were performed in trickle flow in a commercial 16-reactor setup between 80 and 120 °C. In a typical experiment, the reactor system is loaded with 15 calcined catalysts, 50 mg each. The remaining reactor is left empty, to obtain a reliable measurement of conversion and probe for the uncatalysed reactions. The catalysts are first reduced at 300 °C using a mixture of hydrogen and nitrogen. After cooling down to 80 °C, each reactor is supplied with a feed of substrate solution corresponding to a LHSV of 0.032 mol g^{-1} h^{-1}. The samples are collected in the liquid phase and analyzed[9] offline using GC.

RESULTS AND DISCUSSION

High-throughput experimentation is a valuable tool to speed up development, to reduce costs and improve safety. High-throughput integration in a multi-step catalysis research program is perhaps best exemplified by Avantium's own Furanics research effort. Figure 2 depicts a biorefinery concept using wood as the starting point and having Avantium Furanics at the heart of the sugar conversion technology.

Multiple carbohydrate feed sources are produced from woody biomass, mainly C5 (arabinose and xylose) and aldose-type C6 (glucose, mannose, galactose) sugars, but also lignin and humins, which are carbohydrate degradation products and side products in the Furanics process. Further upgrading to some of the valuable products, especially in the bio-fuels area, requires considerable amounts of H_2 and alcohols (for etherification). An option would be to use lignocellulosic bio-ethanol,[10] but this would use the same C6 sugar stream necessary for Furanics production, thereby lowering the yield of Furanics/kg of biomass. A convenient alternative would be to use the lignin and humin side streams as a source for syngas production. *Via* the water gas-shift reaction, it would produce the required H_2, but *via* well-established catalytic processes it can be also used to produce methanol or a mixture of lower alcohols with ethanol as the main component, as well as paraffins and olefins (outside the scope of the Furanics concept) – namely, *via* well-established Fischer-Tropsch technologies.[5]

Costs

In the first example, the influence of feedstock composition on the dehydration of C6 sugars into hydroxymethylfurfural (HMF) was investigated. The miniaturization of the experiments often produces important cost benefits. The amount of reactants and solvents can be strongly reduced, and the amount of man-hour per experiment is small. In this example, the benefits of High-throughput technology are shown when costly (ketose) substrates are used for reference purposes. Three different ketose- and three different aldose-containing feeds were dehydrated under various process conditions and catalyst concentrations. The program, consisting of 96 experiments, was performed within 3 weeks by one person. There was a strong difference between the behavior of aldose and ketose sugars, confirming literature data.[8,9] However, within the aldose and ketose group, no significant difference was observed in the selectivity of the desired products. For each of the three feeds within the ketose group, an optimum of 45% HMF at around 90% conversion could be observed (Figure 3), with selectivity dropping fast at higher sugar conversion levels, in favor of the formed levulinic acid. Interestingly, it was, however, observed that the three ketose feeds had significantly different reactivities. In Figure 4, the first-order observed reaction rate constant $k_{observed}$ is plotted against the reciprocal reaction temperature and acid concentration, in a 3-dimensional Arrhenius plot for the different ketose feeds employed. From this plot, it is clear that feed 1 is more active than feeds 2 and 3, but it can be also observed that the three planes are nearly parallel to each other. This is a strong indication that all feeds run through the same chemical pathways and the lower rates should be assigned to a lower activity of the catalytic system, due to differences in the stereochemistry of the used ketoses.[5]

Speed

Catalytic biomass conversion is a highly competitive area so that the speed of development is crucial for any part, for remaining a front-runner in the development, and to guarantee a solid intellectual property position. The following example illustrates the strength of High-throughput technologies on the speed of developments. To develop biofuels from Furanic intermediates, new catalytic systems for the selective reduction of furanic molecules should be found. As shown in Figure 2, YXY furanics are complex molecules possessing several groups that can be hydrogenated. For example, in the hydrogenation of EthoxyMethylFurfural (RMF, R = Ethoxy) in the route to new bio-fuels[10] hydrogenation of the furan ring, aldehyde moiety and ethyl ether moiety are possible. Using a 3-month High-throughput screening program consisting of 576 experiments, a group of Iridium-based catalysts could quickly be identified as an active and selective metal for the hydrogenation of the aldehyde group.[6,7] It is clear that this small-scale High-throughput approach using expensive noble metal catalysts has also important costs benefits during the R&D phase.

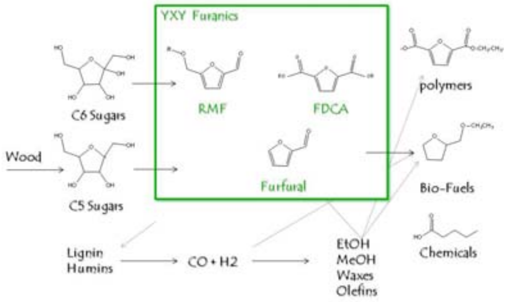

Figure 2: A biorefinery concept using Avantium Furanics technology for converting wood to high-value products. Red arrows indicate reactions discussed in more detail

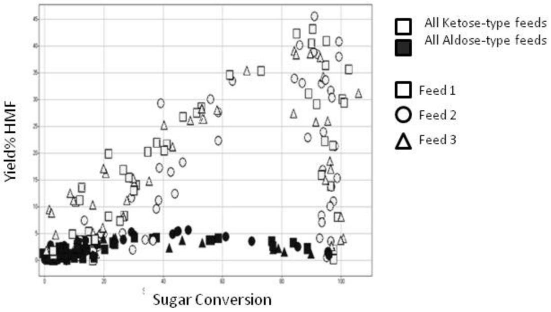

Figure 3: Yield of HMF dehydration product as function of sugar conversion for several ketose and aldose feeds

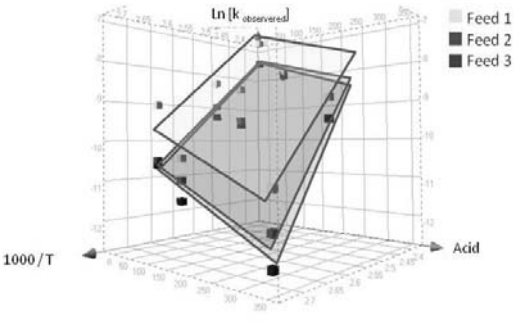

Figure 4: 3-Dimensional Arrhenius analysis of three different sugar feeds. The observed kinetics first order rate constant is plotted against 1000/T [K] and acid catalyst concentration applied

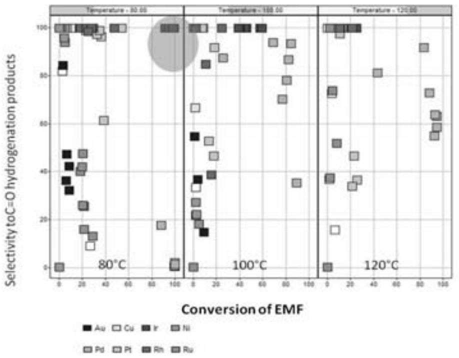

Figure 5: Screening of catalysts for selective hydrogenation of aldehyde moiety in EMF

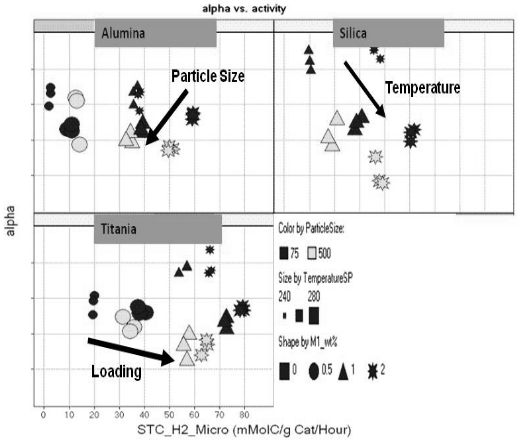

Figure 6: High-throughput study of several physical catalyst properties on α value and H_2 consumption rate

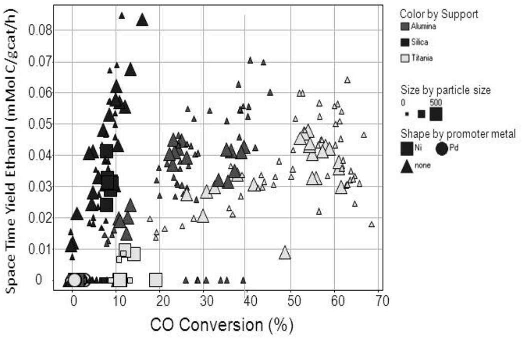

Figure 7: Production of ethanol by-product as a function of support (color), catalyst particle diameter (size) and active metal promoter (shape)

Safety and Ecological Footprint

The screening of new catalytic materials often results in promising leads. However, it will still require further optimization of the new catalysts' composition, to obtain an industrially relevant catalyst. Miniaturization has also major advantages, as to safety and ecological footprint. Because of the small-scale size of the experimental setup, the amount of solvents and reactants is strongly reduced, with associated positive effects on the amount of generated waste. Small-scale experimentation has also benefits regarding safety aspects.

In Figure 6, an example of catalyst optimization is given for a Fischer-Tropsch catalyst. Fischer-Tropsch chemistry uses CO and H_2 as feedstock, toxic and explosive chemicals. Small-scale makes it easier to accommodate to the rigorous demands associated with this kind of chemistry. From the data obtained in a single, 1 week run, one can tailor the catalysts required, depending on the desired Anderson-Flory-Schultz α-value and production rate of product waxes. The α-value is the ratio of chain growth over the termination in Fischer-Tropsch chemistry, and higher values are typically sought after, as they give more valuable products. In Figure 6, several trends can be easily identified. The α-value is improved by using smaller particle sizes, lower reaction temperatures and, to a lesser extent, lower catalyst loading. On the other hand, productivity is improved when using higher temperatures, smaller particle sizes, higher catalyst loadings and titania as a support.[8]

In wax production, the formation of minor amounts of ethanol normally needs to be minimized. Figure 7 shows clearly that the amount of ethanol is strongly related to the catalyst support used. The highest amounts of ethanol are obtained with silica as a support.

CONCLUSIONS

Chemo-catalytic processes will play an important part in the biorefineries of the future. However, a proper design, optimization and operation of these biorefineries will require significant research efforts. The present study shows that the use of High-throughput methodologies offers a fast, cost-efficient, accurate, safe, flexible and therefore powerful tool to address the needs of biorefineries. The integration of the High-throughput technology in a multi-step catalysis research program is very well exemplified by iHighAvantium's own Furanics research effort. In a biorefinery concept using wood as the starting point and having Avantium Furanics at the heart of sugar conversion, High-throughput technologies has been successfully used to study several of the key catalytic steps.

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