Catalysis for biorefineries – performance criteria for industrial operation

Journal:	*Catalysis Science & Technology*
Manuscript ID	CY-PER-02-2016-000431.R1
Article Type:	Perspective
Date Submitted by the Author:	19-May-2016
Complete List of Authors:	Lange, Jean-Paul; Shell Chemicals Int.,

Catalysis for biorefineries – performance criteria for industrial operation

Jean-Paul Lange

Shell Research and Technology Center, Amsterdam, The Netherlands; University of Twente, Enschede, The Netherlands

e-mail: jean-paul.lange@shell.com

Table of contents entry

Make sure your biorefinery catalyst meets the performance criteria required for industrial application!

Summary

Past analyses of industrial processes for fuel and chemical manufacturing led to a few performance criteria that are critical for viable industrial operation. The present paper reviews these factors and provides a target window for each of them. It then illustrates their relevance for biorefineries through a dozen of cases studies based on selected scientific papers.

Keywords: renewable feedstock, biomass, biorefinery, industrial operation, catalysis

1 Introduction

The last decade has witnessed an explosion of research in the catalytic conversion of bio-based feedstock to fuel and chemicals. The number of annual publications in this area has indeed exponentially grown from ~10 in 1990, to ~100 in 2000 and ~1,000 in 2010. Catalyst scientists were, initially, focused on developing novel catalysts to maximize conversion and selectivity, as reported in [1-6] and illustrated in the case studies below. More recently, however, they increasingly extend the discussion to complementary topics that are also of industrial relevance such as catalyst deactivation,[7-9] product recovery [10,11] or other process parameters [12,13]. Nevertheless, the catalysis literature seems to still be missing a broad and general discussion on what catalysts need to deliver to be industrially applicable. The present paper is attempting to fill this gap.

To this end, it seemed valuable to look back to decades of industrial practice in oil and petrochemical manufacturing to review sets of catalyst performance that have proven critical for industrial practice, as they will, most likely, apply to biomass conversion processes as well. This will be done by revisiting some economic and industrial guidelines that were formulated some 15 years ago upon analysing a large set of industrial processes [14]. More specifically, we'll discuss four criteria for catalyst operation: catalyst selectivity, activity and stability (i.e. catalyst consumption) as well as product concentration. We will then discuss a dozen of case studies on biomass conversion to illustrate the insight and guidance provided by these criteria.

The guidelines that resulted from this study do not pretend to allow for quantitatively determination of the economic competitiveness of novel processes. The aim is to help identifying the factors that are most critical to the economic viability of processes under study.

2 Industrial operating window

Many factors need to be considered to assess the technical and economic feasibility of catalytic conversion processes. A few of those are directly related to the catalytic step itself (Table 1), and will be the focus of our attention here. Other engineering considerations such as reactor design, heat management, product separation and recovery, health and safety, etc. will remain out of scope here.

Table 1 – Performance windows applied in oil and petrochemical industry (adapted from [14] and [8])

Criteria	Industrial window	Comments
Selectivity	70-100 w%	*Selectivity (per pass) > (feed price + CC)/product* price CC = conversion cost (e.g. ~\$200/t_{feed} for single step)
Activity	0.1-10 $t_{prod.}/(m^3_{react}\cdot h)$	Catalyst with low activity <1 t/(t·h) require high concentration (~1 $t_{cat.}/m^3$); catalyst with high activity >100 t/(t·h) can afford low concentration (<1 kg/m^3)
Catalyst consumption	1-100 $t_{prod.}/kg_{cat.}$	Catalysts with low activity <1 t/(t·h) require long life (>1 y); catalysts with high activity >100 t/(t.h) can afford short life (<1h)
Product Concentration	3-100 w%	Undiluted feed and high conversion per pass are preferred; feed dilution can be acceptable for highly endo/exothermic ($\lvert\Delta H_{react}\rvert$ >10 kJ/g_{prod}) and fast reactions.

2.1 Catalyst Selectivity

Selectivity is often the most critical performance for a catalytic process, particularly when using expensive feedstock: the lower the selectivity, the higher the feed consumption and feed cost. Hence, industrial processes are typically operating with selectivity above 70 w%.

This targets can be rationalized in terms of feed price, product price and conversion cost. With the risk of oversimplification, one can state that the product cost depends mainly on feed price, conversion cost (CC) and overall product yield (eq. 1). It should be mentioned here that feed price and conversion cost are expressed as cost (USD or Euro) per ton of feed and, consequently, the yield is expressed as weight fraction (ton product per ton feed) and not as mole fraction.

$$\text{Product cost} \sim (\text{feed price} + \text{CC})/\text{yield} \qquad (1)$$

When unconverted feed can be recycled for further conversion, selectivity nearly equals the overall yields, as it is exceeded only by the small fraction of feed and product that is eventually lost during processing. Obviously, the product price, which is documented in the literature, needs to be higher than the product cost, to allow for some profit. Substituting the overall yield and product cost by selectivity and product price allows us to transform eq. 1 into a selectivity requirement eq. 2. As for the yield, the selectivity is here expressed as weight fraction.

$$\text{Selectivity} > (\text{feed price} + \text{CC})/\text{product price} \qquad (2)$$

Typical figures for renewable feed prices are \$50-100/t for lignocellulose, \$300-400/t for sugars and \$1000-2000/t for platform molecules, including vegetable oils. Biofuels and commodity chemicals are also expected to fall within the window of \$1000-2000/t. Conversion cost may amount to \$100-300/t_{feed}, depending on the complexity and scale of the process. Typically, conversion cost can be estimated based on the energy transfer duty applied in the conversion and separation segments, as discussed elsewhere [14].

Some refinements of eqs. 1-2 are worth mentioning here. Firstly, the co-production of multiple products requires a more complex equation that consider individual selectivities and prices for the various products. Secondly, processes that consist of numerous process steps are not properly described by eqs. 1-2 using overall process yield and overall conversion cost. More realistically, each conversion step should be 'sized' for the yields of all *subsequent* steps (not of the preceding ones!). Accordingly, eq. 1 should be rewritten as eq. 3, where CC_i and Y_i represent the conversion cost and yield of step i.

$$\text{Product cost} \sim (\text{feed price}+CC_1)/(Y_1.Y_2\ldots Y_n) + CC_2/(Y_2.Y_3\ldots Y_n) + \ldots + CC_n/Y_n \qquad (3)$$

Even with such refinements, these equations should be viewed as crude and preliminary indicators. They indeed offer a poor accuracy, due to the variability of feed and product prices as well as the inaccuracy of the conversion cost estimates. They can nevertheless be very insightful, as we can see with the example of the conversion of sugar to ethylene via ethanol fermentation (eq. 4):

$$C_6H_{12}O_6 \rightarrow 2\ C_2H_5OH + 2\ CO_2 \rightarrow 2\ C_2H_4 + 2H_2O + 2\ CO_2 \qquad (4)$$

According to eq. 2, the conversion of sugars (\$300/t) to ethylene (e.g. \$1000/t) requires an overall selectivity of 70 w% when assuming an overall upgrading cost of ~\$400/t for the 2-step process. This target is well above the theoretical selectivity of 31 w% allowed by the stoichiometry of the reaction (eq. 4). Hence, the process requires either cheaper sugar, cheaper processing and/or more expensive ethylene to become profitable. The reader is invited to play a bit with the refined eq. 3, using the theoretical selectivities of 50 and 60 w% for the first and second step, to determine the sugar price, conversion cost and product value that are necessary to make this process economically attractive.

This example leads to a very important learning: biomass deoxygenation is expensive. The oxygen, which was indeed paid for with the feed and processed in the plant, is now wasted. Moreover, the removal of oxygen often proceeds with significant energy consumption or release (e.g. during hydrodeoxygenation), which further increase the conversion cost. This details are out of the scope of this paper, and discussed in more depth in [14] and applied to biorefineries in section 3 of [15].

2.2 Catalyst activity

Industrial practice can accommodate a large window of catalyst activity that stretches over four orders of magnitudes: from ~0.2 to >1,000 ton product per ton catalyst per hour [14]. Looking per reactor volume, the productivity window is much narrower, however. It covers only two order of magnitude, from 0.1 and 10 ton of product per m^3 reactor per hour, because of an effective balance between catalyst activity and loading catalyst hold-up (Figure 1a). Catalysts with low activity (<1 t/(t.h)) are generally operating as millimeter-size particles in fixed bed reactor at high catalyst hold-up (>0.5 t/m^3). In contrast, catalyst with high activity (>1 t/(t.h)) are generally used as micron-sized particles or smaller that are suspended or dissolved in a fluid medium (gas or liquid) at much lower concentrations (from 0.01-0.1 t/m^3 or even lower). The lower limit of reactor productivity of 0.1 $t/(m^3.h)$ apparently defines affordable reactor size. The upper limit of 10 $t/(m^3.h)$ is more likely set by heat transfer limit as it corresponds to a heat exchange duty of ~5 MW/m^3 for processes with moderate (absolute) heat of reaction of ~2 GJ/t_{prod}, irrespective of being endothermic or exothermic [14].

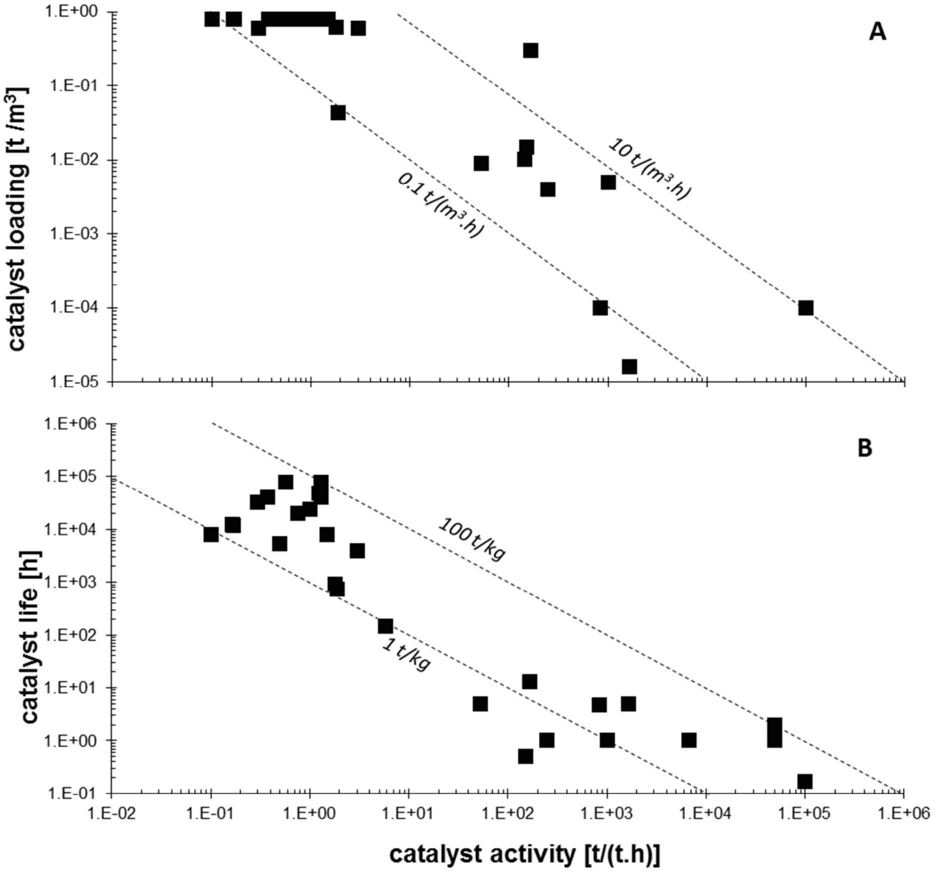


Figure 1 – Catalyst loading, activity and life time encountered in industrial process. Processes operates with overall reactor productivity of 0.1-10 t_{prod}/m^3 (A) and overall catalyst consumption of 1-100 t_{prod}/kg_{cat} (B) – adapted from [14]

As we will see later in the case studies, biomass conversion processes are occasionally challenged on their reactor productivity. This can be the case for processes that are operating at fairly mild temperatures (e.g. <250°C) with significant dilution of the feed, being lignocellulose or sugars in water, and low catalyst hold-up. In contrast, the upgrading of well-defined platform molecules can often be carried out with high reactor productivity.

2.3 Catalyst consumption

Industrial processes are also operating within a large window of catalysts life-time. The window covers seven order of magnitudes, from seconds to years. Some catalysts are used in single pass and are discarded after reaction, possibly after neutralization (e.g. for homogeneous acids and bases) or by being left as 'contaminant' in the product (e.g. in polymerization or fat hardening). Other catalysts may last for a years, optionally through multiple regeneration cycles to compensate for deactivation.

However, the overall catalyst life-time seems to be limited to two order of magnitude when expressed as catalyst consumption, i.e. as amount of catalyst that is required to make one ton of product. Industrial catalysts appear to become disposable after having produced 1,000 to 100,000 times their own weight of product (Figure 1b). Catalysts are generally >100 times more expensive than the product they manufacture: heterogeneous catalyst often cost $40-200/kg while commodity chemicals are rather prices at $1-2/kg. Hence, the catalyst consumption starts to affect the economics of the process when consumed at more than 1/1000 of the product output.

The overall consumption of catalysts in biomass conversion can be affected by three main mechanisms: catalyst poisoning, catalyst fouling and catalyst degradation such as sintering or leaching.[8] Poisoning is related to the deposition of electropositive contaminants (e.g. alkali and alkali earth) on acid sites or the deposition of electronegative contaminants (e.g. N and S) on hydrogenation sites. Fouling is generally related to the deposition of insoluble components that are either present in the feed or formed by degradation of the feed or of the intermediates. Catalyst destruction results from the thermodynamic instability of most oxidic supports, solid acids/bases and hydrogenation functions under hydrothermal conditions (see also [7,9]). The various mechanisms may affect homogeneous and heterogeneous catalysts differently. Catalyst poisoning and destruction affect both homogeneous and heterogeneous catalysts. Fouling is particularly critical for heterogeneous catalysts.

Obviously, homogeneous catalysts also need efficient recovery and recycle processes to reach affordable consumption rates. They are often used at loadings of 1-10w% of biomass feed intake, i.e. 10-100 times above the ratio needed to meet the consumption target of 1/1,000 to 1/100,000 in a single pass operation. Cheap catalysts such as acids and bases may still be affordable (if not sustainable!) at the lower end of the window, even after considering the cost of the additional chemical needed for neutralization. In contrast, expensive catalysts such as organometallic complexes of noble metals may require productivities at the higher end of the window or even beyond. Examples will be provided in the coming case studies.

2.4 Product concentration

The fourth and last key factor for catalyst operation is the product concentration. The industry can accommodate a large window of product concentrations; from a few percent to nearly pure product. Low product concentration are the result of either feed dilution or operation at low conversion per pass (i.e. product dilution in unconverted feed). Whenever possible, the product dilution should be minimized as it comes with significant processing costs. It requires larger equipment to contain, move and heat/cool the larger stream. It also requires larger equipment and higher duties to recover the desired product form the diluted stream. Indeed, the investment cost of manufacturing plants have been shown to largely depend on the amount of energy transfer through heater, coolers, pumps and compressors in the process.[14] Moreover, product dilution also results in lower yields and additional costs as the recycled stream, eventually, becomes contaminated with impurities that need to be purged together with feed and products. The clean-up of this purge stream can also add severely to the cost, e.g. in the form of large waste water treatment plant [13].

Despite the economic penalty, operation at low product concentration may be imperative e.g. for safely accommodating highly exothermic reactions. Indeed, feed concentrations as low as a few w% are often encountered for exothermic reactions that release more than 5 kJ/g product [14]. The most exothermic reactions generally consist of oxidation reactions, which can liberate more than 2 kJ/g product. This family of reactions may be less common with renewable feedstock than with petrochemical ones as the renewable feedstock is already rich in oxygen. However, the second family of exothermic reaction, namely hydrogenation and other addition reactions on double bonds, are very common with bio-based feedstocks. They may still liberate 1-3 kJ/g product and, thereby, may require operation in diluted streams.

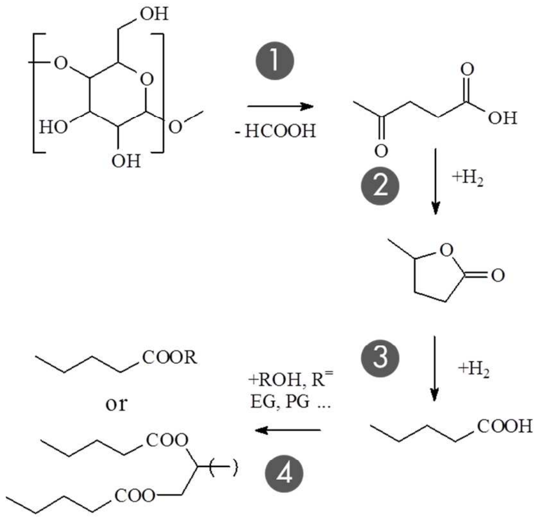
2.5 Trade-off

Obviously, these four parameters are not operating in isolation. Industrial practice often needs to find a real sweet spot. For instance, the conversion of reactive feedstock such as sugars is often accompanied by undesired condensation reactions. High selectivity may then call for high feed dilution and, consequently, low reactor productivity. In other cases, the desired reaction product may be sensitive to degradation either by thermal decomposition or by oligomerization reactions. High selectivity may require moderate reaction temperature and/or moderate conversion per pass, which inevitably results in lower reactor productivity and, possibly, also lower product concentration. Examples of such trade-offs will be provided below in case studies.

3 Case studies with Renewables

The performance criteria discussed above were derived from manufacturing processes that convert fossil resources into fuel and chemicals. However, there is no reason why they would not apply to biomass conversion processes as well. A good example of such application and resulting insight is found in the multi-step conversion of lignocellulose to levulinic acid and, subsequently, to valeric biofuels as illustrated in Figure 2 [16]. Applying these criteria to each step of the process indeed helped identifying the challenges presented by this manufacturing route. These challenges appeared to all reside in the very first step, the conversion of lignocellulose to levulinic acid ('1. Hydrolysis' in Figure 2), which proceeds with low selectivity, low reactor productivity and low product concentration. For instance, the 50 mol% selectivity (based on contained hexose) corresponds to an overall yield of 25 w% when using an hexose-rich feedstock such as soft wood. The first step appears also to proceed with high catalyst loading of about 1 kg of catalyst per kg of product [17], which results in high catalyst consumption of 1 kg/kg if levulinic acid is recovered by neutralizing the acid and distilling of the water. This stresses the need for developing a smart product workup scheme that allows to recover the H_2SO_4 catalyst for recycling back to the reactor. In contrast to the first step, all subsequent steps (#2-4 in Figure 2) were shown to perform within the industrial window, with high selectivity, high productivity and high product concentration.

Eq. 2 readily illustrates the economic challenge of valerate-based biofuels. With a feed cost of \$50/t, a biofuels target price for \$1460/t, i.e. twice the crude price (oil at \$100/bbl and 7.3 bbl/t), and a conversion cost of 4x\$200/t, we find a target selectivity of 58 w%. Such target is already twice the 25w% selectivity observed for the first step only. Similarly, Eq. 3 results in an approximate biofuels around \$2300 per ton of contained valeric acid, using the same feed cost of \$50/t and a conversion cost of \$200/t for each steps and converting the selectivities of Figure 2 from mol% to w%.



		1. Hydrolysis	2. Hydrogen.	3. Hydrogen.	4. Esterific.
Catalyst		H_2SO_4	Pt/TiO_2	Pt/ZSM-5	IER
Selectivity	mol%	50-60%	>95%	>90%	>95%
Productivity	$t\ m^{-3}\ h^{-1}$	>0.1/h	>10/h	>1/h	>0.02/h [(a)]
Concentration	wt %	<5%	>90%	>50%	>50%

Figure 2 – Reaction scheme and key performance factors for converting lignocellulose into valeric biofuels (adapted from [16]; [(a)] the low productivity of step 4 is due to the reactive distillation which integrates reaction and separation)

Such pattern appears to be quite common in lignocellulose conversion: the largest manufacturing challenge resides at the first step of the manufacturing chain, at the conversion of the lignocellulose. In contrast, the conversion of platform molecules is often much less demanding. This trend and the typical challenges encountered in biomass conversion will be illustrated below using a dozen of examples found in literature. We should acknowledge upfront that the papers referred to present new leads for biomass valorisation without claim about commercial viability. The coming analyses may then provide guidance on how to develop these breakthroughs towards commercial viability.

3.1 Lignocellulose conversion

Catalytic pyrolysis has been proposed to convert lignocellulose into olefins and aromatics in a single step. Accordingly, lignocellulose is contacted with an acidic zeolite catalyst, e.g. a Ga-doped ZSM-5 zeolite, at 550-600°C for 30 min, after which the catalyst is regenerated by coke burn-off [18]. The combined yield of olefins and aromatics is reported to amount to ~32 C% (i.e. ~15 w%) of the wood intake.

Let us check the various targets of Table 1 in detail for this very first case. Subsequent cases will be discussed more succinctly.

- Eq. 2 is defining a selectivity target of ~25 w% (i.e. ~50 C%) using feed and product prices of $50 and $1000/t, respectively, using a conversion cost of $200/t. Such target clearly exceeds the 15w% reported for the catalytic pyrolysis.
- Under the conditions evaluated, the reactor productivity can be estimated at ~5 $kg_{prod}/(m^3.h)$, based on a biomass feed rate of 0.35 $t/(t_{cat}.h)$, a yield of 15 w% and a presumed catalyst density

of ~0.1 t_{cat}/m^3 for fluidized bed operation. Such productivity falls about two order of magnitude below the target window of 0.1-10 t_{prod}/m^3.

- The process is operated with a fairly diluted product of ~10 w%. This number is calculated from a feed that consists for about 50w% in biomass and 50w% in lift gas, a product yield of ~15 w% and the deposition of 20 w% (40C%) of the biomass as coke on catalyst.
- With a yield of 15 w% and a catalyst feed ratio of 5.7 w/w, the catalyst consumption amounts to 40 t_{cat}/t_{prod} per cycle. This corresponds to a target of about 2.5 years of operation (40,000 cycles of 30 min) to reach the target consumption of 1 kg of catalyst per t of product.

In conclusion, further developments should mainly aim at increasing the yield and reactor productivity. Increase of product concentration and reduction of catalyst consumption warrant also attention, though to a lesser extent.

Another interesting case study is the production of furfural by acidic steam stripping of bagasse – the lignocellulosic residue of cane sugar production [15]. Here, a gaseous stream of steam containing 1w% HCl is passed through a bed of bagasse at 160°C to dehydrate the contained xylose to furfural and to hydrolyse acetate groups to release acetic acid. Yields are reported to respectively amount to 60 and 90 mol% of the theoretical yield for furfural and acetic acid. When expressed as fraction of the biomass intake, the furfural and acetic acid yields amount of 10 and 3 w%. This is significantly below the ~20 w% yield target (based on \$50/t for bagasse, \$1200/t for furfural and \$900/t for acetic acid). The reactor productivity appears to be two orders of magnitude below target, at 0.5-1 $kg_{furfural}/(m^3_{reactor}.h)$, based on the data reported and a presumed bagasse loading of 20 $g/L_{reactor}$. The product concentration was not very high either, being about 10 and 6 w% for furfural and acetic acid in steam, respectively. Significant improvements are required in these areas.

A third example on lignocellulose is its conversion to bio-oil under acidic hydroliquefaction conditions [19]. Here, 10 w% of birch wood is slurried in a water/organic medium (e.g. water/acetic acid in 40/60 weight ratio) in the presence of 0.4 w% H_2SO_4 and a hydrogenation catalyst (e.g. Pd acetate). The slurry is digested for 1.5h at 200°C under 80 bar H_2 to produce a hydrogenated bio-oil with ~50 w% yield and marginal amount (5w%) of solid residue. The remaining product stream consists of water and smaller amounts of gaseous products. The desired product, the bio-oil, is produced at reasonable yield (50 w%) but consists of a low-value bio-oil rather than of a high-value intermediate. This bio-oil is produced at low concentration of ~5 w% (in the liquefaction solvent) and at modest reactor productivity of ~33 $kg/(m^3.h)$.

These three examples support the conclusion drawn earlier for the valeric biofuels: the challenge in lignocellulose conversion resides in achieving high product yields and high reactor productivity. Wet processes such as the hydrolysis or liquefaction may face the additional challenge of achieving acceptable product concentration. Although not discussed here, overall catalyst consumption is likely to be challenging as well due to the production of aggressive by-products such as carboxylic acids and the presence of electronegative and electropositive contaminants in the lignocellulose, as discussed in more depth elsewhere [8].

3.2 Sugar conversion

Challenges in sugar valorisation will be illustrated through three examples: fructose dehydration into 5-hydroxymethyl furfural (HMF), hydrogenolysis to ethylene glycol and cleavage to alkyl lactates.

The dehydration of fructose into HMF is known to proceed with modest yields when carried out in water. Operation in bi-phasic water/organic media leads to improved yield and easier recovery of HMF from the reaction medium by means of liquid-liquid extraction.[20] Building on these findings, Dumesic et al. reached ~70 mol% HMF yield by processing a 30 w% aqueous solution of fructose at 180°C for ~3 min in the presence of 0.25 M HCl using water/MIBK/SBA as biphasic medium.[21] HMF was then extracted by the organic phase with a distribution coefficient of 1.6. Besides the reasonable selectivity of ~70 mol% (i.e. ~50 w%), the reaction also showed a good reactor productivity of ~1.4 t/(m^3.h). However, the process was run at high dilution and potentially high catalyst consumption. Indeed, fructose was processed at an overall concentration of ~10-15 w%, based on total liquid (i.e. water+organic), and HMF was extracted at ~5 w% in the organic phase. Moreover, the reaction proceeds with high catalyst/feed ratio of 3:1, which implies that some 300 recycles of the HCl-containing water phase are required to achieve the target productivity of 1 t/kg.

In a second example, cellulose was converted into ethylene and propylene glycol with 69 w% glycol yield upon hydrogenolysis at 235°C and 60 bar H_2 using Ni-promoted W_2C/C catalyst operating batch-wise for 30 min [22]. The reaction was operated at high dilution (1 w% cellulose in water), which resulted in a low product concentration of ~0.7 w% and a low reactor productivity of ~14 kg/(m^3.h). No information was provided on catalyst stability but later paper from the same group revealed significant deactivation through Ni and W leaching.

As third example, sugars was converted into methyl lactate in the presence of a Sn-doped beta zeolite slurried in methanol at ~160°C [23]. Yields were reported to reach ~40 mol% from fructose and glucose but ~70 mol% from the dimeric sucrose, which correspond to 40 and 70 w% of contained lactic acid. Such yield looks reasonable as they would allow to produce the methyl lactate at a reasonable cost of ~$800/t of contained lactic acid according to eq. 1, using a sucrose price of $300/t. More challenging is the low product concentration, the low reactor productivity and the high catalyst consumption. The reaction was carried out with low feed and catalyst concentrations (2.5 w% and 1.9 w% in Methanol), likely to minimize undesired condensation of sugars to humins. This results in a low lactate concentration of 1-2 w% only. As the reaction seemed to take 20 hours to reach completion, the resulting reactor productivity did not exceed ~0.8 kg/(m^3.h). Finally, the Sn-Beta catalyst was reported to deactivate by coking, despite the low feed concentration. It could be regenerated by coke burn-off but would likely need some 1,000 regenerations to reach the catalyst productivity of 1 t/kg catalyst, which might prove challenging as the Sn-zeolite would then also need to retain its crystallinity and Sn sites over so many cycles.

These few examples show that the conversion of sugars can present significant challenges for commercial operation. Because of the high functionality and reactivity, acceptable molar yield may require high feed dilution and, thereby, result in diluted product stream and modest reactor productivity. Further development should be focused on raising the feed concentration without losing the selectivity. Catalyst consumption may also be an issue. The conversion of sugar is often run at high catalyst/feed ratios and is often accompanied by the formation of heavy components, often called humins, which are prompt to deactivate the catalyst. Measures should be taken to minimize deactivation and, when necessary allow for regeneration to reach affordable catalyst consumption [8].

3.3 Platform molecules upgrading

The opening example presented various technologies for upgrading levulinic acid, a direct dehydration product of hexoses. We'll discuss here additional examples with platform molecules, some based on the upgrading of furanic intermediates such as furfural and HMF, others based on the upgrading of vegetable oil components, namely glycerol and fatty acids.

Furfural is a potential co-product of levulinic acid as both can be produced simultaneously by acid hydrolysis of cellulosic material that contains both pentoses and hexoses. Interestingly, furfural can be converted into levulinate esters via hydrogenation to furfuryl alcohol and subsequently into acid-catalysed ethanolysis. The ethanolysis reaction was shown to be catalysed by strongly acidic resins and by some zeolites [24]. The reaction proceeded with a yield of 90 mol% (i.e. 106 w% on contained levulinic acid) when carried out at high EtOH/furfuryl alcohol ratio, e.g. in semi-batch or CSTR operation. The conditions allowed a good product concentration (>40w%) and high reactor productivity (750-1500 kg/(m^3.h)). Clearly, all documented factors fall within their commercial window.

Similarly, the hydrogenation of HMF to dimethyl furan was reported to operate within the commercial window. Dumesic et al. combined the 2-phase dehydration of fructose to HMF discussed above with a hydrogenolysis step of the extracted furfural using a CuRu/C catalyst at 200-220°C [25]. The hydrogenolysis step proceeded with good yields of 80 mol% (60 w%). Under gas-phase operation, the hydrogenolysis step proceeded at modest feed concentration (10w% HMF in butanol) but at high rate (~1 $g_{HMF}/(g_{cat}.h)$). This delivered a modest product concentration (~7 w%) but a high reactor productivity (<500 kg/(m^3.h)). Obviously, pre-concentration of the feed to 20-50w% could deliver higher product concentration and even higher reactor productivity.

As for the upgrading of vegetable oil components, glycerol (36 w% in water) was dehydrated to acrolein using a ZrO_2-supported $H_3PW_{12}O_{40}$ catalyst operating at 315°C and a glycerol GHSV of 400 h^{-1} [26]. Here, the selectivity was moderate (70 mol% or 42 w%) and so was the product concentration (~15 w%). However, the reactor productivity was high at 1500 kg/(m^3.h). The conversion dropped from 100% to ~70% within 10 h of operation, indicating the need for frequent regeneration. As reported in another paper [27], a more diluted feed is likely to deliver a higher selectivity at the cost of lower product concentration.

Finally, the other component of vegetable oil, the fatty acids and esters, were decarboxylated to the corresponding C_{n-1} alkanes with ~70 mol% yield (60 w%) over Pd/C operating at 300-360°C and 17-40 bar H_2 or H_2/He mixture within.[28] The reaction was performed batch-wise using undiluted feed and a combination of catalyst loading and reaction time (i.e. 2 w% on feed for ~3h) that corresponds to a reactor productivity of 180 kg/(m^3.h). Raising the catalyst loading to 10 w% (on liquid) for slurry reactor or even to 0.5 t/m^3 for fixed bed trickle-flow reactor would raise the reactor productivity to 900 or >5,000 kg/(m^3.h), respectively. By avoiding feed dilution, the product concentration reached a comfortable level of >60 w%. Regrettably, the batch operation did not provide information on catalyst longevity.

In summary, the upgrading of well-defined platform molecules does not need to present additional challenges when compared to the upgrading of oil and petrochemical intermediates. Yields, productivity and concentration are often within the window of commercial practice.

3.4 Lignin and bio-oils upgrading

As last set of examples, we will consider lignin and bio-oils, which consist of a complex mixture of components, mainly aromatic or phenolic components. These oils often tend to polymerize when processed at high temperature, due to the presence of unstable carbonyl-components. Upgrading of these streams often consist of hydrotreating or hydrodeoxygenation.

As first example, kraft lignin was hydrotreated undiluted using NiMo-catalysts supported on basic oxides (e.g. $MgLaO_x$) under 100 bar of H_2.[29] The desired product consisted of about 50 w% of CH_2Cl_2-soluble components, half of which are valuable monomeric components - phenols, aromatics and (cyclo)alkanes. The other half of the CH_2Cl_2-soluble components are mainly less desirable oligomers with molecular weight up to 2,000-3,000 Da. Taking the whole CH_2Cl_2-soluble fraction as valuable product, the authors achieved a yield and product concentration of both about 50 w%. When operating for 4 h with low catalyst loading (5w% on feed), the authors achieved an acceptable reactor productivity of about ~100 kg/(m^3.h). Even higher reactor productivity, up to 200-300 kg/(m^3.h), may be within reach upon increasing the catalyst loading to 10-15 w% (on liquid) or beyond (e.g. in fixed bed operation).

In a second example, pyrolysis oil was converted into distillate product using a two-stage hydrotreating-hydrockracking process.[30] Hydrotreating was performed over a Pd/C catalyst operating at 340°C and a feed rate of 0.3 L/(L.h), whereas the hydrocracking was performed over an undisclosed metal sulphide catalyst operating at 400°C and a feed rate of 0.4 L/(L.h). The final product was obtained with an overall yield of ~50 w% (based on pyrolysis oil) and exhibited a very low O-content (O/C < 0.01) and an attractive H/C ratio of about 1.6. As the feed was processed undiluted, the overall product concentration amounted to ~50 w% on total effluent (including gas and water). With a yield of 50 w% and feed rates of 0.3 and 0.4 L/(L.h), the reactor productivity of the individual stages were around 100 and 150 kg/(m^3.h). However, the overall productivity dropped below the target of 100 kg/(m^3.h) when calculated over the sum of the two catalyst beds. The paper also reported severe catalyst deactivation and reactor plugging for the hydrotreating stage. Considering the moderate feed rate applied, the catalyst will likely need a full year of operation to reach the target catalyst consumption of 1 kg of catalyst per ton of product.

These two examples illustrate some of the challenges encountered in lignin and bio-oil upgrading, particularly challenges in yield and, likely, in catalyst consumption. These challenges result from the chemical complexity and poor thermal stability of these feeds. Although not discussed in the papers, the potential poisoning of catalyst with contaminants of the bio-oil should not be forgotten.[**Error! Bookmark not defined.**] When processed in undiluted form, the product concentration and reactor productivity may not be as critical.

3.5 Window mapping

The examples discussed in this paper can be used to map the performance window of biomass upgrading to illustrate the potential challenges of the various feedstock (Figure 3). For the sake of clarity, the window has been limited to selectivity, reactor productivity and product concentration. As mentioned earlier, this window mapping does not want to diminish the merits of these pioneering studies but only intents to provide guidance on how to develop these breakthroughs towards commercial viability.

Lignocellulose and, to a lesser extent, bio-oil conversion processes generally deliver low selectivity and productivity. The low selectivity is largely due to the chemical heterogeneity of the feedstock, i.e. the presence of reactive carbohydrates (hemicellulose), recalcitrant carbohydrates (cellulose) and lignin. Lignocellulose fractionation attempts to alleviate this challenge by providing several more homogeneous streams that can be converted with higher selectivity. However, it also increases the complexity and overall conversion cost of the biorefinery. Dilution of feed, e.g. for liquid-phase processing, generally leads to poor product concentration as well and, thereby, further reduces the reactor productivity. This unfortunate combination of challenges explains why lignocellulose biorefineries have a hard time to breakthrough.

As sugar feedstock is chemically more homogeneous, it can converted with better selectivity. This particularly holds for processes that retain the oxygen in the product. Their high reactivity also allow for reasonable reactor productivity when operating at high catalyst loading. However, sugar conversion processes often require high feed dilution to secure good selectivity and, thereby, suffer from low product concentrations.

Well-defined platform molecules may often be processed within the industrial window, in terms of selectivity, product concentration and reactor productivity.

Although not illustrated in Figure 3, catalyst deactivation and consumption can also be a point of concern, being due to fouling, poisoning or destruction.[**Error! Bookmark not defined.**]

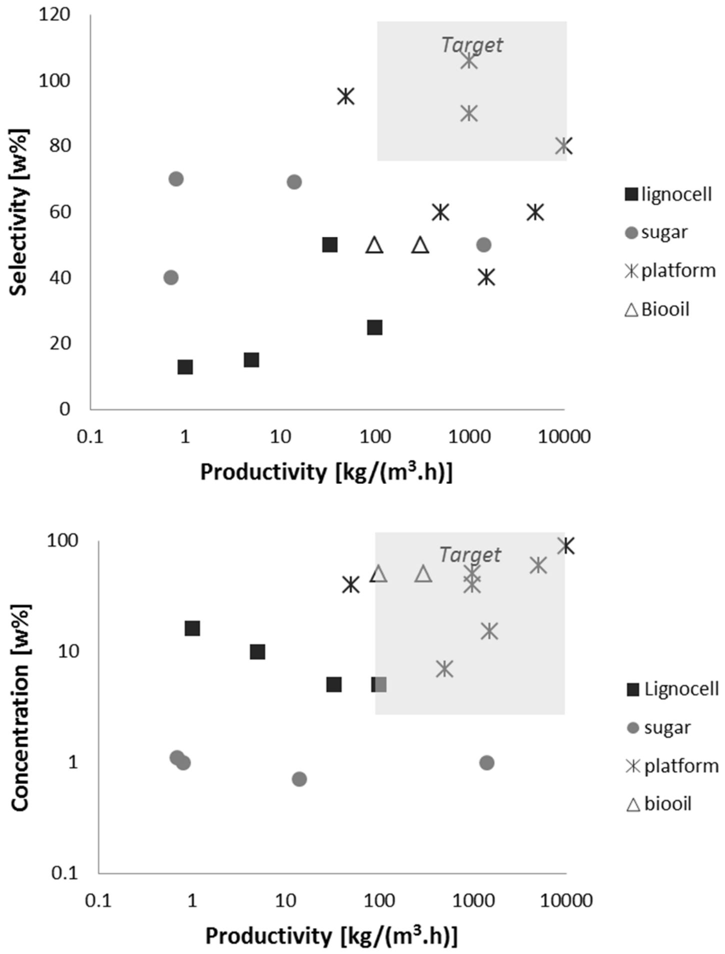


Figure 3 – operating window of biomass upgrading processes

4 Conclusions

Over numerous decades, the oil and petrochemical industry has learned to run conversion processes at industrial scale and industrial economics by meeting a few specific performance criteria: namely selectivity, reactor productivity, product concentration and catalyst longevity (Table 1). Meeting these criteria appeared essential in lowering the cost of feed, energy, catalyst and equipment to affordable levels. There is no reason why these criteria would not equally apply to biorefineries.

Using a dozen of case-studies taken from open literature, we have tried to illustrate how biomass conversion processes perform against these industrial criteria. A few key learnings are worth summarizing:

- Feedstocks that are chemically heterogeneous or over-functionalized such as lignocellulose, sugars and bio-oils, may deliver modest product yields upon upgrading. The value of the resulting products needs to be high enough to compensate for the significant selectivity losses.
- Feedstock that are thermally sensitive (e.g. sugars or bio-oils) may degrade upon high temperature processing and, thereby, lead to catalyst deactivation and poor longevity.
- Well-defined platform molecules do not differ severely from present chemical intermediates in terms of functionality, stability and reactivity. Of all the bio-based streams, they are the easiest to process under industrially relevant conditions.
- Operation with diluted streams, e.g. upgrading of lignocellulose or sugars in liquid phase, generally results in low product concentration and low reactor productivity. It thereby requires large processing equipment and expensive product recovery and purification.
- Overall, biomass deoxygenation is expensive because it results in modest selectivity on weight basis. Indeed, a significant fraction of the biomass is purchased and processed at significant cost but eventually gets disposed of as CO_2 or water waste stream without delivering any return. It seems therefore preferable to use biomass for the production of oxygen-rich products, e.g. chemical intermediates, rather than using it for fuel and base chemicals (olefins and aromatics).

Much research is still needed to push biomass conversion processes into the commercially relevant window (Figure 3). For instance, biorefineries will need technologies that operate with concentrated streams while maintaining high selectivity. They'll need treating technologies that remove contaminants from the feed or, more preferably, conversion technologies that are insensitive to such contaminants. Biorefineries will need a range of catalysts that are performant in and resistant to aqueous media.

The field of biomass conversion is no new research field. It was already an exciting field of research in the 1970s and 1980s, when crude oil reached prices unseen till then. Much can be learned from reading this pioneering literature, starting e.g. with [31,32] and reference therein. Of course, since then the field has made much progress. However, it is still in need of numerous breakthrough to secure humankind with sustainable fuel, chemicals and materials from biomass for the decades to come.

References

1. A. Corma, S. Iborra, A. Velty; Chem. Rev. **2007**, 107, 2411-2502
2. J.-P. Lange, Biofuels, Bioprod. Bioref., **2007**, 1, 39-48
3. J.C. Serrano-Ruiz, R. Luque, A. S. lveda-Escribanoa; Chem. Soc. Rev., **2011**, 40, 5266–5281
4. J.-P. Lange, E. van der Heide, J. van Buijtenen, R.J. Price, ChemSusChem **2012**, 5, 150-166
5. Z. Strassberger, S. Tanase, G. Rothenberg; RSC Adv., **2014**, 4, 25310-25318
6. R. Beerthuis, G. Rothenberg, N.R. Shiju; Green Chem. **2015**, 17, 1341–1361
7. H. Xiong, H.N. Pham, A.K. Datye, Green Chem. **2014**, 16, 4627–4643
8. J.-P. Lange; Angew. Chem. Int. Ed. **2015**, 54, 13186–13197
9. L. Shuai, J. Luterbacher, ChemSusChem **2015**, DOI: 10.1002/cssc.201501148

10. S. Ramaswamy, H.-J.Huang, B.V. Ramarao, in ‘Separation and purification technologies in biorefineries’, Wiley, Chichester, UK, **2013**
11. A.A. Kiss, J.-P. Lange, B. Schuur, W. Brilman, A.G.J. van der Ham, S.R.A. Kersten, submitted for publication (**2016**)
12. Y.-C. Lin, G.W. Huber, *Energy Environ. Sci.* **2009**, 2, 68–80
13. J.-P. Lange, I. Lewandowski, P. Ayoub, in “Sustainable Development in the Process Industry – cases and impacts”, (Harmsen, Powell, eds) Wiley, **2010**, 171-208
14. J.-P. Lange, *CatTech* **2001**, 5, 82-95
15. J. van Buijtenen, J.-P. Lange, L. Espinosa Alonso, W. Spiering, R.F. Polmans, R.J. Haan, ChemSusChem **2013**, 6, 2132 –2136
16. J.–P. Lange, R. Price, P. M. Ayoub, J. Louis, L. Petrus, L. Clarke, H. Gosselink, *Angew. Chem. Int. Ed.* **2010**, 49, 4479 –4483
17. J.-P. Lange, J.W. Gosselink, R. Lee, E. van der Heide, C.J. Schaverien, J.B. Powell, in ‘Industrial Biorenewables: A Practical Viewpoint’ (ed. Pablo Dominguez de Maria), Wiley, **2016**, ISBN: 978-1-118-84372-7
18. Y.-T. Cheng, J. Jae, J. Shi, W. Fan, and G.W. Huber, Angew. Chem. Int. Ed. 2012, 51, 1387 –1390
19. K.L. von Hebel, J-P. Lange, patent application WO 2011/141546 (Shell Int.)
20. B.F.M. Kuster, Starch/Staerke **1990**, 42, 314-321
21. Y. Roman-Leshkov, J.N. Chheda, J.A. Dumesic, Science **2006**, 312, 1933-1937
22. N. Ji, T. Zhang, M. Zheng, A. Wang, H. Wang, X. Wang, J.G. Chen, Angew. Chem. Int. Ed. **2008**, 47, 8510-8513
23. M.S. Holm, S. Saravanamurugan, E. Taarning, Science **2010**, 328, 602-605
24. J.-P. Lange, W.D. van de Graaf, R.J. Haan, ChemSusChem **2009**, 2, 437 – 441
25. Y. Roman-Leshkov, C.J. Barrett, Z.Y. Liu, J.A. Dumesic, Nature **2007**, 447, 982-986
26. S.-H. Chai, H.-P. Wang, Y. Liang, B.-Q. Xu, Green Chem. **2008**, 10, 1087–1093
27. B. Viswanadham, V. Pavankumar, K.V. R. Chary, Catal. Lett. **2014**, 144, 744-755
28. I. Kubickova, M. Snare, K. Eranen, P. Maki-Arvela, d.Y. Murzin, Catal. Today **2005**, 106, 197-200
29. C.R. Kumar, N. Anand, A. Kloekhorst, C. Cannilla, G. Bonura, F. Frusteri, K. Barta and H.J. Heeres, Green Chem. **2015** (DOI: 10.1039/c5gc01641j)
30. D.C. Elliott, T.R. Hart, G.G. Neuenschwander, L.J. Rotness, A.H. Zacher, Environ. Progress & Sust. Engineering **2009**, 28, 441-449
31. H.H. Szmant,, in “Industrial utilization of renewable resources, an introduction’ Technomic Publ. (Lancaster) **1986**
32. D.L. Klaas, in “Biomass for renewable energy, fuels and chemicals, Academy Press (San Diego) **1998**