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PERSPECTIVE

Catalysis for Lignocellulosic Biomass Processing: Methodological Aspects

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Preface

Gabor Somorjai

The Perspective entitled "Catalysis for Lignocellulosic Biomass Proceedings" addresses many of the challenges and opportunities of catalytic conversion of biomass to fuels and chemicals. It should be considered in light of the history of woody biomass conversion for fuels and chemicals both in Finland, where this Perspective originates, and in Sweden, dating back to the Second World War. Of course, the technologies of producing paper from wood without catalysis have a considerable longer history. This description of the chemical structures of lignocellulosic biomass, the catalysts used for selective depolymerization, the analysis of the reactants and products, the catalyst preparation and overview of kinetic and mechanistic studies utilizing different reactor technologies, provides readers with a valuable overview of the challenges of catalytic biomass conversion as it becomes an ever-growing contributor to produce fuels and chemicals.

Abstract Increasing value of lignocellulosic biomass through catalytic approaches is an area, which recently attracted a lot of attention. Due to specific features of such catalysis, different from more traditional heterogeneous catalysis in transformations of petrochemicals, the authors considered important to address various methodological issues, such as product analysis, catalytic measurements, influence of mass transfer, development of kinetic expressions, reactions intensification by application of microreactors and technology development in general. Potential pitfalls, challenges and research opportunities are highlighted.

Keywords · Heterogeneous catalysis · Methodology and phenomena · Processes and reactions

1 Introduction

One of the authors was approached by the editors of *Catalysis Letters* to provide some thoughts about important directions—past, present and future—in the field of catalysis science. Any review (perspective) of this type is pretty subjective, it would take, therefore, an effort of many scientists to formulate more or less balanced view on the future perspectives in catalysis. Such an endeavor was for example recently undertaken by a group of Dutch scientists working in the field of catalysis [1]. The authors [1] formulated a number of research topics for the coming years, such as (a) nanostructured heterogeneous catalysis; including control of catalysts on an atomic scale, precise synthesis, understanding structure/environment/performance relationships, (b) molecular catalytic systems; (c) predictive catalysis, (d) new catalytic conversions emphasizing sustainable/green chemistry approach.

Processing of biomass was mentioned in Ref. [1], as one of the novel conversions (along with other reactions, such as valorization of CO_2 for example) which have attracted a lot of attention recently. This area of biomass utilization is considered nowadays as a promising way to diminish the negative impact on the environment. Moreover, in some future scenarios, renewable raw materials are thought to be able to replace finite mineral-oil-based raw materials before 2050 [2]. This means that new synthetic routes, which should desirably adhere to the principles of green chemistry, need to be developed for production of chemicals.

The structure of biomass-derived starting materials, such as cellulose is totally different from that of present crude

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oil which is the basis of today's fuels and chemicals. It is fair to state that biomass conversion is largely at the infancy, therefore a lot of research is required to implement the concept of biorefinery which could compete with modern refinieries, which were optimized along many decades.

Due to the importance of this topic, hundreds of articles and many dozens of reviews have appeared recently addressing various issues of biorefineries and biomass processing [2–38], confirming a renaissance in this area, which in fact has a long tradition. For example, Rudolf Diesel could be mentioned, who used vegetable oils while developing the engine, which bears his name, one hundred years ago. In many places during the Second World War, such as Sweden and Finland, woody biomass was used as fuel and as a source of chemicals.

As mentioned above, quite a number of papers have appeared in the literature on catalysis in biomass conversion. The authors of the present contribution have also co-authored several reviews [26–31], where different type of reactions, related to catalytic transformation of (lignocellulosic) biomass, have been addressed. Thus we do not feel a need to discuss once again various types of reactions and corresponding catalysts.

An essential part of the research related to catalytic transformations of biomass is connected, however, to a number of other important methodological and engineering issues, which are very seldom covered in the literature and, what is more important, lead to significant drawbacks and deficiencies in many recent publications. Bearing in mind that many scientists turned their attention to catalysis in the biomass conversion, having their background in other fields, there is an urgent need to discuss such issues, even if to some readers the paper will resemble at several places textbook knowledge.

2 Lignocellulosic Biomass

Despite a wealth body of literature on biomass few words could be still mentioned. Lignocellulose (Fig. 1) is the fibrous material that makes up the cell walls of plants, containing cellulose (≈40 wt%), hemicellulose (≈25–30 wt%), lignin (ca. 20 %), extractives (fatty acids, terpenes, stilbenes, and lignans) and inorganic components, including metals.

Cellulose is a linear polysaccharide consisting of glycoside units, the number of which can be as high as 15,000. Such units are linked by β-1,4-glycoside bonds resulting in the formation of the crystal structure of cellulose with intra- and intermolecular hydrogen bonds. The access of homogeneous or heterogeneous catalysts to this bond is limited due to the limited space around the glycosidic bridging oxygen in cellulose, thus cleavage of this bond is a big challenge and it has been a subject of intensive research. Another challenge in the transformations of cellulose through functionalization is related to a possibility of performing reactions in suitable solvents, since cellulose is soluble only in some rather unusual solvents, such as DMSO, concentrated $ZnCl_2$ solutions and ionic liquids. Especially discovery of a possibility to dissolve cellulose in ionic liquids opened a new perspective in utilization and functionalization of cellulose.

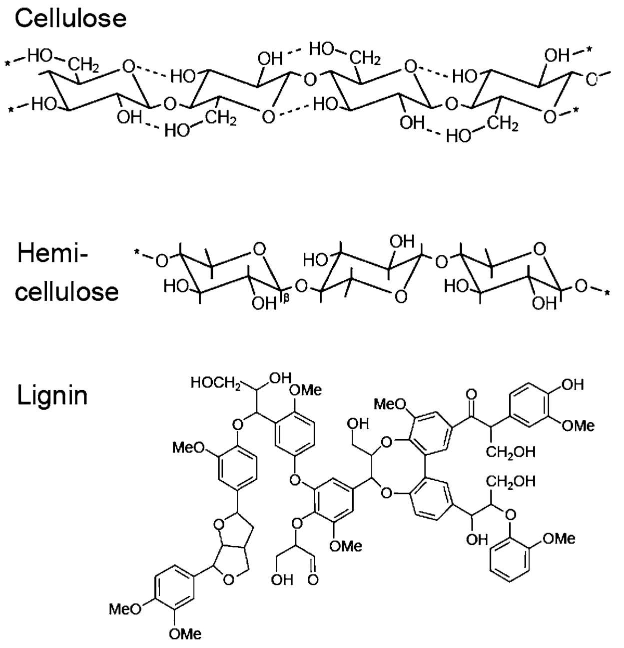


Fig. 1 Structure of lignocellulosic biomass

Hemicelluloses are composed of several monomers, for example arabinogalactan of larch (Fig. 2) has bonded (1, 3) β-galactopyranose as its backbone and D-galactopyranose, L-arabinofuranose, and D-glucuronic acid units in the side chain. The average ratio of galactose, arabinose, and glucuronic acid is close to 5:1:0.08; the molecular mass is (2–10) × 10^4 g/mol. The C6 carbohydrates in hemicellulose are composed of mannose and galactose in addition to glucose; and C5 carbohydrates contain xylose in addition to arabinose. Steric hindrance, due to the presence of side chains and axial hydroxyl groups in different sugars of hemicelluloses, prevents the formation of a crystal structure, promoting reactions with different biomass components, including cellulose.

Once a polymer (cellulose or hemicellulose) is depolymerized, the corresponding monomers can be transformed into valuable chemical substances through various catalytic routes, which could involve homogeneous, heterogeneous, or enzymatic catalysis. Lignocellulose contains not only polysaccharides, but also lignin (see Fig. 1), which is a three-dimensional polymer composed of propylphenol units with coumaryl, coniferyl and sinapyl alcohols as monomers,

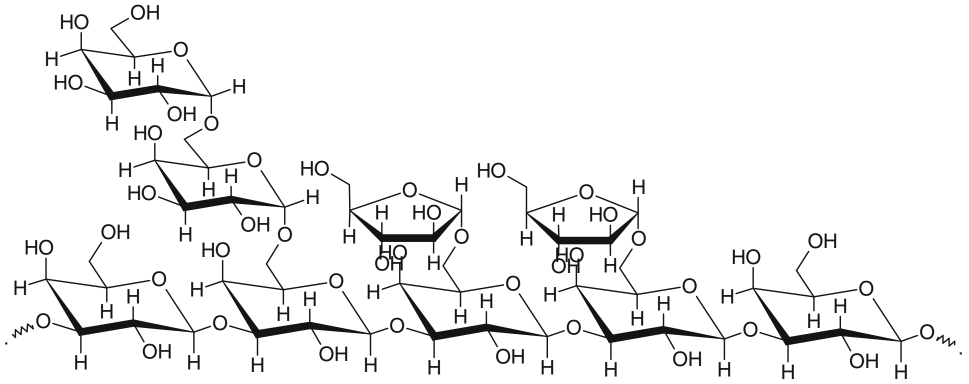


Fig. 2 Arabinogalactan

which are heavily cross-linked leading to complex structures of large lignin molecules. Lignin acts not only as a binder but protects lignocellulose from various microorganisms.

Due to natural variations in the feedstock, any research in biomass conversion should address the following issues: details on where the species/cultivar were harvested—(geo-coordinates), their age—location in the plant where the samples were taken from, their method of storage and processing along the chain of custody from forest or field to the reactors equipment with an aim to allow the research work to be repeated.

In fact preparation of the samples and their retreatment could be very demanding and time-consuming. Since in catalytic transformation of lignocellulosic biomass often wood or various streams from pulping are used as raw materials, a special attention should be devoted to sampling. Inappropriate sampling could undermine the value of the whole study, therefore it should be carefully planned. Sampling and sample storage is important, since samples may be altered or destroyed due to temperature, light, presence of oxygen, humidity, enzymes or microbes (bacteria, fungi, etc.). For instance, enzymatic and microbiological attack can happen for samples of fresh wood, wet pulp and paper, sludge, process waters and effluents, while polyunsaturated extractives such as abietic acid could be subjected to oxidation. Storage in a frozen state (less than −20 °C) gives structural changes in wet, solid materials and physicochemical changes in process waters. Biocides could be added to preserve moist samples. Drying of samples could bring a risk of oxidation, therefore freeze-drying is usually recommended.

Another important issue is variation of impurities depending on the feedstock. Sitosterol hydrogenation could be mentioned as an example. In [39–41] hydrogenation of sitosterol to sitostanol has been studied (Fig. 3). The raw material sitosterol is a product of the pulp and paper industry and contains besides *β*-sitosterol (94 %) also ca. 6 % campesterol (structure 1 in Fig. 3 with R = CH_3) and several impurities such as sulphur (<50 mg/kg), chloride and phosphorus (<20 mg/kg). The products, e.g. phytosterols, such as sitostanol, are known inhibitors of cholesterol absorption and are widely used as functional food ingredients.

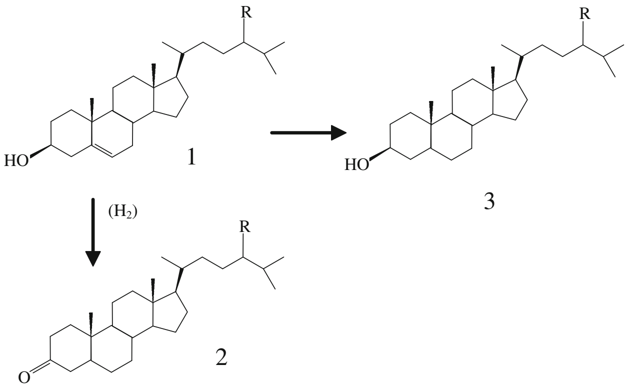


Fig. 3 Reaction scheme of *β*-sitosterol (*1*) transformations into *β*-sitostanol (*3*). R = C_2H_5

As shown in [40] there were significant variations in catalytic activity of the feedstock, associated with its purity.

Another example is pyrolysis of woody biomass, which is sensitive to the presence of such impurities as alkali and alkali-earth metals.

It is, therefore misleading (although often seen by the authors in the literature) to describe reactions of some model compounds, which are petroleum derived and supplied from commercial suppliers, and refer to them as “biomass derived” even if in principle they could be derived from biomass.

It should be also mentioned that in particular biomass from side streams of pulping is not an ideal raw material, because it contains a lot of inorganic impurities originating mainly from pulping chemicals. Selective fractionation of lignocellulosic biomass would be a better way (compared to pulping) to obtain valuable chemicals and fuel components.

3 Reactions and Catalysts

Chemical treatment of lignocellulosic biomass in general, and wood in particular, can have several targets. One of the options is delignification of the biomass leading to cellulose and some residual hemicelluloses, which are further applied in production of paper or board, or cellulose derivatives.

Thermal (or catalytic) treatment of biomass, e.g. thermal or catalytic pyrolysis, is a route to bio-based synthesis gas and biofuels. Milder depolymerization results in the formation of low-molecular-mass components (sugars, phenols, furfural, various aromatic and aliphatic hydrocarbons etc.), e.g. unique building blocks for further chemical synthesis.

Wood biomass contains many valuable raw materials for producing fine and specialty chemicals. These raw materials are carbohydrates, fatty acids, terpenoids and polyphenols, such as stilbenes, lignans, flavonoids and tannins. Some of them can be exuded directly from living trees, while others are extracted and purified via chemical methods. Several reactions of biomass processing such as oxidation, hydrogenation, cracking, etc. are similar to the processes widely utilized in the refining and chemical industries. However, due to the large number of functional (hydroxyl and other) groups, processing of biomass requires also other reactions, such as dehydration, ketonization, aldol condensation, decarboxylation, etc. Moreover in petroleum refining, petrochemistry and chemical industry reactions are often conducted in the gas or in the liquid phase using organic solvents. Contrary to this, catalytic reactions of sugars and polyalcohols occur in aqueous solutions, having specific features. For example, acid catalyzed reactions in chemical industry often involve such solid acids as alumosilicates. These materials (e.g. zeolites) might have insufficient stability in aqueous media, moreover adequate methods are needed for studying their physicochemical properties, which would reflect the state of surfaces in liquid media. The activity and selectivity of such catalysts can be determined as mentioned above by impurities present in the lignocellulosic feedstock, which depend substantially on the type of wood biomass and place of origin.

Criteria for selecting heterogeneous catalysts to be applied in biomass transformations were considered in detail [34]. The selection of carriers for the catalytic reactions of the transformation of alkanes (i.e. for oil refineries) is driven by the requirements to perform these processes at high temperatures. Such inorganic oxides as Al_2O_3 or SiO_2 certainly meet such requirements. At the same time, a number of the processes of biomass treatment (alcohol oxidation or hydrogenation of aldehydes, hydrolysis, and even hydrogenolysis) can take place at much lower temperatures in polar solvents. Such requirements imply that catalysts supports must be stable at different pH in highly polar liquids. Those supports which are only of limited use in classical catalysis due to their low temperature stability, such as for example various polymer carriers, can satisfy the requirements [42]. It could be even advantageous to use such polymeric supports in aqueous solutions as they undergo profound swelling in organic solvents [35], while swelling can be insubstantial in water. The most popular polymer supports are polystyrene and polyethylene, and a particularly interesting carrier could be cellulose, which was reported to be used in several reactions [43].

The pore sizes of micro- and mesoporous carriers are most likely sufficient for the transformation of carbohydrates, while the penetration of microporous materials by polymers or oligomers of biomass can be problematic. Therefore some inhibition of diffusion can be expected, unless terminal groups of these oligomers get access to the actives sites. When such penetration is hindered only external surface of catalysts is available for catalysis. Although from the viewpoint of pore sizes, utilization of macroporous materials could be optimal, however, their pores are too large to provide stearic hindrances, which might be necessary for some selective transformation of organic molecules.

An important feature of carriers is their stability (hydrothermal in particular), which limits the use of some metal oxides, mesoporous materials, and zeolites. For example, alumina can be subject to precipitation and dissolution, depending on the medium. Although activated carbons are usually more stable than alumina, presence of a large number of micropores can prevent reagents to access the active centers. Therefore, utilization of such materials as mesoporous Sibunit and carbon nanotubes and nanofibers could be very promising. The acidity of these carriers (catalysts) could be insufficient for some reactions of biomass transformation, therefore, functionalization of their surfaces with for example sulfonic groups as well as the search for new catalysts are of great interest.

4 Analysis of Reactants

Because of the complexity associated with processing of biomass per se or transformations of biomass-derived chemicals, in depth chemical analysis of all components and their reactions is difficult to perform. Therefore, most analytical methods will be a result of a compromise between information depth and available resources. In industrial processes only a limited number of rather fast analytical methods can be utilized as a large number of samples should be processed.

To have in-depth and molecular-level understanding of the chemical reactions occurring during transformation of biomass not only advanced analytical methods are required, but additionally a broad spectrum of these methods needs to be applied. Let us consider as an example catalytic conversion of cellulose [44] in the presence of hydrogen leading to sugar alcohols. During such depolymerization reaction not only the concentration of carbohydrates and other products in the liquid phase should be measured, but also the crystallinity of cellulose, its morphology, molecular mass distribution and presence of sugar oligomers. The analysis is even more complicated if in this reaction wood is used directly instead of cellulose.

Gas chromatography allows accurate quantification based on internal standards and has a possibility to be combined with a mass spectrometer. On the other hand, only molecules up to about 1,000 mass units can be analyzed, as they should be stable at high temperatures. Therefore, sometimes samples should be processed before the analysis. The last point is important for polar compounds, like for example acids, which should be derivatized. GC and GC–MS analysis in the vapour phase require volatile derivatives that do not adsorb onto the column wall. Different derivatizations for different substances are recommended, e.g. silylation or methylation for extractives, methanolysis and silylation for carbohydrates [45].

Separation by liquid chromatography is performed often at high pressure (HPLC) with solvent velocity controlled by high-pressure pumps, giving a constant flow rate of the solvents. Another important form of HPLC is size-exclusion chromatography, which is widely applied for determination of molecular-mass distributions of dissolved lignin and hemicelluloses, and even cellulose dissolved in ionic liquids. The same method can be used for analysis of extractives and their derivatives, for instance dimers and trimers of fatty acids. In SEC, solutes in the mobile phase (for example THF) are separated according to their molecular size. Smaller molecules penetrate far into the porous column packing material and thus elute later than larger ones.

Among the advantages of LC its non-destructive character could be mentioned as well as absence of derivatization. This technique can handle both small and large amounts and it can be used also for preparative isolation of compounds from mixtures. Contrary to GC there are almost no, or at least much less, limitations in terms of the molecular size. LC in addition can be combined with mass spectrometry, once again without derivatization.

LC–MS provides better sensitivity and selectivity than GC–MS and can be used for quantification of selected substances in complex mixtures. On the other hand, this technique is not very suitable for rapid and reliable identification of unknown compounds. The reason for it is sparse fragmentation as the conditions of ionization are mild. Moreover, spectra libraries enabling identification are not available. Other shortcomings of LC–MS such as rather low sensitivity of the detectors for certain compounds could be mentioned.

The choice of analytical method depends on many issues, including complexity of the reactant mixture. It could be also mentioned that chromatography can be used for both separation of a compound from the mixture and for quantification and identification. What should be also considered that no heavies (leftovers), which are difficult to vaporize, should remain in GC column and significantly influence subsequent analyses. Thus regular control of retention times and response factors, as well as column cleaning or replacement in due time should not be overlooked.

Another example worth considering is the gas-phase catalytic transformation of levoglucosan over zeolites. In [46] for HPLC analysis of reaction products an acid Aminex cation H+ column with sulfuric acid (0.005 M) as a mobile phase with a flow of 0.5 ml/min at 338 K was used, in addition to an Aminex HPX-87C column and mobile phase—calcium sulfate (1.2 mM) with a flow rate of 0.4 ml/min at 353 K. Figure 4 illustrates that the separation is very much dependent on the analytical conditions.

Stability of the samples is another important issue, which should be also carefully considered, as illustrated in Fig. 5. Samples stored in a freezer exhibited another peak, which is certainly a result of transformations happening during storage.

The analytical procedures reported in the literature sometimes are very incomplete, because of the objectives of a particular study and available resources in terms of instruments, time, costs and human skills.

The main hurdles on the way of developing a reliable analytical method for a particular application are associated with a lack of time to check methods described in the literature, a certain trust in already published procedures, even if they are far from being perfect, as well a pressure from granting agencies/sponsors to get “real” catalytic results rather than developing or checking analytical methods. In the latter case there is certainly more glory in developing new methods, compared to just checking the old ones [45].

5 Catalytic Measurements

Since catalysis is a kinetic phenomenon, elucidation of kinetics is a vital part of any catalytic research, including transformation of biomass. A heuristic approach includes first collecting all the possible data during the experiments as a function of the parameters which are deemed to be important, i.e. concentrations, temperature, pressures, pH, catalyst concentration, volume, etc. Then the rate constants are estimated by regression analysis and the adequacy of the model is judged based on some criteria (like residual sums and parameter significance).

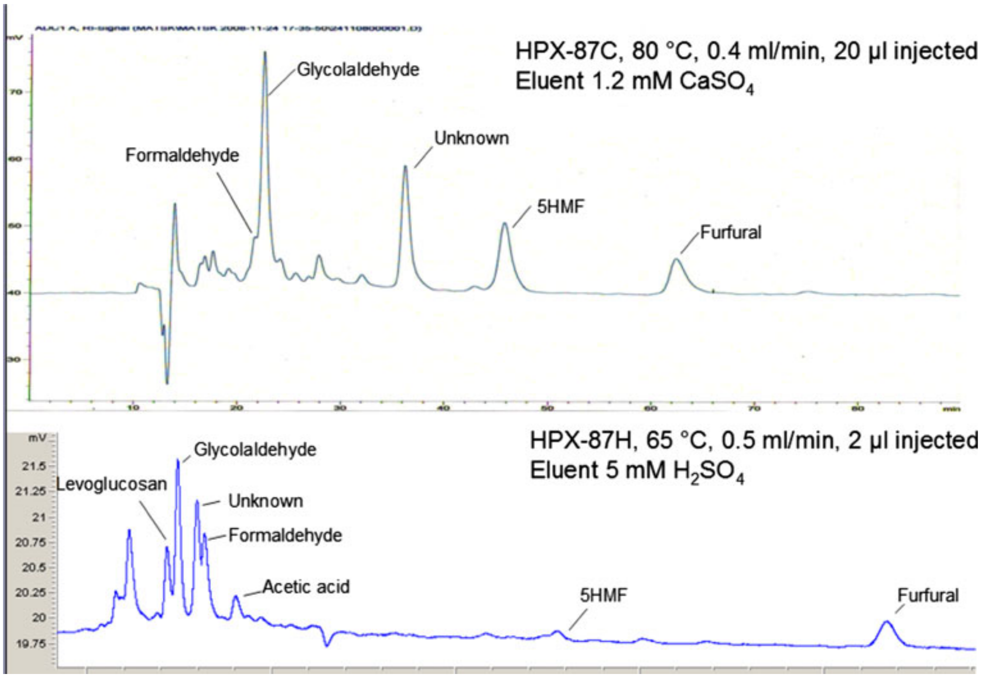


Fig. 4 Analysis of a levoglucosan transformation mixture by HPLC with two different columns

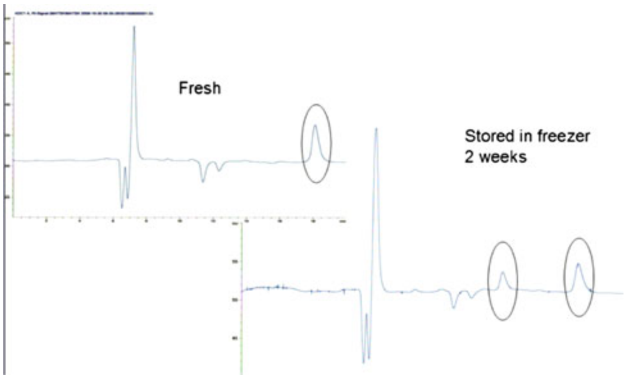


Fig. 5 HPLC data showing instability of reaction products in levoglucosan transformations

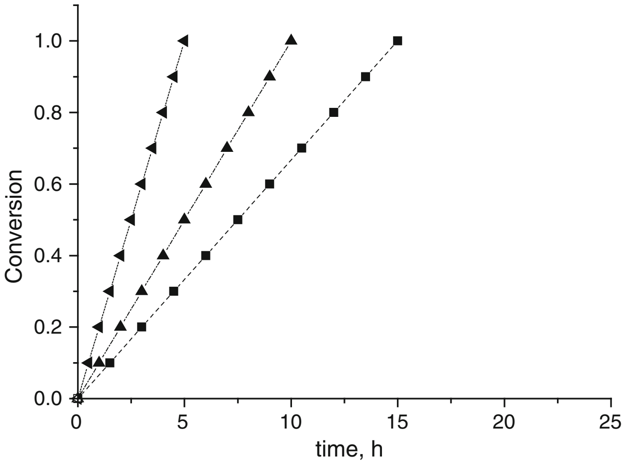


Fig. 6 Concentration versus time dependence for difference catalysts (see explanations in the text)

Unfortunately on many occasions kinetic calculations are based on erroneous data. Let us consider as an example Fig. 6. As obviously follows from this figure conversion after a certain period of time reaches 100 % independent of the catalyst applied. Often reported values of 100 % conversion after say 24 h and TOF values are thus misleading, since catalysts have very different activity.

Traditionally, in designing kinetic experiments, it is believed that kinetic data should be obtained under isothermal conditions. Nowadays, it is possible technically to perform experiments under for example rising temperature gradient to the set temperature, as the temperature profile can be followed on-line. The temperature dependence of the kinetic model is incorporated in the temperature dependencies of the rate and equilibrium constants and the parameters are determined by non-linear regression.

As very well known the first task in the design of experiments for a reaction system is to define the feasible area of the experimental domain, which is typically constrained by temperature, pressure, concentrations, solubilities, slurry density, mixing effects, kinetic rates, mass transfer rates, reaction enthalpies, heat transfer rates and the thermal stability of the species in the reaction medium. The preferable procedure is to try to separate the reaction kinetics from transfer phenomena and to carry out kinetic experiments under mass transfer free conditions to measure the real chemical kinetics and not the apparent mass transfer limited pseudo-kinetics. This means in practice that the experiments should carried out at lower temperatures and at lower catalyst loadings with small catalyst particle sizes and with efficient mixing to ensure that the rate limiting step is pure reaction kinetics and slower than the slowest mass transfer phenomena (dissolution rate, gas–liquid- or liquid–solid-transfer rate or intraparticle transfer rates).

In any catalytic system not only chemical reactions per se but mass and heat transfer effects should be considered. For example, mass and heat transfer effects are present inside the porous catalyst particles as well as at the surrounding fluid films. In addition, heat transfer from and to the catalytic reactor gives an essential contribution to the energy balance. The core of modeling a two-phase catalytic reactor is the catalyst particle, namely simultaneous reaction and diffusion in the pores of the particle should be accounted for. These effects are completely analogous to reaction–diffusion effects in liquid films appearing in gas–liquid systems.

Gas–liquid diffusion is present in heterogeneous catalysis for three-phase systems (three-phase catalytic hydrogenations or oxidations) as illustrated in Fig. 7 [47]. Moreover, the mechanism for the transport of mass and heat is different from the one for chemical reaction, therefore different dependences on concentration can also be expected. Mechanistic interpretations of catalytic results should be thus done with a clear understanding about the influence of mass transfer.

In a porous catalyst particle, the reacting molecules must first diffuse through the fluid film surrounding the particle surface. This is followed by diffusion into the pores of the catalyst, where a chemical reaction takes place on active sites. For most common reaction kinetics, the reaction rates, therefore, inside the pores have lower values than what would be expected with the concentration levels of the main bulk.

In general, a numerical solution of the catalyst particle model is necessary to obtain the concentration profiles inside the particle. For some isothermal steady state systems and ideal geometric forms (slabs and spheres), it is possible to obtain analytical solutions of the model. Typically the results are presented in form of the effectiveness factor, which for an isothermal irreversible first order reaction in a spherical catalyst particle becomes

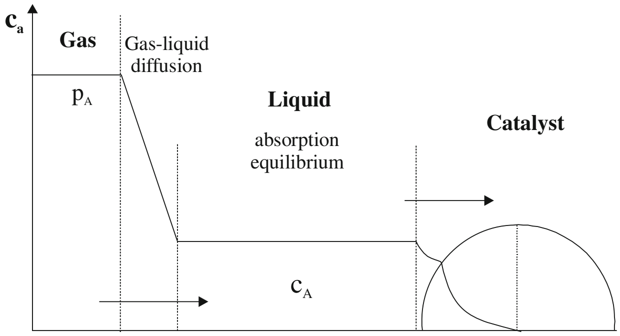


Fig. 7 Mass transfer processes in three-phase systems [47]

$$\eta = \frac{3}{\phi}\left(\frac{1}{\tanh(\phi)} - \frac{1}{\phi}\right) \tag{1}$$

where Thiele modulus (φ) is given by

$$\phi = R\sqrt{\frac{k\rho_p}{D_e}}. \tag{2}$$

In the equation above the units for the rate constant are [m^3/(s kg)] and R is the radius of catalyst particles, D_e is the effective diffusion coefficient. Equation (2) shows that the Thiele modulus and consequently the effectiveness factor depend strongly on the size of catalyst grains. When $\varphi \gg 3$, the following dependence is valid $\eta \propto 1/\phi$. Obviously in laboratory scale reactors the size of catalyst particles can be rather small to diminish the impact of internal diffusion, while in fixed bed pilot reactors due to increased pressure drop the size of catalyst grains is unavoidably much higher resulting in significant influence of internal diffusion. For slurry reactors, even at the pilot stage the size of catalyst powder could be still in the range of 50–100 μm, which in most cases (i.e. when catalytic reactions are not very fast) is sufficient to eliminate internal diffusion. However, external diffusion limitations can still play a role.

It is worth mentioning that in many papers even in the journals with a high impact factor, size of catalysts grains is not even mentioned, thus influence of internal diffusion remains obscure.

Considering the effect of internal mass transfer limitations on the observed kinetics it was shown [47] that not only activity but kinetic regularities (reaction orders/selectivity) can also change when going from a lab to pilot scales, e.g. increasing the size of catalyst particles.

Probably the most widely applied criterion to elucidate the influence of mass transfer is the one for internal mass transfer limitations in an isothermal catalyst particle, i.e. for pore diffusion. Due to Weisz and Prater [48] no pore diffusion limitation occurs, if the Weisz modulus

$$\Phi = \frac{r_{obs}R^2}{c_s D_e} = \phi^2\eta \tag{3}$$

for the first order reaction is below unity ($\Phi < 1$), for zero-th order reaction $\Phi < 6$ and for the second order reaction the Weisz modulus is below 0.3. In Eq. (3) r_{obs} is the observed reaction rate.

An experimental approach, which is usually recommended to verify the impact of internal diffusion, is to perform experiments with catalyst of different particle sizes.

The liquid–solid mass transfer coefficient can be estimated from the correlations provided in [48]. The method is based on the estimation of Sherwood number (Sh), starting from Reynolds (Re) and Schmidt (Sc, $Sc = \nu/D$) numbers,

$$Sh_i = a\mathrm{Re}^{\alpha}\, Sc_i^{\beta} \qquad (4)$$

where Sh = $k_{Li} \cdot d_p/D$.

For fixed bed reactors the following correlations [47] were proposed in case of gas–solid $Sh = 0.357/\varepsilon_p\ \mathrm{Re}^{0.641} Sc^{1/3}$ ($3 < \mathrm{Re} < 2{,}000$) and liquid–solid reactions $Sh = 0.25/\varepsilon_p\ \mathrm{Re}^{0.69} Sc^{1/3}$ ($55 < \mathrm{Re} < 1{,}500$) and $Sh = (1.09/\varepsilon_p\ \mathrm{Re}^{1/3} Sc^{1/3}$ ($0.0016 < \mathrm{Re} < 55$). Here ε is the interparticle void fraction of the bed of particles. If the values of Re and Sc numbers are known, then the Sherwood number can be calculated and consequently the mass transfer coefficient (k_{Li}) can be determined.

For slurry reactors several correlations were proposed in the literature, which relate the dimensionless Sherwood number to the Reynolds and Schmidt numbers. Data, collected in [49] for various slurry reactors, where high agitation velocities are used, showed that the Sherwood number can be described by the following equation $Sh = 1.0\mathrm{Re}^{1/2} Sc^{1/3}$. In the case of low Reynolds numbers, this equation should be modified to contain a correction term, which accounts for mass transfer in the absence of stirring, as in the correlation of Sano $Sh = 2 + 0.4\mathrm{Re}_d^{0.5} Sc^{1/3}$. The dependence of the Reynolds number on the local velocity can be established in terms of Kolmogorov theory of turbulence

$$\mathrm{Re}_d = \left(\frac{\varepsilon d}{\nu^3}\right)^{1/3} \qquad (5)$$

which leads to the following equation

$$k_{LS} = \left(\frac{\varepsilon D^4 \rho}{\eta\, d_p^2}\right)^{1/6} \qquad (6)$$

where ε denotes the specific mixing power, D^o_{AB} is the mutual diffusion coefficient of solute A in solvent B, ρ is solvent density, η solvent viscosity, d_p is the diameter of the catalyst particles (instead of it for gas/liquid mass transfer d_{bu}, i.e. the diameter of gas bubbles, should be applied). Theoretical calculations of the maximum specific mixing power are based on the assumption that all of the energy of the impeller is dissipated in the liquid.

A common test to verify if mass transport controls a catalytic reaction in three phase systems is to vary the rate of agitation. Agitation of a reaction mixture is usually done by stirring, although reactors in the form of shakers are also used for laboratory purposes. The mass transfer coefficient depends on the energy dissipation (as seen in Eq. (6)), the latter is a function of mixing power W, often related to the stirring speed according to $W = K\rho_{\mathrm{liquid}} n^3 d^5_{(\mathrm{stirrer})}$, where n is the stirring speed, K is a constant and d_{stirrer} is the stirrer diameter. The dependence of the mass transfer coefficient on stirring speed is therefore $k_{LS} \propto n^{1/2}$. If the rate is independent on the agitation efficiency at sufficiently high stirring speed, then it is conventionally assumed that the mass transport effects are minimized.

However, it should be kept in mind, that energy dissipation can have a more complex behavior depending on the selection of solvent, stirring rate, liquid volume and design of the reactor internals. Experiments with a 0.5 l autoclave [50] demonstrated that the dissipation power at high stirring rates in fact does not follow the square root dependence of mass transfer coefficient on the stirring speed. Moreover, the energy of dissipation depends on the liquid load in an autoclave or a shaking reactor [51]. At higher liquid load, increasing the shaking frequency did not lead to improved energy dissipation [51], therefore the rate of catalytic reactions could be independent of the agitation simply due to the fact that the mass transfer coefficient is the same. This shows an apparent danger of establishing the kinetic region based exclusively on the results of catalytic experiments at different stirring speeds, since the independence of catalytic activity on the agitation could be explained simply by the fact that higher stirring speed or shaking frequency does not necessarily influence the specific mixing power. Therefore, experimental verification of the absence of mass transfer should be combined with calculations.

Not only catalytic activity but also selectivity can be influenced by mass transfer phenomenon. Analytical treatment is available for simple reactions and as the complexity increases, numerical treatment becomes necessary. For a consecutive reaction sequence A ⇒ B ⇒ C in a batch reactor when the rate equations are of the first order the differential selectivity towards intermediate B is lower when internal diffusion plays a role.

6 Kinetic Analysis

Derivation of kinetic equations, including a microkinetic approach, is a part of many textbooks in heterogeneous catalysis and reaction engineering, thus there is no need to comment in detail on these issues and we would like to stress few selected topics, such as for example incorporation of multi site adsorption in kinetic modelling, catalyst deactivation and cluster size dependences in kinetic equations.

It should be mentioned that the size of organic molecules derived from lignocellulosic biomass is ca. 0.5–1 nm. The size of reacting molecules and multicentred nature of adsorption is rather seldom taken into account in kinetic modeling [52–54]. Cabrera and Grau investigated methyl oleate hydrogenation and isomerization and established that *cis*- and *trans*-methyl oleate could cover up to eleven sites [55, 56].

In [57] the number of Pd surface atoms needed for the adsorption of a single molecule of a natural lignan hydroxymatairesinol, extracted from wood knots, was elucidated to be equal to 20 by molecular modeling and this number was utilized in kinetic modeling. As an area of ca. 1.6 nm^2 is thus required for adsorption of hydroxymatairesinol and the size of a metal cluster is typically in the range of 1–4 nm, only few molecules could be adsorbed on the surface. Even for smaller reactants like carbohydrates or levoglucosan the size of such reactants could be in the range of 0.5–0.7 nm, imposing a severe restriction on the number of adsorbed molecules per cluster.

In catalysis involving complex organic molecules with different functional groups, not only the number of sites, but also the mode of adsorption, requiring different number of catalytic sites, is important and should be taken into account in kinetic modelling.

Another important feature of catalytic reactions in biomass processing is deactivation leading to time-dependent catalyst activity factor (a). Due to the industrial importance of deactivation, various kinetic models that account for the deactivation have been advanced. Probably the most frequently used approach is based on different empirical and semi-empirical equations, with activity having the form

$$-\frac{da}{dt}=f(c_i,T)\varphi(a) \tag{7}$$

where $\varphi(a)$ is a function of catalyst activity, e.g. deactivation function, often expressed in terms of time. Time, however, is not a true variable, as it can lead to incomplete predictions. More correctly, the deactivation function has to be expressed in terms of the deactivating agent itself: the coke precursor or the poison, which means that the amount of coke (or poison) on the catalyst site should be known. The determination of a rate equation for the formation of the coke precursor is thus an integral part of a kinetic study.

Contrary to experiments in fixed bed continuous reactors, where the activity changes are easily observed as a function of time on stream, deactivation of catalytic reactions performed in batch modes can be obscured, as the observed behavior can resemble first order kinetics or reversible kinetics. It is advisable, therefore, to perform experiments under identical conditions recycling the catalyst.

Due to the progress in the physical methods of nanomaterials characterization and advances in synthesis procedures there is a revival of the interest to the problem of structure sensitivity, i.e. dependence of the rate on the particle size [58–65].

It should be noted that variations in the activity in the domain of 2–20 nm could be dependent not only on the size of cluster per se, but can be influenced by the size of reacting molecule as well.

Size-dependent kinetics on a quantitative level is very rarely described in the literature. A chemical explanation for the cluster size effect was discussed in [66], where a cubo-octahedral representation was utilized, and the reasons for the cluster size effect was attributed to differences in the activation energy for low and high coordinated surface atoms (edges and terraces). The TOF (v) as a function of the cluster size for a two step sequence

$$\begin{aligned}&1.\ \mathrm{Z}+\mathrm{A}_1\leftrightarrow\mathrm{ZI}+\mathrm{B}_1\\&2.\ \mathrm{ZI}+\mathrm{A}_2\rightarrow\mathrm{Z}+\mathrm{B}_2\\&\quad\mathrm{A}_1+\mathrm{A}_2\leftrightarrow\mathrm{B}_1+\mathrm{B}_2\end{aligned} \tag{8}$$

where A_1, A_2 are reactants, B_1, and B_2 are products, Z is the surface site, I is an adsorbed intermediate and step 2 is irreversible, could be written [66]

$$v(d)=\frac{p_1e^{(1-\alpha)\chi/d_{cluster}}}{1+p_2e^{\chi/d_{cluster}}} \tag{9}$$

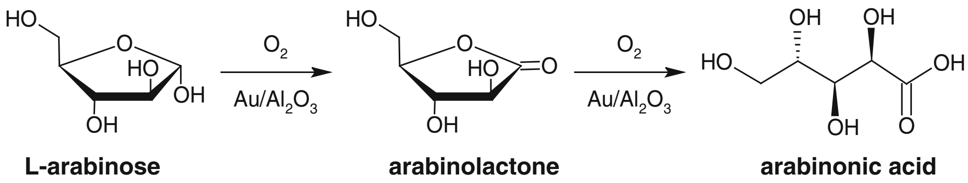
where $\chi=(\Delta G_{ads,edges}-\Delta G_{ads,terraces})/RT$. Theoretical analysis of Eq. 9 demonstrated [66] that the position of the maximum in turnover frequency depends on the cluster size and that reaction parameters (partial pressures of reactants) can influence this position.

An example of cluster size dependence of the activity on the cluster size related to catalytic transformations of biomass derived chemicals, is oxidation of sugars over gold catalysts [67, 68], in particular selective oxidation of arabinose to arabinonic acid (Fig. 8). Au/Al$_2$O$_3$ catalysts with varying metal dispersion were synthesized using different preparation methods and conditions [67]. An increase of the particle size was observed with an increase in the concentration of the initial HAuCl$_4$ solution as well as calcination temperature [67, 68]. It was demonstrated that arabinose as well as galactose oxidations are structure sensitive. The activity has a volcano relationship with a maximum at the cluster size 2.3–2.6 nm. This relationship was explained by the cluster size depending availability of low-coordinated atoms, which are the active sites for the oxygen activation, the arabinose adsorption and the dehydrogenation of the anomeric carbon. A kinetic model, explicitly considering the cluster size, was based on a theoretical approach [66] and was utilized in [67, 68] to obtain a quantitative description of the cluster size dependence data (Fig. 9).

7 Preparation of Tailor Made Nanocatalysts

Structure sensitivity and changes in selectivity depending on the cluster size call for a development of new tailor

Fig. 8 Oxidation of arabinose



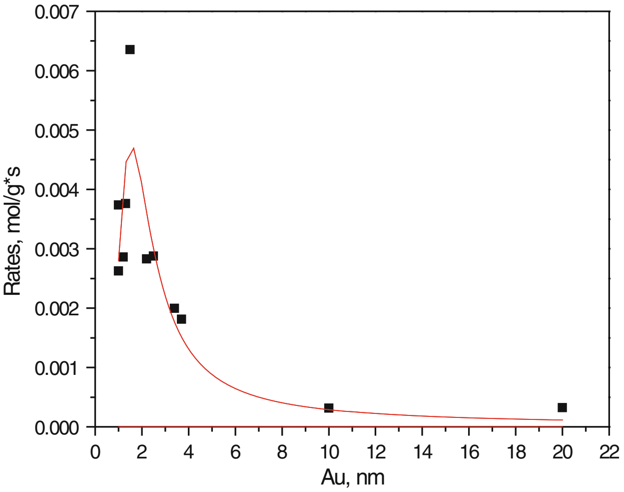


Fig. 9 Dependence of initial rates in arabinose oxidation on the gold particle size of Au/Al_2O_3

made heterogeneous catalysts with high activity and selectivity [63, 64, 69]. Cluster size distribution as well as the shape control is difficult to achieve at industrial level using conventional wet method. One of the emerging strategies for catalyst preparation leading to uniform particles distribution, is to apply colloidal medium in preparation of monodispersed metal particles [63, 70].

Although on a conceptual level it is clear that nucleation and growth theory is the cornerstone of preparation methods, there is surprisingly very little quantitative description in the contemporary catalytic literature of the size evolution of metal clusters, that would relate the final size of nanoparticles with the preparation parameters, such as for instance number of hydroxyl groups on the support, point zero charge, precursor concentration, energy dissipation during stirring, etc. An excellent text book [71] contains just one equation. Not only textbooks but often original publications devoted to catalyst preparation lack any quantitative analysis. Another example worth mentioning is a collection of contributions from a conference on scientific bases of heterogeneous catalyst preparation [72]. An otherwise comprehensive snapshot of current activities in the field (1,000 pages) does not contain a single equation, related to catalyst preparation.

At the same time there is a significant body of literature devoted to kinetic and thermodynamic analysis of nanoclusters nucleation and growth, described in monographs and textbooks [73, 74]. An excellent review on the kinetics and mechanism of formation of supported nanoparticle heterogeneous catalysts appeared recently [75].

A thermodynamic approach to evaluate the cluster size evolution was adopted in [76] and was concerned with the preparation of several gold catalysts supported on various inorganic supports with different point zero charge by deposition precipitation with urea, showing inverse dependence of the cluster size on relative point zero charge (difference between *pzc* and deposition precipitation pH in relation to *pzc*). The key element in the thermodynamic model was the dependence of the interfacial energy on the electrostatic interactions of nanoparticles with the support, which were in turn related to relative approach to *pzc* during deposition precipitation. Experimental data were compared with the theoretical model, showing a possibility to utilize the theoretical approach to predict the cluster size of gold particles supported on titania, silica, alumina (e.g. materials with pH higher than point zero charge *pzc*) having monomodal distribution, while trimodal distribution, theoretically predicted for alkaline magnesia with *pzc* close to 12, was in line with experimental data.

8 Mechanistic Studies

It is fair to state, that understanding of catalytic chemistry on the molecular level is required for further progress in using catalysis for biomass processing.

Several important issues of catalyst development for biomass processing including characterization aspects were nicely summarized in [34]. Many surface science techniques require removal of moisture and were mainly used in studying catalytic transformations in gas phase reactions. For biomass related research such methods as IR, UV, and Raman spectroscopy, as well as attenuated total IR reflectance are applied, in particular for reactions of carbohydrates and their derivatives.

Characterization of catalysts and their surface properties should be preferably done in situ or in conditions relevant to catalysis, since surface properties can depend on the pH of the solution, presence of surfactants, type of solvent, and ionic strength of the solution. While surface properties of such materials as zeolites are usually elucidated by means of temperature programmed desorption or adsorption of such probe molecules as pyridine or ammonia from the gas phase, the relevance of such properties to catalytic measurements in the liquid phase should be carefully considered not only for zeolites, but even for alumina, which is hydroxylated in water media.

Theoretical (DFT) calculations, which are used in parallel with catalyst characterisation and kinetic data to reveal underlying reaction mechanisms should consider rich conformational behavior of biomass derived molecules [77], size of clusters, which could be of the same dimension as the size of reacting molecules [78] and presence of water [79].

9 Intensification Aspects

During the recent years, a lot of research activities were devoted to carrying out reactions in a small scale. The development of manufacturing technology has enabled to produce miniature components for micro- (micro-structured, microchannel) reactors with dimensions of channels typically ca. 10 µm–2 mm. Microreactors can easily provide short residence time, provide or remove the heat and allow sufficient mass transfer. The reduced dimensions in microreactors and high ratio of surface area to volume make them applicable for reactions, which need efficient heat and mass transport properties. This in turn allows utilization of catalysts during highly endothermic or exothermic reactions, which otherwise will result in deterioration of catalyst activity. Thus, reactions can be performed under more aggressive conditions with higher yields that can be achieved with conventional reactors and new reaction pathways can be pursued in microreactors.

On-site production enables the use of chemicals at the place of production, thus avoiding the transportation and storage of dangerous materials. These factors besides improving safety may also improve economics. Safety of microreactors is based on a small reaction volume, which leads to a small inventory of dangerous chemicals. In addition, the efficient heat transfer resulting from the high surface-to-volume ratio improves temperature control and therefore, decreases the risk of run-away reactions. Therefore, it is also possible to use higher operating temperatures safely. This increases the reaction rate and might lead to a smaller reaction volume. Applying microreactors to on-site production should combine the above mentioned advantages and introduce new ones.

One of the main challenges in micro fluidic chemistry is in the introduction of catalytic particles in microreactors, therefore substantial efforts in the microreactor community are put on catalyst preparation methodology [80]. Conventionally catalysts are prepared by impregnating metal compounds from aqueous or organic solutions, although other techniques as catalyst powder deposition, sputtering, atomic layer deposition were also reported.

For particular cases of biomass processing it can be mentioned that stability of the washcoating in water solutions of for example carbohydrates can seriously deteriorate catalytic performance. As illustrated in Fig. 10 the catalytic washcoat has been almost totally removed from the lower plate, and, in the upper plate, an estimated washcoat loss was 30 % after hydrogenation of water solution of galactose at 120 °C (experimental data of Dr. Kalle Arve from Åbo Akademi University).

Another important issue in microreactors is maldistribution of the reactants, which could be even more severe for gas–liquid–solid reactions, than for gas–solid reactions. As shown in Fig. 11, the liquid and gas flows inside the microplate are not evenly distributed, which is related to the washcoating thickness and the mode of gas/liquid introduction in the reactor. Thus gas was preferentially flowing through some channels (darker ones in Fig. 11) of the microplate, while the liquid goes mainly through the rest of the channels (whiter channels in Fig. 11).

One might pose a question: are microreactors really the future of basic biomass conversion? The authors are rather cautious in giving a positive answer and suppose that maybe other structured reactors, including solid foams, are more probable alternatives to conventional slurry reactors.

10 Technology Development

Sometimes in the literature related to catalysis in biomass processing there are claims about developing a new technology. It should be kept in mind that many processes are controlled by other factors than the catalysis per se. A detailed overview of these factors was recently discussed [81] pointing out that market situation, costs of equipment changes and development of a new catalyst, investments costs, energy costs, the added processing costs of operations like compression, distillation, purification, separation, can have an impact on implementation of a novel process into the commercial scale.

Fig. 10 Microreactor after experiments with galactose hydrogenation

Fig. 11 Non even flow pattern in a microreactor

A very important point which should be accounted is the quality of the feedstock at the various stages of technology development. There is probably no general opinion how this issue should be handled. It is generally recognized in industry that preliminary laboratory studies, aimed for instance at initial screening of potential catalysts, could be performed with a model feedstock. Studies on intrinsic kinetics and evaluation of the influence of internal mass transfer could be done with the laboratory feedstock as well. In case of batch operations there is not only a desire from the end-user of process development to utilize the real feedstock, but rather often a possibility to utilize such feedstocks as early as possible in scaling-up. It should be, however, kept in mind that utilization of real feedstocks can mask the intrinsic kinetics, since it may influence for instance catalyst deactivation.

Considering as an example scaling up a three phase catalytic reaction to a pilot, often catalyst screening is done in autoclaves with a model feedstock. This gives a possibility to study experimentally intrinsic kinetics and internal diffusion. Thereafter, it could be recommended to utilize a real feedstock already at this lab scale. The following step of investigating external diffusion could comprise experiments in an autoclave containing a basket with a catalyst in the form of pellets or/and in a trickle bed/upflow reactor. While model feedstocks are advised to use at this stage to get a picture on internal/external mass transfer it is important to perform at least some experiments with the real feedstock already at this stage.

11 Final Remarks

We would like to summarize some challenges and perspectives in biomass processing in general.

- Separation of the components of lignocellulosic biomass is far from being trivial and should be done with selective extraction.
- Each fraction should be treated in a specific ways: cellulose, lignin, hemicelluloses and extractives using catalysis (homogeneous, heterogeneous and enzymatic)
- More knowledge on the specific catalysis for transformation of lignocellulosic biomass is urgently needed
- Deactivation of traditional heterogeneous catalysts used in biomass processing is a very serious issue
- Products separation can be a bottleneck, since conventional methods of separations used in chemical and petrochemical industry (e.g. distillation) cannot be readily applied in many instances, therefore such methods as preparative chromatography, nanofiltration, ion-exchange, etc., should be utilized.

Thus research on catalytic transformations of biomass should consider the process in its entity, e.g. not only the catalytic reactions per se (which certainly brought new exciting chemistry to the research community, specializing in catalysis), but other essential steps, such as feedstock purification/separation as well as separation of products.

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