Reaction Network upon One-pot Catalytic Conversion of Pulp

Johan Ahlkvist[a], Samikannu Ajaikumar[a], William Larsson[a], Johan Wärnå[a,b], Tapio Salmi[b] and Jyri-Pekka Mikkola*[a,b]

[a]Technical Chemistry, Department of Chemistry, Chemical-Biochemical Centre, Umeå University, SE-901 87 Umeå, Sweden
[b]Laboratory of Industrial Chemistry and Reaction Engineering, Process Chemistry Centre, Åbo Akademi University, FI-20 500 Turku/Åbo, Finland
*jyri-pekka.mikkola@chem.umu.se

Nordic sulphite and sulphate (Kraft) cellulose originating from Nordic pulp mills were used as raw materials in the catalytic synthesis of green platform chemicals, levulinic and formic acids, respectively. The catalyst of choice used in this study was a macro-porous, cationic ion-exchange resin Amberlyst 70 for which the optimal reaction conditions leading to best yields were determined. For this system, maximum yields of 53 mol-% and 57 mol-% were obtained for formic and levulinic acid, respectively. The reaction network of the various chemical species involved was investigated and a simple mechanistic approach involving first order reaction kinetics was developed. The prototype model was able to describe the behaviour of the system in a satisfactory manner.

1. Introduction

The chemical industry of today is under increased pressure to develop novel green materials, bio-fuels as well as sustainable chemicals for the chemical industry. Indeed, the endeavour is to move towards more eco-friendly cost efficient production processes and technologies and chemical transformation of renewables has an important role in terms of future sustainable supply of chemicals and energy needed for societies. In the Nordic countries, the importance of pulping and paper industry has been particularly pronounced and the declining European demand on these products as a result of our digitalizing world has forced the industry to look at alternative sources of revenue and profitability.

Lignocellulosic biomass such as wood is an excellent raw material for converting renewables into fuel components and chemicals, since the utilization of this kind of biomass does not compete with food or feed production. Chemical products based on food-crops, such as corn is ethically compromised because corn is also an important source of nourishment. In addition, other sugar crops like e.g. sugarcane is often grown for non-food purposes (primarily transportation fuel blends) on farmland that competes with human related food production. After the initial boom of first generation biochemical and fuels made from edible biomass, the so called second generation biofuels produced from non-edible biomass (e.g. agricultural residues, lignocellulosics and other waste materials) are starting to emerge and have entered the market. Development of new processes for woody biomass or other lignocellulosic materials have been under intensive investigation for some time now. In fact, many commercial operations and pilot units are currently integrated as biorefineries combined with adjacent pulp and paper mills that aim at utilizing e.g. black liquor and other secondary streams as sources of new products. These emerging biorefineries combine and re-invent the material streams of the old industry together with other processes and practices of chemical industry in an effort of utilizing the existing and new technology solutions to produce the fossil-free necessities of future.

In this paper, both sulphite and sulphate (Kraft) cellulose from Nordic pulp mills were used as raw materials in the synthesis of green platform chemicals, levulinic and formic acids, respectively. Albeit today the alkaline sulphate process dominates, the older, acidic, sulphite process has a number of advantages

over the currently dominant industrial approaches. In particular, the sulphite process is easily adapted to produce highly pure, essentially lignin and hemicellulose-free pulp. The catalyst used in this study was a solid acid: macro-porous, cationic ion-exchange resin, Amberlyst 70.

Since the catalyst particles typically used in industrial sugar chemistry are relatively small (slurry reactors), one could easily consider that any such system is in fact on the kinetic regime. For example, our earlier simulation results obtained for sugar hydrogenations (Salmi et al., 2006) evidently suggest that this is not necessarily the case. Carbohydrates are large, organic molecules with molecular diffusion coefficients in the magnitude of order of $4.0 \cdot 10^{-9}$ m^2 s^{-1}. Moreover, the porosity-to-tortuosity factor can become small (<<0.5) and, therefore, the effective diffusion coefficient can be rendered small resulting in internal diffusion resistances to become an important factor. Moreover, external diffusion resistances can often be of crucial importance due to inefficient supply of reactant(s) due to less than perfect mixing (improper stirrer or reactor vessel design; unbaffled reactor). This, in turn, can result in more prominent formation of by-products. All of the above mentioned factors are even more pronounced when considering large, industrial-size cellulose cookers which easily accommodate tens of tons of material.

2. Experimental

2.1 Materials and methods
The commercially acquired reagents and chemicals used were of analytical grade and used without further purifications or other treatment procedures. D-glucose (VWR International, >99 %), 5-hydroxymethylfurfural (Aldrich, 99 %), levulinic acid (Janssen Chimica, 98+ %) and formic acid (Sigma-Aldrich, 98-100 %) were used to facilitate the calibration curves needed to follow the reaction kinetics. HPLC grade sulfuric acid (Fluka, 50 %) was used for eluent preparation. Whenever water was used, deionized water (MilliQ) was used to prepare all the solutions. The polymeric catalyst, Amberlyst 70, was obtained from the Rohm and Haas Company. The catalyst is a macro-porous, polymeric, cationic ion-exchange resin material applicable in high-temperature applications and is designed to be used in various processes such as olefin hydration, esterification and aromatic alkylation. In the aforementioned applications, Amberlyst 70 offers good performance over conventional resins due to its high thermal stability, catalytic activity and good mechanical strength. Importantly, very low sulphonate leaching has also been confirmed. The catalyst has an appearance as dark brown and spherical particles with an effective particle size of around 0.50 mm. The average pore diameter was measured and corresponded to 220 Å (22 nm). The nitrogen physisorption (in accordance to the B.E.T. method) confirmed a specific surface area in the range of 36 m^2 g^{-1} (Siril et al., 2008; Bringue et al., 2006; Rohm and Haas Company, 2005). The catalytic material was studied as fresh and after carrying out the kinetic reactions by means of Scanning Electron Microscopy (SEM, Cambridge Stereoscan 360) and nitrogen physisorption techniques (Micromeritics TriStar 3000 porosimeter) to undermine the changes occurring to the material upon exposure to the experimental conditions. Surface areas were calculated by the B.E.T. method and pore volumes were calculated from desorption isotherms.

2.2 Cellulose pulps utilized
Nordic, bleached, industrial pulp obtained from the Aditya Birla Domsjö pulp mill in Sweden (a mixture of softwoods Norway Spruce and Scots Pine) as well as Metsä-Serla kraft pulp from Finland (hardwood birch, Betula pendula) were compared as the starting materials. The softwood pulp utilized has a typical degree of polymerization (DP) in the range of 950 as an average whereas the DP of hardwood approaches 1900 on the basis of viscosity measurements. Kraft (sulphate) cellulose typically contains significant amounts of residual hemicelluloses (16 wt-% xylose pentose) whereas sulphite pulp is lean on hemicelluloses (sum of xylose and mannose pentoses comprise 4.2 wt-%). The pulps were utilized without any prior chemical treatments but both the sulfite and sulphate pulp were initially grinded to an average particle size of 0.35 mm in order to facilitate a realistic comparison. Since the degradation and transformations of the cellulose polymers initially proceeds via hydrolysis to glucose, also transformation of pure D-glucose was investigated (Sundberg et al., 1996; Strunk et al., 2011; Ahlkvist et al., 2013).

2.3 Chemical analysis of the product mixture
The composition of the samples was analysed off-line with high-performance liquid chromatography (HPLC, Agilent Technologies 1200 Series) equipped with a refractive index (RI)-detector, a degasser, a double-channel binary pump and an auto sampler. The analytical column of choice (Bio-Rad Aminex HPX-87H) is a 300 x 7.8 mm, a pre-packed HPLC carbohydrate analysis column supplied in hydrogen form containing 9 µm particle size with 8 % cross linkage and is designed to operate at a pH range of 1–3. 5 mM H_2SO_4 was utilized as the mobile phase with a flow rate of 0.5 cm^3 min^{-1} and temperature of 60 °C. For the sake of the clarity, instead of more commonly applied UV-vis detector, refractive index (RI)

detection is a must upon analysis of carbohydrates and their derivatives since UV detection is not capable of resolving most of the species.

2.4 Study of reaction kinetics

The kinetic experiments were carried out in a standard 300 ml laboratory scale, three-phase stainless-steel autoclave (Parr Inc, USA) designed for high pressures and temperatures. The temperature was measured with a thermocouple and automatically adjusted with the inbuilt temperature regulator (Parr 4848 Reactor Controller). The setup was equipped with a sampling outlet fitted with a 2 μm metal sinter frit designed to prevent the catalyst particles as well as pulp pieces to leave the reaction vessel upon sampling of the liquid phase. The hydrolytic degradation of wood pulp took place in the presence of catalysts in an aqueous media and high stirring rates (1000 rpm) were applied in order to eliminate any external mass transfer limitations. The reaction parameters studied, such as the reaction time, temperature, pressure as well as the nature of the catalyst was of crucial importance in terms of optimal conversion of the biopolymers to platform chemicals. Each and every experiment was commenced by charging the reaction vessel with 3.0 g of pulp dispersed in 147 ml of deionized water along with the catalyst. Before heating the reaction mixture to the intended temperature (150–200 °C), the system was degassed (<0.01 atm) with a high power vacuum pump to remove any residual air in the solution. After reaching the preset temperature the agitation was engaged thus marking the start of the experiment. Furthermore, also experiments upon which the reaction vessel was pressurized with various gases (CO_2, Ar, H_2; 3-50 bars) to counter-effect vaporization of water were carried out. Throughout the experimental run, samples were taken at suitable intervals and the sampling line was flushed with small volumes of the reaction solution in between the samples to avoid any contamination between consecutive samples. For the sake of precaution, the samples were once more filtered and the composition was determined by means of high-performance liquid chromatography (HPLC).

3. Results

3.1 Modeling of the reaction system

An ultimately simplified model was concerned here to obtain a physical feeling of the behavior of the model and to illustrate the central features of the kinetics. In the initial approach only the experimental runs at higher temperature range, i.e. 180–200 °C, was concerned since the reaction proceeds extremely sluggishly at lower temperatures and batch experiments lasting for several days had to be carried out. Nevertheless, the preliminary modeling and simulation revealed that a first order reaction kinetics model could describe the reactions in the reaction scheme. Batch reactor model was applied ($dc_i/dt=r_i$). For the parameter estimation, Modest[®] software was used (Haario, 1994). The reactor model containing the ordinary differential equations was solved with the backward difference method and a hybrid Levenberg-Marquardt method was applied to estimate the unknown parameters (rate constants and activation energies) in the kinetic model. Rate equations for the proposed elementary reaction kinetic model and batch reactor model were implemented in the Modest software which also provides the graphical interface. On the basis of the mentioned model, the kinetic parameters for the studied reaction system were estimated. Reasonably good agreement between the model fit and the experimental data was obtained although a very simple approach was used in this first approach. The model agreement with the experimental data exceeded 93 % and a sample fit is depicted in Fig. 1.

The modeling approach chosen verified that the experimental results obtained at 180–200 °C in the heterogeneously catalyzed reaction scheme displayed prominent Arrhenius-type temperature dependence demonstrated for the reaction products identified. For the parameter estimation the following objective function was minimized:

$$Q = \sum_t \sum_i (c_{i,t,exp} - c_{i,t,model})^2 w_{i,t} \tag{1}$$

where $c_{i,t,exp}$ and $c_{i,t,model}$ are the experimentally recorded concentrations and the concentrations predicted by the model, respectively. The weight factors, w_i, were at this time set equal to unity (1) for all experimental data.
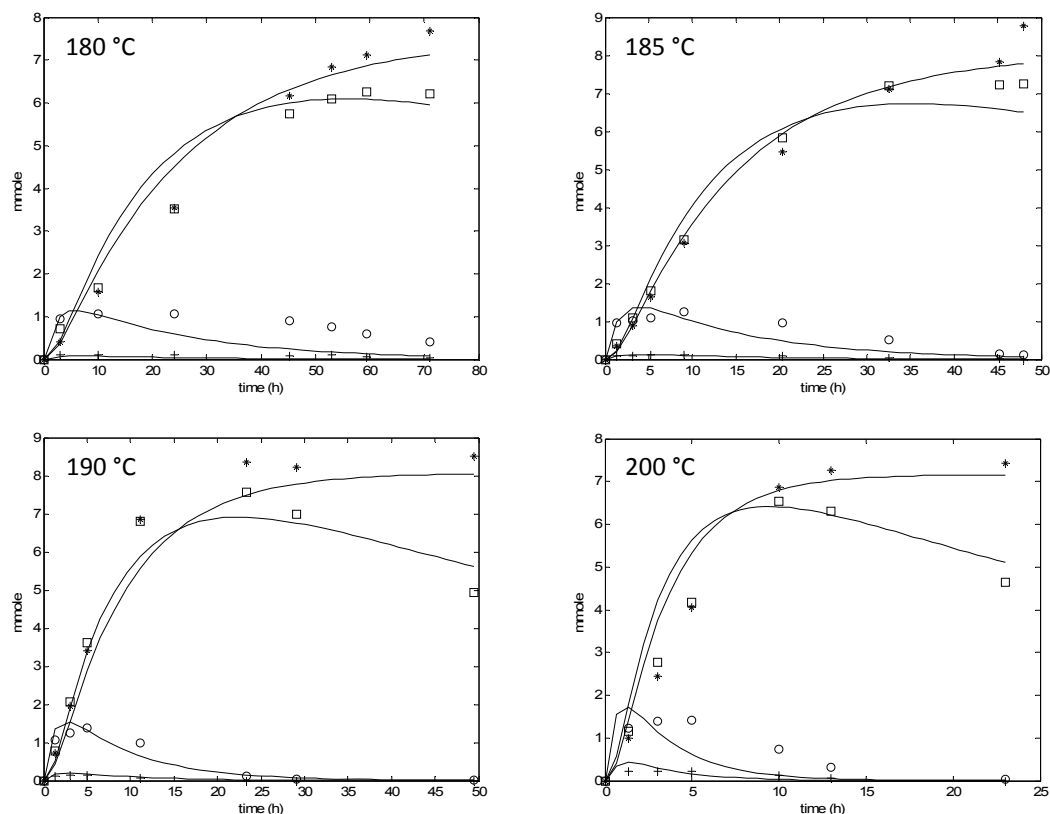
Figure 1: Fit of model to the experimental data; concentration evolvement of products formed: Levulinic acid (*), Formic acid (□), Glucose (○) and 5-HMF (+) vs. time.

3.2 Reaction network

A simplified reaction network for the acid-catalyzed hydrolysis of wood pulp to levulinic and formic acids is introduced in Figure 2. In fact, the complete reaction network involves a sequel of hydrolysis hydration-dehydration reactions where, at first, the biopolymer chains (cellulose and hemicelluloses present in the pulp) are cleaved into low molecular weight, oligomeric species followed by hydrolytic degradation reactions. Two reaction pathways are involved: degradation of cellulose results into formation of glucose, while the degradation of hemicelluloses generates xylose. The glucose formed is under the experimental conditions further transformed to 5-hydroxymethylfurfural (HMF) which, in turn, is further converted in a consecutive hydration-dehydration reaction sequence to levulinic (LA) and formic acids (FA). The xylose pentoses originating from the hemicellulose fractions transform to furfural which is finally decomposed to formic acid. The formation of xylose confirms the presence of hemicelluloses in the pulp since native Birch wood (Betula pendula) has been reported to contain 23 % of xylose, bound in the form of the hemicellulose xylanes (Willför et al., 2005). Monosaccharide's originating from hemicelluloses of four different bleached birch pulps from Finnish paper mills has been studied earlier and it was found that the average amount of xylose found in the pulps resides in the range of 14.3 wt-% (Sundberg et al., 1996). Furthermore, HMF can be decarbonylated into furfural (Käldström et al., 2011). Also, formation of humins (or tar like species) directly from cellulose and sugars typically occurs due to kind of charamelization reactions when the carbohydrate fractions are getting in contact with the hot walls of the reaction vessel. Throughout all kinetic experiments, black insoluble-substances known as humins were found on the reactor walls and the amount was visibly increased with reaction time. These are well known products of side-reactions upon acid-catalyzed decomposition of pulp.
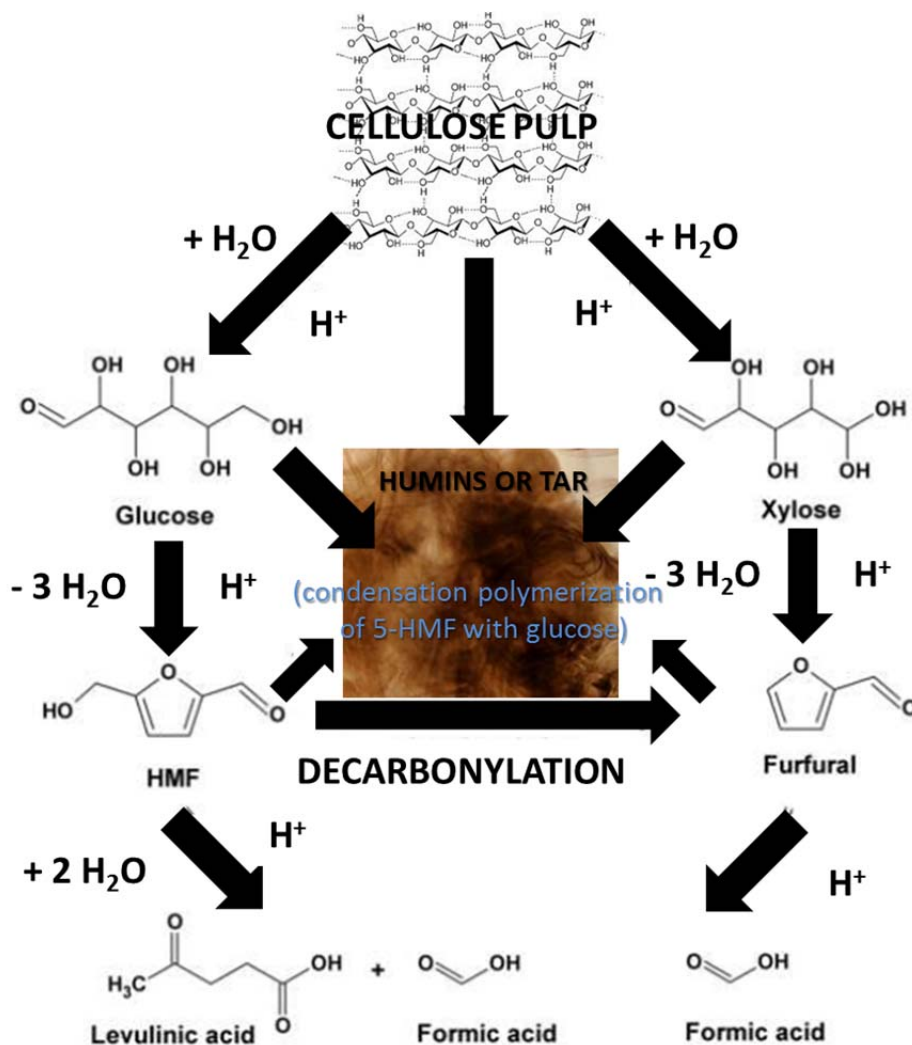
Figure 2: The reaction network upon production of the platform chemicals levulinic and formic acids from cellulose.

4. Conclusions

Solid acid catalyzed degradation of Nordic industrial pulp was studied under batch wise reaction conditions to yield platform chemicals levulinic and formic acids. The optimal reaction conditions were determined and a simple, first order kinetic approach was demonstrated to describe the experimental data with satisfactorily accuracy. The study revealed that cellulose obtained from different processes, i.e. sulphite vs. sulphate processes, yields pulps with different potentials for the production of chemicals. Sulphite pulp, being lean on pentose sugar containing hemicelluloses was revealed as the preferred raw material resulting in notably higher yields of the more valuable end-product, levulinic acid, since formic acid tends to degrade to carbon dioxide and water upon prolonged reaction times.

654

References

Ahlkvist J., Ajaikumar S., Larsson W., Mikkola J-P., 2013, One-pot catalytic conversion of Nordic pulp media into green platform chemicals, Applied Catalysis A: General, 454, 21-29.

Bringué R., Iborra M., Tejero J., Izquierdo J.F., Cunill F., Fité C. and Cruz V.J., 2006, Thermally stable ion-exchange resins as catalysts for the liquid-phase dehydration of 1-pentanol to di-n-pentyl ether (DNPE), Journal of Catalysis, 244, 33-42.

Haario H., 1994, Modest User's Guide, Profmath Oy, Helsinki, Finland.

Käldström M., Kumar N. and Murzin D.Y., 2011, Valorization of cellulose over metal supported mesoporous materials, Catalysis Today, 167, 91-95.

Rohm and Haas Company, 2005, Product data sheet <www.amberlyst.com/literature/a4/70.pdf> accessed 06.04.2013.

Salmi T., Kuusisto J., Wärnå J., Mikkola, J.-P., 2006, Alternative Sweeteners: La Dolce Vita. La Chimica e l'Industria (Milan, Italy): 8, 88, 90-96.

Siril P.F., Cross H.E. and Brown D.R., 2008, New polystyrene sulfonic acid resin catalysts with enhanced acidic and catalytic properties, Journal of Molecular Catalysis A: Chemical, 279, 63-68.

Strunk P., Eliasson B., Hagglund C., Agnemo R., 2011, The influence of properties in cellulose pulps on the reactivity in viscose manufacturing, Nordic Pulp and Paper Research Journal, 26, 81-89.

Sundberg A., Sundberg K., Lillandt C., Holmbom B., 1996, Determination of hemicelluloses and pectins in wood and pulp fibres by acid methanolysis and gas chromatography, Nordic Pulp and Paper Research Journal, 11, 216-219.

Sundberg A., Emet S., Rhen P., Vähäsalo I. and Holmbom B., 2005, Estimation of Proportions of Different Pulp Types in Recycled Paper and Deinked Pulp by Acid Methanolysis, Proc. 13th International Symposium on Wood, Fibre and Pulping Chemistry, Auckland, New Zealand, 361.

Willför S., Sundberg A., Pranovich A. and Holmbom B., 2005, Wood Science and Technology, 39, 601-617.