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## Liquefaction of humins from C6-sugar conversions using heterogeneous catalysts

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## 6. Summary

Biomass is considered an important resource for the production of carbon based chemicals to be used for important daily life products (plastics, paints, etc.). Platform chemicals such as furfural, 5-hydroxymethylfurfural (HMF) and levulinic acid (LA) have been identified as interesting biomass derived chemicals with high application potential. However, conventional processes for these chemicals, e.g. the acid-catalysed dehydration of the biomass source in water, are associated with the formation of large amounts of carbonaceous, insoluble humin byproducts formed by polymerisation reactions of substrates, intermediates and products. The amount of humins formed in e.g. the Biofine process for LA, also known as Biofine char, can be as high as 30-40%. The formation of these humins reduces the carbon efficiencies of the processes. As such, there is a strong incentive to either reduce the amount of humins formed or to develop efficient valorisation technologies for these solid materials. In this respect, it is of high importance to have insight in the molecular structure of humins and their formation mechanism. Moreover, the conversion of humin substances as starting material for bulk-chemicals and biofuels has to the best of our knowledge not been described in the open and patent literature.

In this research project catalytic routes for the conversion of humins derived from glucose conversions to bulk chemicals were explored with an emphasis on catalytic liquefaction in the presence of hydrogen or a hydrogen donor.

The formation, morphology and molecular structure of humin byproducts were studied as a function of feedstock and processing parameters in *Chapter 2*. The amounts of humins are a function of the sugar source. Humin yields from xylose were slightly higher than from glucose. Addition of 1,2,4-trihydroxybenzene to the feed led to an increase in humin formation indicating that this molecule is included in the humin structure as a cross-linker. This result shows that humin formation also involves reactions other

than aldol condensations. The influence of acid concentration, sugar intake and temperature on the formation of humins from glucose was studied using a DoE-based approach. The data show that humin formation is strongly influenced by reaction temperature and acid concentration, but statistically hardly depends on sugar concentration. Humin samples prepared from different feedstock were characterised by several analytical techniques. SEM indicated that the humin by-products have a spherical morphology, of which the exact size strongly depends on feedstock and processing conditions. A study on the molecular structure of humin by-products using elemental analysis, IR, solid state  $^{13}\text{C}$  NMR spectra and pyrolysis-GC-MS revealed a furanic structure with alcohol, acid, ketone and aldehyde functional groups, which is formed via a dehydration pathway. Based on this information a model for the molecular structure for glucose-derived humins was proposed. It was also found that xylose-derived humins have a more conjugated molecular structure. This can be explained by the free 5-position of furfural which leads to direct linking of the furan leading to less aliphatic groups and a more condensed network of furans moieties.

The models for the molecular structure of the humins derived from  $\text{C}_5$  and  $\text{C}_6$  sugars that are presented here will aid the development of catalytic routes for the valorisation of these by-products. The analogy can be made with the development of valorisation strategies for lignin, another example of a recalcitrant, highly heterogeneous, aromatic biopolymer with limited solubility. The considerable advances in the structural characterisation of lignin, in particular the type and occurrence of specific linkages and the influence of pre-treatment on the lignin structure, have clearly guided the development of catalytic lignin conversion strategies. Similar advances are to be expected for the valorisation of humins. Catalytic pyrolysis, a process that has been quite extensively studied for lignin, of humins is a promising example of this. Alternatively, the insights gained in humin formation and structure can aid in managing the extent of humin formation, or can improve our understanding and application of related materials such as biochars.

In *Chapter 3*, an extensive catalyst screening study using various (noble) metals (Pt, Ru, Ni, Rh) on a range of supports (C,  $\text{Al}_2\text{O}_3$ ,  $\text{TiO}_2$ ,  $\text{ZrO}_2$ ,  $\text{CeO}_2$ ) is reported for the reactive liquefaction of humins in isopropanol (IPA). Experiments were carried out in a batch reactor using an artificial model humin derived from glucose with isopropanol as the solvent at  $400\text{ }^\circ\text{C}$  for a 3 h batchtime. Initial studies using noble metal catalysts (Rh, Pt, Pd, Ru) on a carbon support revealed that Pt was the best catalyst in terms of humin conversion (77%) and amounts of alkylphenolics and aromatics in the product oil (GC $\times$ GC-FID). Subsequent support screening studies ( $\text{TiO}_2$ ,  $\text{ZrO}_2$ ,  $\text{CeO}_2$ ) were performed using Pt as the active metal and the results were compared with Pt/C. The best results were obtained with Pt/C when considering humin conversion. However, Pt/ $\text{CeO}_2$  was shown to be more attractive when considering the amounts of alkylphenolics in the product oils (20.4 wt% based on humin intake). Detailed liquid product analysis (GPC, GC-MS, GC $\times$ GC) including blank reactions in the absence of humins revealed that the humins are mainly converted to monomeric and oligomeric alkylphenolics and aromatics (GPC, GC). IPA was shown not to be inert and is converted to acetone and hydrogen, and the latter is the hydrogen source for the various metal catalysed hydrogenolysis and hydro(deoxy)genation reactions. In addition, acetone is converted to aldol condensation products (like methylisobutylketone, MIBK) and hydrogenation products derived thereof. Though a complex reaction mixture is obtained with product both from humins and the solvent, the development of efficient separation technology may allow the separation of the aldolcondensation products (like MIBK) and alkylphenolics from the mixture. Both components are commercially available bulk chemicals with a high application range. For instance MIBK is used as a solvent whereas mixtures of alkylphenolics may be used as a replacement of phenol in phenol based adhesive formulations. In addition, mixtures of alkylphenolics may also be used as biofuel blending agents to improve diesel engine performance.

Detailed studies on the catalytic liquefaction of humin substances using a Pt/C catalyst in IPA are reported in *Chapter 4*. IPA is not inert and acts as a hydrogen donor in the Pt catalysed dehydrogenation to acetone.