Eliminating the Pathway of Humin by Acid Catalyzed Hydrolysis of Glucose

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Abstract

Recent hydrolysis of carbohydrates to valuable fuels such as 5-(hydroxymethyl)furfural (HMF), furan, and levulinic acid (LA) is carried out in biphasic systems to allow products to be removed from an aqueous to an organic phase, whereby products are protected from degradation. Due to the presence of water in current systems, humin formation occurs, which is undesired and significantly lowers the yield of products formed. This present study aims to optimize HMF and LA production by focusing on the use of solvents, co-solvents, catalysts, and desiccants by which the presence of water can be decreased. In general, our system uses glucose as the carbohydrate source and a non-aqueous solvent with a desiccant that traps/removes water during reaction. The reaction ceases after HMF forms so that humins do not form downstream. Different solvents such as formic acid, acetic acid, propionic acid, levulinic acid, and γ-valerolactone and co-solvents such as HMF, formic acid, and water have been tested. Additional Brønsted acids such as H2SO4 and HCl have been tested as catalysts. Two different 5 Å and 3 Å molecular sieves have been tested as desiccants. Several variations of systems were tested with each of the variables, yielding different outcomes and exposing certain limitations.

Figure 9: Humin from 7 wt.% glucose solution with 5 Å catalyst in GVL.

Figure 10: Humin from 7 wt.% glucose solution with 5 Å catalyst in GVL.

Conclusions

Using formic acid as a solvent is a novel idea. Dry formic acid should theoretically be able to produce HMF with no humin formation. However, due to formic acid decomposition, CO + H2 or CO + H2O are formed. The first reaction allows for hydrogenation of both LA into GVL and HMF into 2,5-dihydroxymethylfuran (DHMF) and subsequently 2,5-dihydroxy methyltetrahydrofuran (DHMT), a desired reaction. However, the latter reaction allows for humin production, negating the purpose of using non-aqueous solutions. Furthermore, formic acid can readily fit into a 5 Å pore due to its length of approx. 2.9 Å. While 3 Å sieves were tested, they consistently yielded a lower amount of HMF. This may be due to the lower H2O capacity of 3 Å over 5 Å sieves along with the rate at which they can remove H2O. Due to these drawbacks, there has not been any convincing data demonstrating that formic acid is capable of high selectivities to valuable products. Other carboxylic acids suffer from lower solubility of glucose, along with higher Ks. Acetic acid and propanoic acid also suffer from esterification of glucose which may alter HMF formation. Levulinic acid as a solvent has poor solubility of glucose and is believed to caramelize glucose, rather than hydrolyze. γ-Valerolactone as a solvent resolved the issues incurred with formic acid in regards to stability and physical properties, however, it also has a low glucose solubility. γ-Valerolactone cannot hydrolyze glucose without a catalyst. HCl and H2SO4 are the strongest catalysts and under aqueous solutions produce the highest yields of LA. However, they are not capable of producing HMF without humin formation due to the need for H2O. The greatest yield of HMF and LA from an approximate 7 wt.% glucose reaction was 1.44 and 3.05 wt.%, respectively. The use of HMF instead of water to dissolve glucose was not practical with H2SO4 or HCl as the catalyst due to the production of humins at room temperature. HMF may be beneficial when using formic or levulinic acid, however, this has yet to be confirmed. Formic acid as the catalyst in a GVL solution was the only reaction in which the mass balance has been closed with no unwanted products. Although the selectivity has went above 100% in some reactions, this may be due to the fact that glucose and fructose, the isomerisation product of glucose have the same retention time in the HPLC. The HPLC may give false interpretations of the concentration of glucose due to fructose having a larger peak in the HPLC than glucose for similar concentrations. In order to continue this research, an HPLC method that separates all products and reagents must be developed. Overall, this study is the first to demonstrate the highest wt.% yield of HMF as well as the first to convert over 50% of a glucose solution into products without humin formation.

References