



Eliminating the Pathway of Humins by Acid Catalyzed Hydrolysis of Glucose

Jacob Heltzel, Carl R. F. Lund

Chemical and Biological Engineering, University at Buffalo



Abstract

Fuels created from cellulose have garnered significant attention over the past decades. Current research groups have moved away from traditional renewable fuels such as ethanol to fuels that are more compatible with existing infrastructure. However, production of these fuels is accompanied by production of a solid carbon byproduct known as humins. Humins are undesired and lower the yield of the desired fuel products. Our group has studied the mechanism, and it appears that water is necessary for the production of humins. Consequently, our recent focus has involved the use of non-aqueous solvents combined with a desiccant to absorb the water generated by the reaction. The challenges are to find a stable solvent that will dissolve glucose and to find a suitable acid for use in that solvent. Three systems have been studied: gamma-valerolactone (GVL)/sulfuric acid, GVL/levulinic acid and formic acid (as both solvent and acid). The GVL systems suffer from a very low solubility of glucose while the formic acid system suffers from its decomposition.

Proposal

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 gamma-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 5Å and 3Å 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.

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, CO₂ + 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-di-hydroxymethyl-tetrahydrofuran reaction (DHMTHF), 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 5Å pore due to its length of approx. 2.99Å. While 3Å sieves were tested, they consistently yielded a lower amount of HMF. This may be due to the lower H₂O capacity of 3Å over 5Å 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 K_f's. Acetic 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. gamma-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. gamma-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 isomerization product of glucose have the same retention time in the HPLC. This 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 determined. 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.

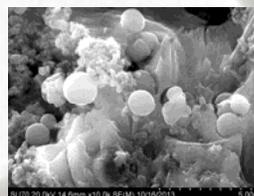


Figure 9: Humins from 7 wt.% glucose solution with SA catalyst in GVL.

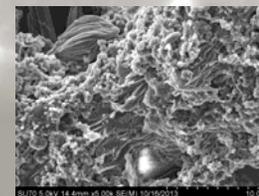


Figure 10: Humins from 7 wt.% glucose solution with SA catalyst in GVL.

Carboxylic Acid Results

Glucose was the most soluble in formic acid systems. Using formic acid as the solvent, a 40-42% yield of HMF was obtained at 58-78% conversion of 0.2M glucose. It is presumed that the residual reacted glucose is either converted to humins or esters due to the number of hydroxyl groups in glucose and fructose. During reaction, formic acid decomposes into either CO₂ + H₂ or H₂O + CO. Use of H₂SO₄ increased the decomposition of formic acid. Only reactions with low conversions of glucose produced no solids using formic acid. When using formic acid, all other solvents with the exception of GVL had negligible yields or very low HMF and LA yields due to ester formation (carboxylic acids) and oxidation/pyrolysis (LA) of glucose. However, they did not form any humins or other solid products.

GVL Results

GVL was used as a solvent due to its physical properties and ability to dissolve cellulose. However, glucose isn't soluble in GVL which caused an issue with some acid catalysts. Upon addition of H₂SO₄ and heat, glucose carbonized in GVL systems. To reduce this, water was added to dissolve glucose prior to reaction and sieve addition. This initially formed a biphasic system of glucose + H₂O and GVL. However, given sufficient amount of time, glucose still came out of solution due to GVL's solubility with water. H₂SO₄ partially decomposed HMF into humins upon contact if there was a small residual amount of H₂O (approx. 1 wt.%). Using HCl (36 wt.%) instead of H₂SO₄ allowed for quicker dissolution of glucose, however, HCl has a low boiling point leading to vaporization from the liquid phase. Due to the high concentration of HCl, any HMF and H₂O can easily decompose into humins either in the vapor phase, or during condensation above the liquid humins. With LA as a catalyst, water isn't required to protect the glucose from carbonizing. After reaction, up to 3 wt.% of HMF was produced from glucose, however, at the time of analysis, glucose wasn't available to determine the selectivity. Depending on reaction conditions, LA either reacted to form another product or was produced from glucose. Formic acid as a catalyst allowed for greater solubility of glucose in GVL. Glucose conversion up to 60 wt.% showed no to very slight amount of humin formation. Using a 7 wt.% glucose in a GVL and approx. 0.9M formic acid solution, reacted at 135°C for 2hrs, HPLC results showed 0.97 wt.% and 1.95 wt.% of HMF and LA, respectively, formed at 55% conversion of glucose, yielding 98% products per mole of glucose reacted with no humin formation. However, similar reactions showed that the glucose concentration may be overestimated.

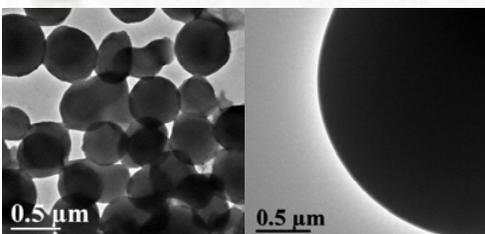


Figure 1: 0.1 M Fructose and SA reacted to 100% conversion. Figure 2: 0.5M Glucose, 1M SA reacted to 100% conversion.

Overall Reaction

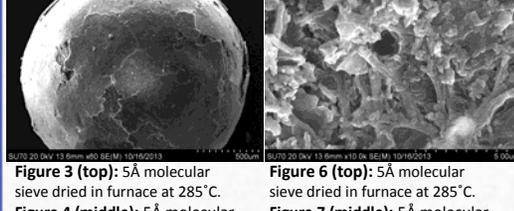
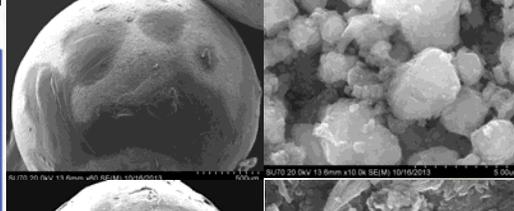
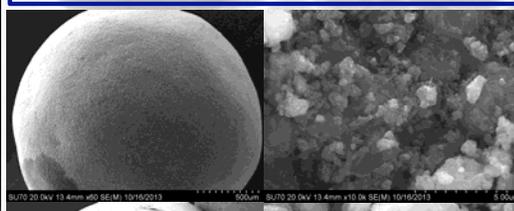
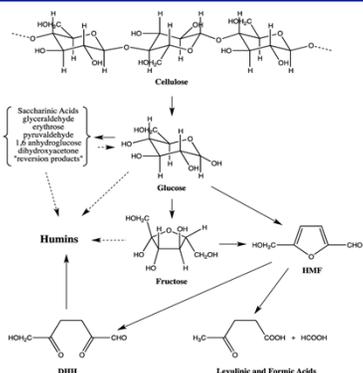


Figure 3 (top): 5Å molecular sieve dried in furnace at 285°C. Figure 4 (middle): 5Å molecular sieve added to reaction solution. Figure 5 (bottom): 5Å molecular sieve after hydrolysis reaction.

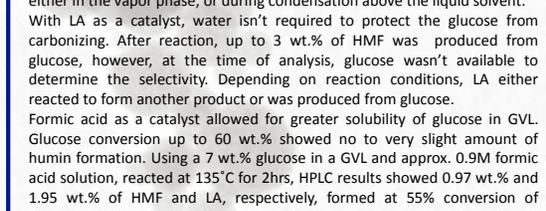
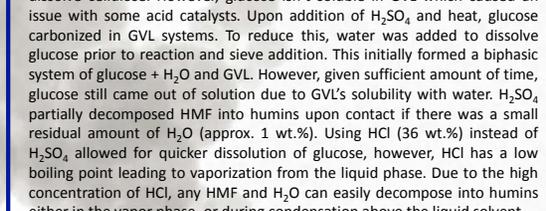
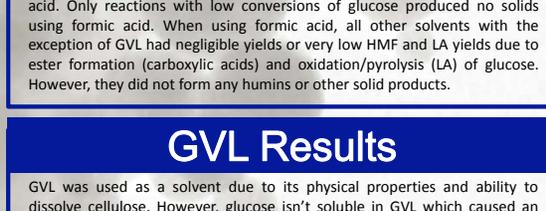


Figure 6 (top): 5Å molecular sieve dried in furnace at 285°C. Figure 7 (middle): 5Å molecular sieve added to reaction solution. Figure 8 (bottom): 5Å molecular sieve after hydrolysis reaction.

References

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