
The dark side of biomass valorization: A laboratory experiment to understand humins formation, catalysis and green chemistry

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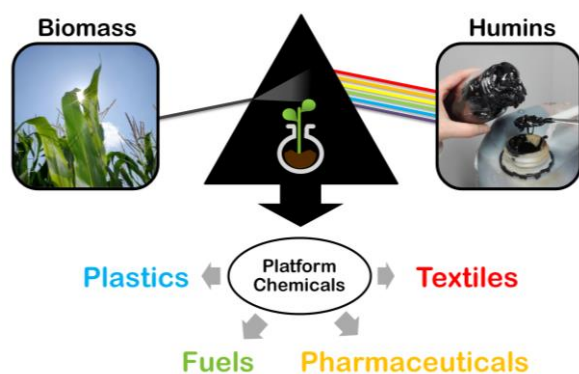
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ABSTRACT

This laboratory experiment introduces students to an important reaction in biomass valorization and allows them to gain a practical understanding of green chemistry. Acid-catalyzed dehydration reactions of fructose to 5-hydroxymethylfurfural, and thus humins, were performed both in aqueous solvent and without, along with two different catalysts (Amberlyst-15 and alumina). Students were able to compare and analyze the effects of these different conditions using Thin-Layer Chromatography, while grasping concepts of catalysis and circular economy. By observing the formation of humins under some of the reactions tested, the students could evidence systems thinking in humins valorization.

GRAPHICAL ABSTRACT



KEYWORDS

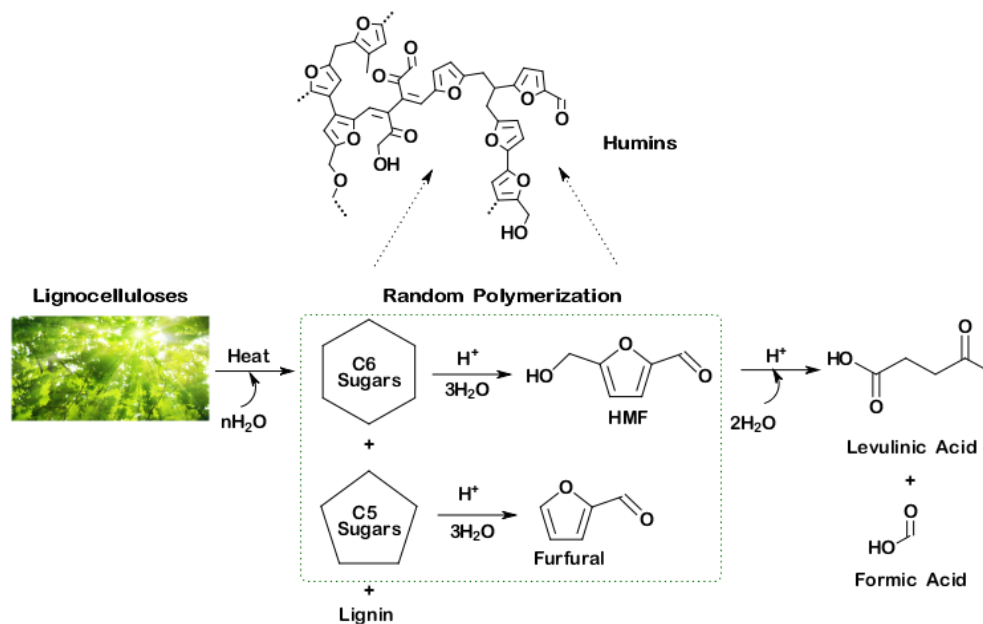
Second-Year Undergraduate, Laboratory Instruction, Interdisciplinary / Multidisciplinary, Hands-On Learning, Aqueous Solution Chemistry, Carbohydrates, Catalysis, Thin Layer Chromatography, Water / Water Chemistry, Green Chemistry, Sustainability, Systems Thinking

There is constant pressure to shift from a petrol-based economy to a renewable and sustainable one due to climate change,¹ impoverishment of traditional sources,² overexploitation, and increased levels of pollution.³ To address this, a variety of renewable resources for energy needs (wind, solar, etc.) are currently being investigated and implemented.⁴ However, renewable options for the production of chemicals are more limited. While some advances have been made with CO₂ (electro) conversion technologies,⁵ biomass valorization is currently taking hold of the scientific community.⁶

Biomass valorization is the process of adding value to different types of plants and residues: food crops (starch-rich) and residues (ex. rice/corn husk), aquatic plants (ex. algae), lignocellulosic plants (ex. grass), municipal waste, animal waste, and so on.⁷ Among all, tendencies are drawn to avoid using food crops as they are intended for human/animal use, particularly given the expected increase of the world population to +9 billion people by 2050.⁸ In fact, higher population density will translate into higher chemical (and energy) use as well as less available food sources (e.g. vegetables, grains). Given this trend, lignocellulosic plants are preferred for the production of plastics, pharmaceuticals and other chemicals because they contain different components that can be valorized for a variety of applications. Another advantage of lignocelluloses is their potential growth in different soils⁹ and their usage will increase crop diversification, thus allowing higher employment in agricultural jobs.

From a chemical point of view, these plants are made of: cellulose, a polymer of glucose (C-6 sugar); hemicellulose, a polymer of different C-5 sugars (xylose, arabinose, etc.); and lignin, an aromatic polymer which confers structural strength to the plant.^{10, 11} While lignin is quite challenging to convert into a selective product,¹² cellulose and hemicellulose may undergo transformation, either with or without pretreatment,¹³ into important bio-based platform chemicals.^{14, 15} As an example, acid-catalyzed dehydration of bio-sugars (e.g. glucose or fructose) can yield 5-hydroxymethylfurfural (HMF) if in aqueous solution. If in alcoholic solutions (e.g., methanol), alkoxymethylfuranics like 5-methoxymethylfurfural (MMF) can be obtained.¹⁶ These furanic products may undergo further modifications into a plethora of chemical products with applications ranging from bulk (plastics, construction materials) to fine chemicals (pharmaceuticals). An example is the formation of 2,5-furandicarboxylic acid (FDCA) *via* oxidation of HMF or MMF. In particular, FDCA polymerizes with monoethylene glycol (MEG) to form polyethylene furanoate (PEF), a 100% bio-based plastic with

exceptional performance properties. However, insoluble by-products known as humins (precisely, humin by-products) form in the acid-catalyzed transformation of sugars to platform chemicals (Scheme 1).

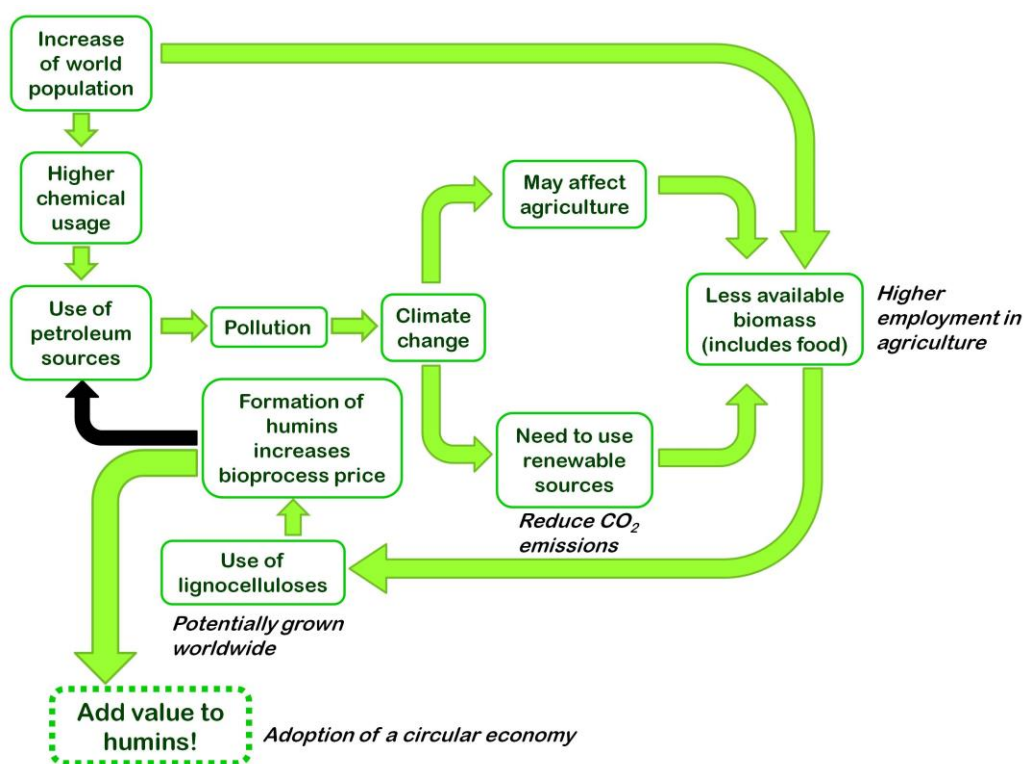


Scheme 1. Acid-catalyzed hydrolysis of biomass to key platform chemicals and humins.

Both the structure and formation mechanism of humins are still a matter of debate,¹⁶ requiring further research. In particular, humins formation (typical yields between 10-50 wt%) significantly reduces the efficiency and economic viability of the process, making the petrol-based processes competitive, thus still used. For this, the laboratory experience proposed herein is to display how humins are formed in a simple way, following green chemistry principles,¹⁷ so that the next generation of scientists can grow familiar with these by-products and liberate their creativity into finding new valorization routes.

Systems thinking, *i.e.* holistic research and learning, is advancing as a complementary approach to a reductionist view of a particular research. Recently, Orgill *et al.* extensively reviewed the history and key concepts of systems thinking,¹⁸ as well as the benefits associated with this comprehensive approach based on key literature examples.¹⁹ As skillfully explained,¹⁸ systems thinking can significantly contribute to improved sustainability at a global level by considering each consequence that may arise from a particular research topic. By applying a systems thinking approach to the

70 formation of humins from biomass, it becomes clear that valorization routes for humins are necessary to achieve a “closed-loop” circular economy²⁰ and improve the system’s sustainability. The overall system thinking of humins valorization is given in Scheme 2. Using systems thinking,²¹ students are able to understand the implications that humins formation has on biomass valorization and how green chemistry can help reduce the different societal challenges mentioned above. In the experiment
 75 proposed herein, students are able to see how green chemistry strategies such as catalysis and solvent selection can help reduce the formation of humins and become familiar with an undefined product that is difficult to handle.



Scheme 2. Systems thinking of humins valorization.

80 Many examples can be found in teaching students green chemistry and waste valorization concepts.²²⁻³⁶ A course on green chemistry with case studies, articles, and a final project with a focus on unconventional thinking can be good for a general background on principles of sustainable chemistry.²³ This course could be coupled to different (dry)²² laboratory experiences present in literature,²⁵ or with a full green chemistry lab activity such as that described by Sharma *et al.*²⁷ Many
 85 laboratory experiences for biomass valorization strategies can be found in literature. Some address

material synthesis from biomass sources with green procedures (enzymatic) for the synthesis of sugar-based gelators²⁸ or bioplastics²⁹ from chitin/chitosan. Looking both at biofuels and materials (*i.e.* sunscreen), a full biomass (cellulose, hemicelluloses, lignin) valorization experiment is given by Zhou *et al.*³⁰ A fermentation experiment for the production of bioethanol was also proposed.³¹ Even
90 experiments for valorizing common, everyday biomass waste such as fruit peels have been proposed for adsorbent²⁹ and shear thinning gel³² applications. A similar reaction pathway considered in this work is given by the homogeneous and heterogenous conversion of fructose to HMF with the use of a quaternary ammonium salt as the first step of HMF purification by precipitation.³⁴ However, humins are not addressed in the work, thus overlooking the current industrial technical challenge.

95 The laboratory experiment outlined in this work is an opportunity for students to apply systems thinking and green chemistry principles to one of the common challenges facing a promising method for sustainability in the chemical industry. The experiment can be completed in a 3-hour lab section and is best suited for courses in advanced general chemistry or introductory organic chemistry. It would be useful to have already covered the information given in the introduction herein, and for
100 students to be familiar with thin-layer chromatography (TLC), vacuum filtration, solvent extraction, and heating under reflux. This experiment has been performed in two different sections by separate groups of second year undergraduate students who had already completed general chemistry courses and were learning the aforementioned techniques. See the supporting information for a student handout and more details about the experiment.

105 **EXPERIMENTAL PROCEDURE**

Laboratory Experience

Students performed four acid-catalyzed dehydration reactions of fructose: three in water with different catalysts and one that is solventless. The three reactions in water were heated in an oil bath at 200 °C for 2 hours under reflux. The reflux condensers were open to atmosphere and had no
110 external gas lines (atmospheric pressure can be assumed). The solventless reaction was performed at 100 °C for 1.5 hours with no stirring (a simple hot plate can be used) in an open vessel. It is recommended that the solventless reaction be done in a small disposable vial, as the product is very difficult to clean and can be safely disposed of. Also, it is only necessary that one solventless reaction

be performed for each lab session. Each of the reactions in water were divided amongst pairs of
115 students in groups of six so that two students were responsible for one of the three reactions. At the
end of the experiment, the students shared their reaction observations and products amongst the
group (e.g. TLC).

For each reaction, students weighed out 5.00 g of fructose to undergo acid-catalyzed dehydration.
The three reactions in water required a magnetic stir bar, 10 mL of distilled water and a 100 mL round
120 bottom flask. Two of these reactions are catalyzed by 100 mg of Amberlyst-15 or Alumina and the
third a blank reaction with no catalyst. When all four reactions had been prepared, 150 μ L of glacial
acetic acid was added to each and heating under reflux was immediately started. Stirring for the
reactions in water was set close to 750 rpm. After 1.5 hours, the solvent-less reaction was stopped and
allowed to cool. Once cooled, 5 mL of acetone was added to the mixture and sonicated for 5 minutes to
125 dissolve some of the product – only a very small portion dissolves. This resulting solution was used to
spot the solvent-less reaction on a TLC plate. The three reactions in water were stopped after 2 hours
and cooled in an ice bath. Once cooled, the catalysts were filtered from the two catalyzed solutions
using vacuum filtration. The filtered catalysts should not be rinsed with water so that any formation of
humins is visible and not washed off. The two filtered solutions and the blank were then extracted
130 with 5 mL of ethyl acetate in order to spot each reaction on the TLC plate. Once all four reactions were
spotted, the TLC plate was run in an eluting solvent mixture of 1:1 pentane to ethyl acetate. RF values
of the obtained molecules are roughly 0.50 for HMF, 0.60 for diformylfuran (DFF), and 0.75 for
levulinic acid. If available and time permitting, students could prepare a sample of each of the
reactions for GC-MS and perform a more in-depth analysis of the product formation as a follow-up
135 during the next lab session.

Materials and lab set-up

D-(-)-fructose (>99%), aluminum oxide-activated-weakly acidic (150 mesh) and pentane (98%) were
purchased from Sigma Aldrich. Amberlyst-15 WET was provided from Dow (Code 69286, Batch
0006759527). Glacial acetic acid (>99.5%), ethyl acetate (99.9%) and acetone (99.5%) were bought
140 from Panreac. Distilled or deionized water was used for all reactions in a solvent.

For a complete laboratory experience, three reflux systems are required. The reflux can be carried with a round bottom flask submerged in an oil bath or in a parallel batch reactor system. For example, these experiments were first performed several times by the authors in a Carousel Reaction Station™ from Radleys Discovery Technologies to optimize reaction conditions and ensure reproducibility. Subsequently, the reactions were performed by undergraduate students who used oil baths and traditional reflux condensers. Results were found to be consistent with each setup. Furthermore, a heating plate and a disposable vial that can withstand high temperatures (at least up to 150 °C) are required for the solventless reaction. Finally, necessary items for running TLC analyses are required (plates, beakers, cover, pipette for spotting).

Safety

All chemicals should be handled with personal protective equipment (gloves, goggles, lab-coat) and with proper ventilation (fumehood preferred, or the use of masks is required). Glacial acetic acid should be handled with extra care as it can cause skin burns and severe eye irritation. If contact is made, flush skin or eyes with water for at least 15 minutes and seek medical aid.

Ethyl acetate, acetone, pentane and glacial acetic acid are all flammable liquids that should be handled accordingly. Chemicals should be discarded as hazardous waste in appropriate bins. More safety information is provided in the supporting information.

RESULTS AND DISCUSSION

One of the biggest factors in improving the *greenness* of a reaction is eliminating, if possible, the use of auxiliary substances, such as solvents, or the use of a solvent with low toxicity to human and animal/plant life. Henderson *et al.* categorized different solvents based on physical and chemical properties such as boiling point, reactivity, and health/environmental impacts (Table 1).³⁷ The scores in each category are broken down as the following: waste accounts for ease of handling and treatment after use (i.e. recycling, incineration, biotreatment); environmental impact accounts for solvent effects on environment; health accounts for acute and chronic effects on human health; flammability & explosion accounts for storage and handling; and reactivity/stability accounts for factors that affect the stability of that material. The low waste value for water is surprising at first glance (especially when compared to toxic compounds such as benzene and tetrahydrofuran), but the issue with water

based reactions lies with the final product separation. Given water's boiling point, the ability to create
170 azeotropes (*i.e.* non-combustible) and the high miscibility with polar compounds, water removal and
recycling can be difficult. In comparison, both benzene and tetrahydrofuran possess lower boiling
points which make them easier to separate from the reaction mixtures. The lower flashpoint and auto-
ignition temperatures of tetrahydrofuran give this solvent a lower waste score as it requires extra
safety in recycling. On the other hand, non-miscibility of benzene with aqueous streams allows easy
175 separation of this solvent easier from reaction mixtures.

Table 1. A green comparison of common industrial solvents. Adapted from GlaxoSmithKline's solvent guide.³⁷

Solvent	Boiling Point (°C)	Waste	Environmental Impact	Health	Flammability & Explosion	Reactivity/ Stability
Benzene	80	5	6	1	3	10
Dichloromethane	40	3	6	4	6	9
Dimethyl carbonate	91	4	8	7	6	10
Dimethyl sulfoxide	189	5	5	7	9	2
Ethanol	78	3	8	8	6	9
Ethyl acetate	77	4	8	8	4	8
Methanol	65	4	9	5	5	10
Tetrahydrofuran	65	3	5	6	3	4
Water	100	4	10	10	10	10

For these experiments, we utilize the best auxiliaries possible: no solvent and water. The absence
180 of a solvent reduces the distance between molecules, favoring polymerization reactions.³⁸ On the other
hand, the presence of water favors the proposed ring-opening hydrolysis of the desired bio-derived
product, HMF, causing polymerization to humins.¹⁶ As the final product of our reactions is humins,
these conditions are not only with the greenest solvents (or absence of), but also can give visual images
of what humins look like.

185 Another important green chemistry concept is the use of a catalyst: by lowering the activation
energies of reaction intermediates, a catalyst can overall accelerate the production of the desired
chemical without being consumed in the reaction. Among all types of catalysts, homogeneous and
heterogeneous catalysts are the most used in biomass conversion.

Homogeneous and mineral catalysts, such as HCl and H₂SO₄ may give high conversions but low
190 selectivity to the desired bio-derived product, HMF.³⁹⁻⁴¹ Mineral acids in particular, produce high
quantities of toxic materials which are difficult to dispose of. In this sense, organic acids, for example
acetic or citric acid, may be used as homogeneous catalysts as they could be mineralized to CO₂.^{39, 40}
In the reactions tested, a small quantity of acetic acid was used to fully drive polymerization to
humins. The overall advantage of homogeneous catalysts relies on the intimate contact between the
195 active sites (in this case, H⁺) and the reactant. However, these catalysts cannot be easily separated
from the reaction media, greatly contributing to the waste of the reaction.⁴² For this reason,
heterogeneous catalysts are preferred because their different state (usually solid in liquid/gas media)
allows for better separation. However, the active part is only given by the superficial area of solid
catalysts, thus high porosity is often looked for to improve the contact between the reactant and the
200 active site.⁴³

Two catalysts were tested in this work, already seen in literature: alumina⁴⁴ and Amberlyst-15.⁴⁵
Alumina as an oxide is an amphoteric material, meaning it could act as a base or as an acid. In the
case of Brockmann's catalyst used in this laboratory experience, the activation of the alumina phase
confers the catalyst weak acidic sites in a range of conditions, without changing the elemental
205 composition of the material.⁴⁶ On the other hand, organic or inorganic materials functionalized with
active groups can act as a catalyst. This is the case of Amberlyst-15, a polymeric resin with sulfonated
groups. The presence of -SO₃ groups on the surface confers this polystyrene-divinylbenzene resin
strong surface acidity.⁴⁷

Most importantly, the difference between the two materials is the type of the surface acidity:
210 alumina is considered a Lewis acid, while Amberlyst-15 acts as a Brønsted acid. Fructose conversion
to HMF undergoes a Brønsted acid-catalyzed mechanism. Literature studies have shown Amberlyst-15
to be active⁴⁵ for these reactions and alumina to be generally ineffective alone.⁴⁴ The difference in
activity also applies to the formation of humins. In our case, this is observed by the darkening of the
reaction mixture and the catalysts. No color change is observed in any of the aqueous reactions within
215 the first 30 minutes (±10 minutes), but a slight yellow color appeared shortly after in the Amberlyst-15
reaction and later intensified to a dark orange upon completion of the reaction. This is the first

symptom of the formation of HMF (yellow), while the darkening shows the formation of humins (Figure 1, S1-S4). A similar trend is observed in the solventless reaction of fructose and acetic acid: upon solubilization of the sugar with heating (melting point of 103 °C), the mixture turned orange before
220 turning completely black after 1.5 h (Figure S8).



Figure 1. Reactions performed in solvent after 1.5 h (Left to right: blank, alumina catalyzed, Amberlyst-15 catalyzed)

The formation of humins can be observed for both of the catalyzed reactions upon filtration, and in
225 the solventless reaction. As shown in Figure 2, Amberlyst-15 beads (originally grey) darkened to a deep brown/black and the alumina (originally white) turned a light brown/orange.

The solventless reaction yielded a sticky and viscous solution that is identified as humin by-products (Figure 3). This is the first point for teaching the effect of a solvent and catalyst on a reaction: the former increases the physical space between reacting molecules, thus reducing the risk of
230 polymerization; the latter, on the other hand, not only improves selectivity to a certain product, but also acts as an adsorbent due to its superficial properties.

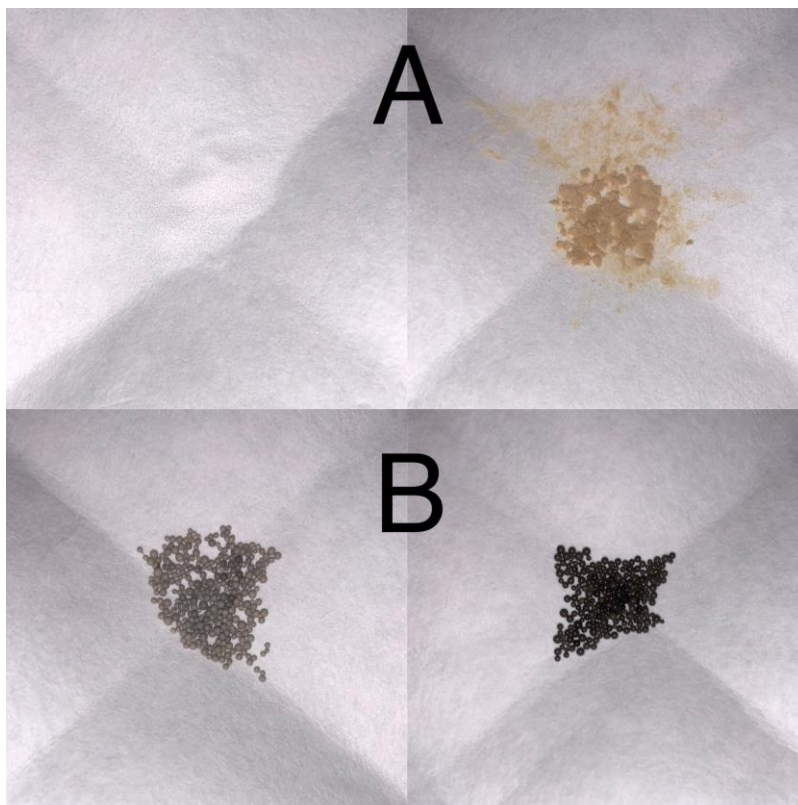


Figure 2. Alumina (A) and Amberlyst-15 (B) catalysts before and after reaction, respectively.



Figure 3. Humins formed in solventless conditions.

After filtration of the heterogeneous catalysts, the students performed an extraction of the aqueous phase with ethyl acetate in order to analyze the reaction results by TLC plates. Under UV light, the

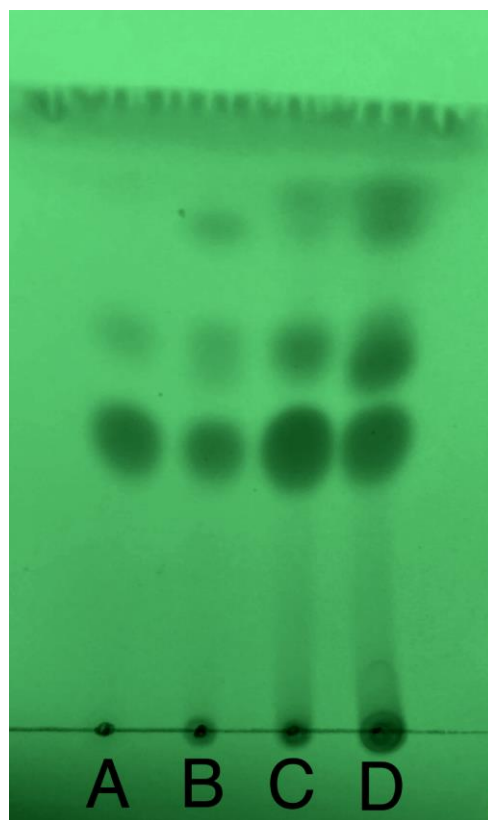
spots of Figure 4 were observed. The intensity of the TLC spots (also the color of the final solution) can
240 give semi-quantitative information and was used as such.

In all cases, the formation of HMF is clearly observed (RF 0.5) with the strongest intensity when
Amberlyst-15 (Fig. 4, C) is used. In fact, being the strongest acidic material, the highest conversion
would be expected given the conditions studied in this laboratory experience. In the case of the weakly
acidic alumina (Fig. 4, B), instead, lighter intensities of the products were observed, contributing to a
245 light color of the final solution. This is a symptom of the adsorption of side-products, including
humins, on the catalyst surface, as previously seen in Fig. 1. This phenomenon where a layer of
carbon is deposited on the catalytic material is referred to as coking.

The formation of DFF is observed at a higher RF value (0.60). This is a result of the acid-catalyzed
oxidation of HMF, a side reaction that occurs in aerobic conditions. This could be avoided by
250 employing an inert atmosphere (*e.g.*, N₂). Lastly, levulinic acid is observed at RF value of 0.75 and is a
product of the acid-catalyzed ring-opening of HMF. Levulinic acid, however, is not observed for the
acetic acid-assisted reaction in water (Fig. 4, A).

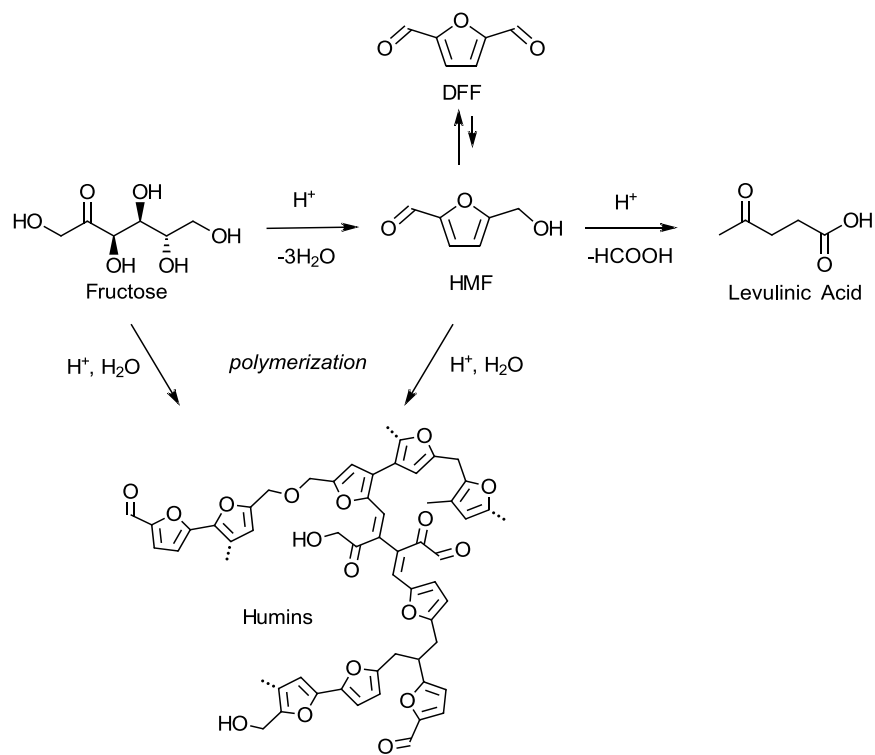
The light spots give a hint of low conversion in the acetic acid-assisted reaction without a
heterogeneous catalyst and in the presence of water. This could be attributed to inefficiency of the
255 small amount of acetic acid to catalyze the dehydration for further decomposition of HMF into levulinic
and formic acid. When the solventless conditions were employed, instead, unidentified peaks were
observed which show the occurring of further side-reactions which decrease the atom efficiency of the
process.

An overall simplified scheme of the reaction mechanism of this laboratory experience is given in
260 Scheme 3. This reaction scheme should be taken as an example that in biomass conversion strategies,
selectivity to one particular product is challenging due to the highly active oxygen containing groups
that can undergo a variety of side reactions, greatly reducing process efficiency.



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Figure 4. TLC results of the four reactions. A: No heterogeneous catalyst in water; B: Alumina in water; C: Amberlyst-15 in water; D: acetic acid-assisted and solventless reaction.



Scheme 3. Overall simplified reaction mechanism from fructose to the observed molecules.

CONCLUSIONS

270 Conclusively, the students were introduced to concepts of green chemistry, systems thinking and biomass valorization with this experiment. This laboratory experiment also provided hands-on practice for common organic chemistry techniques and reactions with sugar dehydration. This should be a step into bringing the students to critically view the traditional acid-catalyzed conversion of biomass from the dark side: the formation of humins.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available on the ACS Publications website at DOI:

10.1021/acs.jchemed.

Notes for Instructors (DOCX)

280 Students Handout (DOCX)

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