

Biomass Conversion into Fuels and Chemicals

One-pot Hydrolytic Hydrogenation of Biomass to Value-added Chemicals

KEYWORDS: Lignocellulosic biomass / One-pot / Hydrolytic Hydrogenation / Heterogeneous Catalysts/ Sorbitol / Ethylene Glycol

The catalytic valorisation of biomass wastes into valuable chemicals is a promising technology that can link the traditional refinery and renewable sources. Sorbitol and ethylene glycol (EG) are extremely important chemicals that are extensively used in food, pharmaceutical, and chemical industries. Great progress was obtained in their selective production over a variety of highly efficient heterogeneous catalysts. Namely, various carbon-supported noble and non-noble metal catalysts have been developed for the one-pot conversion of biomass components and residues. Remarkable sorbitol and EG yields over 60 and 50%, respectively, were reached directly from cellulose using just hot water under H₂ pressure. Furthermore, notable yields of sorbitol and EG up to 48 and 46%, respectively, were attained from the direct catalytic valorisation of agroforestry and urban biomass residues (e.g., tissue paper, cotton wool, corn cob, eucalyptus wood). These results are among the best ever obtained for the catalytic conversion of lignocellulosic biomass by an environmentally friendly process for the production of those compounds of high practical interest. The reported results are very encouraging for large scale application and the accumulated knowledge from these extensive studies will be a valuable guide for tuning the reaction selectivity and meeting the market demand.

Introduction

Biomass is any hydrocarbon that mainly consists of carbon, hydrogen, oxygen and nitrogen, and its resources have a basic structure composed of cellulose (40-50%), hemicelluloses (25-35%), lignin (15-20%) and minor amounts of other organics [1]. Considering the availability of forestry and agricultural feedstocks, aquatic plants and algae, as well as municipal and industrial wastes, there is a great worldwide potential for the production of highly valuable chemicals from biomass. Biomass and its components can be converted into platform chemicals using bifunctional catalysts in one-pot tandem reactions. However, the catalytic processing of biomass-derived feedstocks to chemicals is complex and expensive, so many challenges have to be overcome to replace the fossil-fuel based economy with sustainable technologies. One main difficulty is the first step of hydrolysis, which is extremely difficult due to cellulose's robust crystalline structure. Therefore, some pre-treatments are mandatory to obtain a considerable yield of the desired product, such as ball-milling.

Sorbitol and ethylene glycol (EG) are two of the most important products which can be obtained from biomass, each one with a tremendous growing market and value (Fig. 1). Sorbitol is in the TOP-12 biomass value-added products, while EG has an important role in the synthesis of valuable chemicals that have a large market, such as polymers [2].

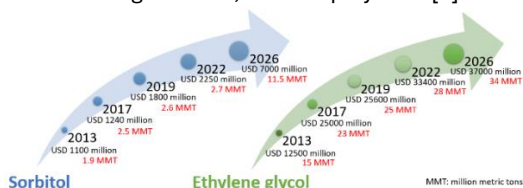


Fig 1. Size and projections of the global sorbitol and EG markets.

Current Development

The direct conversion of cellulose into sorbitol was studied by coupling hydrolysis of cellulose to glucose on acid sites, and its subsequent hydrogenation on metal sites. Sorbitol yields up to 70 and 48% were attained from the one-pot conversion of cellulose and cellulosic wastes (e.g., tissue paper, cotton wool, cotton textile), respectively, over Ru and Ru-Ni catalysts supported on carbon nanotubes (CNT). Following that study, using a catalyst consisting of only 0.4 wt.% Ru supported on carbon (obtained by hydrothermal carbonization of glucose with 2 wt.% of carbon nanotubes), we achieved a remarkable 100% conversion of cellulose with a sorbitol yield of 64% after just 3 h (Fig. 2), which outstood that previously obtained using CNT as support (50.9% sorbitol yield after 5 h: the highest yield reported to date over carbon supports) under the same reaction conditions, indicating that CNT can be successfully replaced by a low-cost support derived from biomass [3]. As a result, not only the highest yield of sorbitol was obtained, but cellulose, one of the most important fractions of biomass, was valorised through two pathways: the cellulose itself as the main raw material of the reaction and its monomer, glucose, for the preparation of the catalyst.

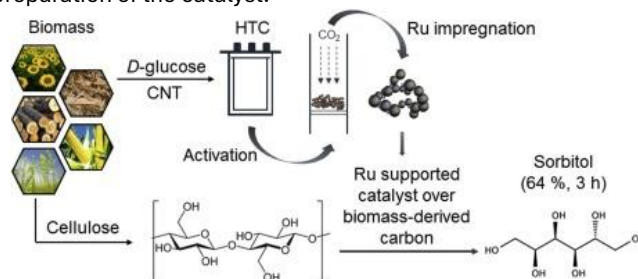


Fig 2. Sorbitol direct production from cellulose over Ru catalysts supported on biomass-derived carbons.

On the other hand, EG was initially produced via the hydrolytic hydrogenolysis of cellulose. This work was done in collaboration with research groups from Spain. A cooperative effect of heteropoly acids and Ru nanoparticles supported on two carbon materials was demonstrated, resulting in EG yields up to 26% [4]. Moreover, the selectivity of the catalyst in the one-pot conversion of cellulose could be controlled by the addition of a second metal to Ru and by the formation of an alloy. For example, the selectivity of the tandem process changes from hexitols (e.g., sorbitol), as main products, to diols (e.g., EG) by the addition of W. Hence, Ru-W/CNT and Ni-W/CNT catalysts were studied for EG direct production from cellulose. Then, the catalytic system and reaction conditions were optimized for the production of EG, resulting in yields around 40% after 5 h at 205 °C and 50 bar of H₂ using a 0.8%Ru-30%W/CNT catalyst, with great stability [5,6]. Moreover, the conversion of biomass wastes, such as eucalyptus wood and tissue paper, was evaluated, and EG yields over 30% were attained [6].

Alternatively, a Ru-W bimetallic catalyst supported on glucose-derived carbon was used for the direct conversion of cellulose to EG, allowing to achieve yields close to 50% in just 3 h (Fig. 3) [7]. As a result, the synthesized catalysts seem to be promising alternatives in order to produce EG directly from cellulose by a more economical (supports derived from

biomass), faster (one-pot reaction) and easier (combined catalyst synthesis) process.

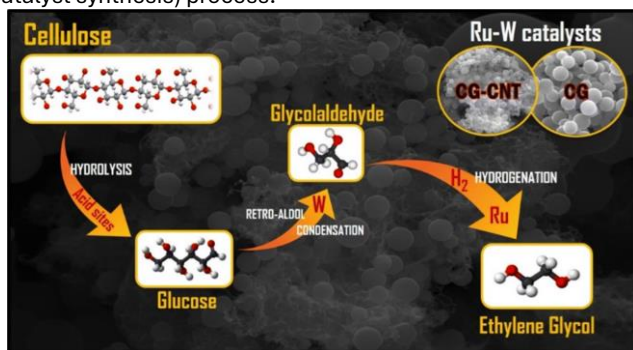


Fig 3. EG direct production from cellulose over Ru-W catalysts supported on biomass-derived carbons.

Furthermore, CNT-supported Ru-W catalysts were tested on the conversion of various forestry, agricultural and urban wastes directly to EG (Fig. 4). Materials such as woods (pine, oak, eucalyptus, etc.), leaves (eucalyptus, lemon), pine cones, cork, corncob, grass, flowers, peanut shells, coffee grounds, cotton wool and paper, were converted as received, after ball-milling and also after lignin removal [8]. While yields between 10-20% were attained directly from the raw wastes, ball-milling the substrates allowed to greatly enhance the conversion rate and the EG yields up to 41%. This highest yield value could be directly obtained from ball-milled eucalyptus wood and cotton wool. These results are amongst the highest ever achieved from the green and sustainable direct conversion of biomass wastes using CNT supported Ru and W catalysts in the presence of H₂ and using only water as solvent, without any acids. Moreover, this catalytic system proved to be reusable for at least four successive runs and also that can be extended to different kinds of biomass wastes.



Fig 4. Photographs of the waste materials before and after cutting/crushing, drying, ball-milling, and lignin removal.

More recently, a cheaper metal such as Ni was found to successfully replace the Ru noble metal for cellulose conversion into EG [9]. An EG yield over 50% was reached in just 5 h over Ni-W/CNT (Fig. 5), which greatly surpassed the previous obtained using Ru-W/CNT under the same conditions that were already amongst the highest ever achieved. Additionally, the catalyst was tested for the conversion of cotton wool, eucalyptus wood and corncob, resulting in EG yields of 46, 28 and 36%, respectively. Thus, Ni-W/CNT catalysts proved to be efficient for the direct EG production from cellulose and biomass wastes as low-cost and sustainable catalytic alternatives.

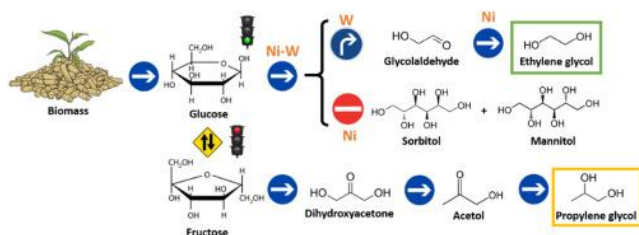


Fig 5. Schematic representation of the catalytic conversion of biomass to EG.

Future Work

We are currently working on the further optimization of a catalytic system for the one-pot conversion of cellulose to sorbitol and EG, taking into account the best previous results obtained: i) Ru catalyst supported on biomass-based material for sorbitol production; ii) Ru-W catalyst supported on biomass-based material for EG production, together with the replacement of Ru by Ni (Ni-W/CNT catalysts). Accordingly, glucose-based materials are already being prepared and evaluated as catalytic supports for cellulose conversion into EG and sorbitol, using non-noble Ni-W and Ni metals, respectively. Afterwards, the main goal will be to replace glucose by biomass residues, such as municipal solid wastes (e.g., food waste), for the production of biomass-based catalytic supports.

Additionally, another interesting and challenging catalytic route is the tandem conversion of cellulose into isosorbide, which is the most promising derivative of sorbitol. An intensive study of the other biomass components (hemicelluloses and lignin) is also an important focus of future studies, as well as the application of the best catalytic systems to the valorisation of a wider range of lignocellulosic residues. The final challenge would be the large-scale application of the developed biomass conversion processes.

Related Sustainable Development Goals



Outputs

Master Dissertations

Marta Noites Sacramento, Sustainable production of aviation fuels directly from biomass, MIEQ, FEUP, 2022

Selected Publications

- [1] L.S. Ribeiro, *Química* 42, 133 (2018)
- [2] L.S. Ribeiro et al., *Materials Today Sustainability* 11-12, 100058 (2021)
- [3] N. Rey-Raap et al., *Applied Catalysis B - Environmental* 256, 117826 (2019)
- [4] M. Almohalla et al., *Catalysis Today* 301, 65 (2018)
- [5] L.S. Ribeiro et al., *Cellulose* 25, 2259 (2018)
- [6] L.S. Ribeiro et al., *Bioresource Technology* 263, 402 (2018)
- [7] L.S. Ribeiro et al., *Cellulose* 26, 7337 (2019)
- [8] L.S. Ribeiro et al., *Industrial Crops and Products* 166, 113461 (2021)
- [9] L.S. Ribeiro et al., *Renewable Energy* 200, 1008 (2022)

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Biomass Conversion into Fuels and Chemicals

One-Pot Oxidation of Biomass to Value-Added Chemicals

KEYWORDS: cellobiose/hydrolysis/hydrolytic oxidation/cascade reactions/gluconic acid/carbon catalys

Carbon xerogels (Cxs) functionalised with varied heteroatoms (i.e., O, P, S, N) were applied as solid acids to hydrolyze cellobiose to glucose. Cx containing 3.4 wt % of phosphorus reached 90 % conversion of cellobiose with 72 % selectivity to glucose under an oxidative atmosphere and in a short reaction time of 4 h. The catalytic performance of the solid acids in hydrolysis of cellobiose depended not only on their total acidity but also on the type of active sites present.

The effect of the type and properties of TiO₂ and the addition of graphene oxide (GO) was studied in Au/TiO₂ bifunctional catalysts, which were applied for cascade conversion of cellobiose to gluconic acid. An exceptional yield of gluconic acid reaching 85% was attained in 2 hours over Au supported on acidic TiO₂. The best catalyst contained "electron-rich" Au metal phase and oxygen vacancies near the metal-support interface. It was found that the strong metal support interaction (SMSI) in Au/TiO₂ can be tuned by adding reduced graphene oxide (rGO), which can be useful in developing bifunctional catalysts for other biomass valorization processes.

Introduction

Lignocellulosic biomass is considered the only suitable source of organic carbon that can be used as an alternative feedstock to fossil fuels for producing chemicals and fuels. Cellulose, a biopolymer composed of d-glucose units linked by β-1,4 glycosidic bonds, is the most abundant component of biomass waste. In all industrially relevant biomass valorization processes, cellulose must first be converted into glucose via mechanical treatments and acid-catalyzed hydrolysis (fig.1). Subsequently, as-obtained glucose can be further transformed via oxidation, hydrogenation, or dehydration into value-added products, applying the strategy of cascade reactions in one pot. Therefore, efficient hydrolysis of cellulose is a crucial entry process to obtain useful sugars that can be converted into a range of industrially important products. Nevertheless, the depolymerization of cellulose continues to be challenging due to its high chemical stability. Conventionally, diluted inorganic acids (e.g., sulfuric or hydrochloric acid) have been used for hydrolysis of cellulose to glucose. However, these technologies suffer from a handful of drawbacks, such as equipment corrosion hazards, generation of toxic waste, and problematic product separation [1]. From the point of view of "green" and sustainable biorefinery processes, it is of great importance to develop efficient and recyclable solid acid catalysts containing

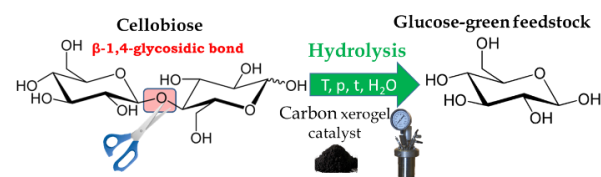


Fig 1. Hydrolysis of cellobiose (model molecule of cellulose) to glucose using carbon xerogels.

suitable strong Brønsted acid sites for the hydrolysis of cellulose to glucose. Carbon materials, such as carbon xerogels (Cxs), are very suitable catalysts for transformations under hydrothermal conditions because of their high surface area, excellent chemical and thermal stability, and tunable

surface chemistry. Many available studies compared different types of carbons as solid-acid catalysts for hydrolysis, but the study comparing types of Brønsted acid sites is lacking.

A wide range of products can be obtained from cellulose/cellobiose via one-pot cascade reactions using multifunctional catalysts. For example, gluconic acid is an important chemical with wide applications as a green chelating agent, an additive in food and pharmaceutical industries, or a monomer of biopolymers. Thus, efforts have been made to develop environmentally friendly gluconic acid production processes for sustainable biorefineries. One of these novel processes is a tandem conversion of cellulose/cellobiose to gluconic acid using bifunctional catalysts. In the cascade process, the acidic sites on the support carry out a cellulose/cellobiose hydrolysis step, followed by oxidation of glucose catalyzed by the metal active sites [2, 3].

Our group has previously obtained promising results in tandem conversion of cellobiose to gluconic acid using Au nanoparticles supported on carbon xerogels (M. Eblagon et al., Appl. Catal. B: Environ. 184 (2016). A remarkably high selectivity of nearly 80% to gluconic acid was obtained in a short reaction time of only 75 minutes using an Au catalyst supported on functionalized carbon xerogel containing larger mesopores. The performance of these bifunctional catalysts in tandem conversion of cellobiose to gluconic acid was tuned by changing the texture and surface chemistry of the support or by modifying the method used to deposit gold. Another type of bifunctional biomass valorization catalyst involves Au supported on reducible metal oxides like TiO₂, where the catalytic activity can be improved by tuning the strong metal support interaction (SMSI) [3].

The current project focusing on cascade valorization of biomass involved two objectives: i) to study the influence of the surface chemistry of solid acid catalysts in the hydrolysis of cellobiose to glucose (first step of the tandem process), ii) explore the influence of SMSI in Au supported on TiO₂ on the catalyst's performance in the tandem process to define the most relevant variables in the design of bifunctional catalysts for biomass upgrading processes involving an oxidation step.

Current Development

The hydrolysis of cellulose using cellobiose as a model molecule was studied in collaboration with our partner from the Faculty of Chemistry at the University of Adam Mickiewicz in Poznan, Poland (AMU). Distinct Brønsted acid sites were incorporated onto carbon xerogel's surface by treatments with inorganic acids (i.e. H₂SO₄, or H₃PO₄), or in the 5% O₂/N₂ flow at elevated temperatures. Gas phase treatment NH₃ was also carried out to study the influence of basic sites in this reaction. The obtained catalysts had different total acidity ranging from 0.13 mmol g⁻¹ for pristine CX to 1.98 mmol g⁻¹ obtained for phosphorylated CX [1].

The optimisation of the reaction conditions using pristine CX showed that the type of the atmosphere significantly influences the conversion of cellobiose, and the glucose yield decreased in order oxygen>air>N₂. The presence of the oxidative atmosphere promotes hydrolysis but also assists in further conversion/degradation of glucose, lowering its final yield. Moreover, the increased air pressure significantly improved cellobiose conversion and the selectivity to glucose.

The catalytic testing was carried out under 5 bar of air at 145 °C for 4 h (fig.2). The blank experiment showed a glucose yield of 15%, which increased to 22% with the addition of pristine Cx. The best results were obtained by phosphorylated Cxs, which were attributed to the electron-donating abilities of P, making the neighboring carbons more negative, inhibiting glucose adsorption and its further conversion/degradation. An outstanding 90% conversion of cellobiose with 72% selectivity to glucose was obtained by a catalyst containing phosphate groups in close vicinity to carboxylic acids and phenols on the surface (fig.2). The results showed that cellobiose conversion is not only affected by the total acidity of the catalysts, but the type of functional groups present on the carbon surface plays an important role. For example, the presence of sulfonic groups and pyridinic/pyrrolic nitrogen promoted the conversion of both cellobiose and glucose, resulting in low glucose yields.

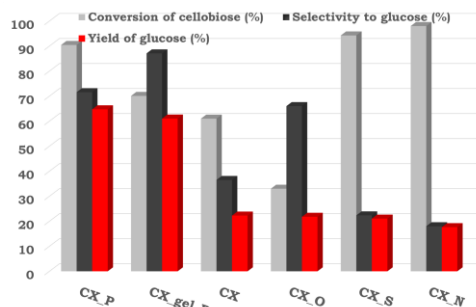


Fig 2. Catalytic results obtained in hydrolysis of cellobiose, using CX post-functionalized with different heteroatoms. CX_gel_P-Cx functionalized in situ with phosphorous [1].

The one-pot oxidation of cellobiose to gluconic acid was studied by applying bifunctional catalysts containing Au supported on different TiO₂ materials, with varied phases, particle sizes, and surface chemistry [2]. The SMSI in these catalysts was controlled by tuning the metal oxide properties or depositing reduced graphene oxide (rGO) onto the TiO₂ materials to form TiO₂-rGO composite supports (fig.3).

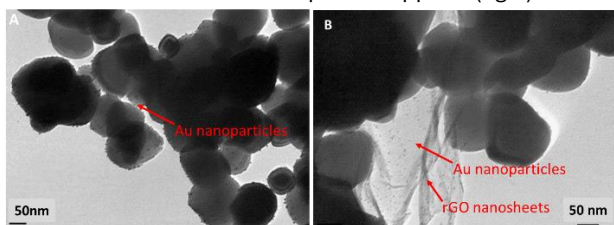


Figure 3. Au nanoparticles supported on TiO₂ (A), TiO₂-rGO (B) [2].

Different interactions between Au and pristine TiO₂ and composite supports were evidenced by varied reduction temperatures of Au in the temperature programmed reduction (TPR) results. The very promising 85 % gluconic acid yield was obtained by Au supported on the acidic TiO₂ (100% anatase phase) in only 2 h. The catalyst was very stable, with only a marginal decrease in gluconic acid yield after 5 consecutive runs. The XPS results showed that the best-performing catalyst contained the electron-deficient gold together with oxygen vacancies situated close to the metal-support interface in Au/TiO₂ (fig.4). Moreover, it was shown that the electrons located on the oxygen vacancies affect the adsorption and reactivity of key adsorbates such as cellobiose, glucose, and oxygen, leading to higher selectivity to gluconic acid of the tandem process. On the other hand, due to the presence of rGO, glucose oxidation in the second step of the tandem reaction was hindered, resulting in much lower yields of gluconic acid obtained (fig.4). This was attributed to the lack of oxygen vacancies and limited charge transfer from the support to gold particles due to the electron-withdrawing properties of rGO [2].

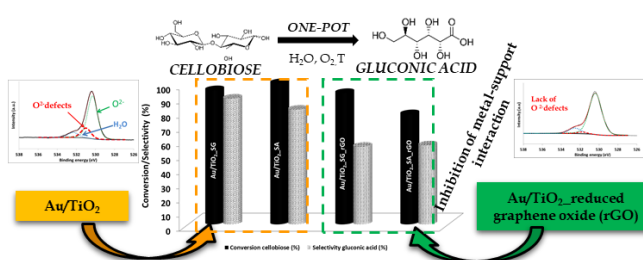


Fig 4. Catalytic results obtained in one-pot conversion of cellobiose to gluconic acid using Au supported on TiO₂ and TiO₂-rGO. TiO₂-SG- obtained by sol-gel method, TiO₂-SA-supplied by Sigma-Aldrich Inserts: XPS O1s spectra of these catalysts, spectrum on the left showing the presence of O₂- defects in Au/TiO₂ catalysts [2].

Future Work

Hydrolysis of cellulose to glucose is the crucial step of many biorefinery processes, however, the low economy and efficiency hinder its commercialisation. Replacing currently used inorganic acids with emerging solid acid catalysts can solve the critical issues connected to the former, including severe equipment corrosion, excessive cellulose degradation, serious environmental pollution, extensive water usage, and difficulties with product separation. Among the studied carbon xerogel-based solid acids, catalysts bearing phosphate functionalities together with -COOH, -OH groups have a strong affinity to cellobiose and make the acid sites closer to the β-1,4-glycosidic bonds. Future research will be focussed on testing the developed solid acids in the hydrolysis of cellulose and real biomass samples and improvement of the yields of glucose by application of microwave heating.

Efficient production of value-added bio-based chemicals from biomass in one-pot tandem processes offers a pathway to achieve the Sustainable Development Goals (SDGs) proposed by the United Nations. The one-pot transformation of cellulose to gluconic acid increases the product's selectivity, decreases the workload and waste production, and shows great potential to replace currently used cost-intensive biochemical oxidation using enzymes or fungi. In the view of industrial application, it is desirable to develop bifunctional catalysts that can convert urban biomass wastes, e.g., food waste and yard waste, into gluconic acid or other value-added products. Another potential research direction in this field is to apply oxidation methods enhanced by ultrasound, microwave, or solar energy in this cascade process.

Related Sustainable Development Goals



Outputs

Selected Publications

- [1] K. Morawa Eblagon et al., ChemCatChem 10, 4934 (2018)
- [2] K. Morawa Eblagon et al., Energy Technology 6, 1675 (2018)
- [3] K. Morawa Eblagon et al., Catal. Today 301, 55 (2018)

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Biomass Conversion into Fuels and Chemicals

Conversion of Biomass to HMF and Other Platform Chemicals

KEYWORDS: 5-hydroxymethylfurfural, cascade reactions, dehydration, glucose, sugarcane molasses, glycerol valorisation

C6 sugars and sugarcane molasses were valorised to 5-hydroxymethylfurfural (HMF) in water using carbon based catalysts. Phosphorylated carbon xerogels were very active in dehydration of fructose, reaching 73.3% yield of HMF. When glucose was used as a feedstock, much lower yields of HMF were obtained, due to the sluggish isomerisation step of glucose to fructose. The strong Brønsted acid sites in the bifunctional catalysts decreased the selectivity of HMF, due to catalysing its degradation to humin under the reaction conditions. Valorisation of industrial grade sugarcane molasses (SCM) resulted in the maximum HMF yield of 28.6 %, obtained with a biomass-derived catalyst containing -SO₃H functionalities. Active solid acid catalysts were prepared from SCM or sugars via partial carbonisation and showed promising results in glycerol valorisation.

Introduction

Biomass emerged as an attractive, abundant, low-cost raw carbohydrate source with carbon-neutral properties. Thus, environmentally friendly novel manufacturing processes can convert sugar-rich biomass or industrial wastes into platform chemicals, like 5-hydroxymethylfurfural (HMF). HMF is a platform molecule that can be upgraded to a wide range of renewable products, including bioplastics, biofuels, or fuel additives (fig.1), replacing conventional petroleum-derived commodities. Despite being a key intermediate in the biorefinery concept, there is still no feasible industrial process to produce large volumes of HMF.

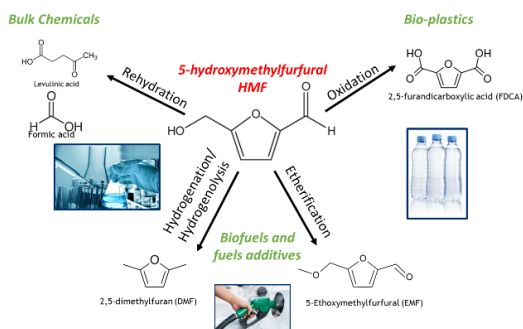


Fig 2. HMF as a platform chemical.

HMF can be produced from sugars, including fructose, glucose, and polycarbohydrates, like sucrose or cellulose. The commercial value of HMF has already been recognized by many companies in the chemical industry market. However, the industrial-scale production of HMF is still strongly limited by the high cost and low availability of feedstock, difficult processing, and insufficient HMF yields [1]. Therefore, finding cheap and widely available waste materials suitable for mass production of HMF is a critical step towards a sustainable biomass-based economy.

It should be underlined that more complex feedstocks containing glucose are difficult to dehydrate to HMF, making the process more challenging due to the increased reaction steps and inherent instability of HMF under the reaction conditions.

In collaboration with our colleagues from the Adam Mickiewicz University in Poland (AMU) and our local industrial partner, sugar refinery RAR in Porto, we explored the possibility

of valorizing industrial-grade sugarcane molasses (SCM) waste as carbon source for production of HMF. Two approaches were considered: i) using SCM as feedstock for HMF production or ii) as a carbon source for solid acid catalysts. SCM is a promising potential feedstock for future biorefineries because it is widely available worldwide and contains a high concentration of sugars, mainly sucrose (up to 50%). SCM also contain large amounts of impurities, including ashes, colorants, organic acids, and proteins. The conversion of SCM to HMF on the bifunctional catalyst involves the following steps: i) the hydrolysis of sucrose into glucose and fructose (catalyzed by Brønsted acid sites), ii) the isomerization of glucose into fructose (catalyzed by Lewis sites), and iii) fructose dehydration to HMF (catalyzed by Brønsted acid sites). The common side reactions include the acid-catalyzed HMF rehydration to organic acids and condensation or cross-polymerization of HMF with hexoses, forming soluble polymers and insoluble humin (fig.2).

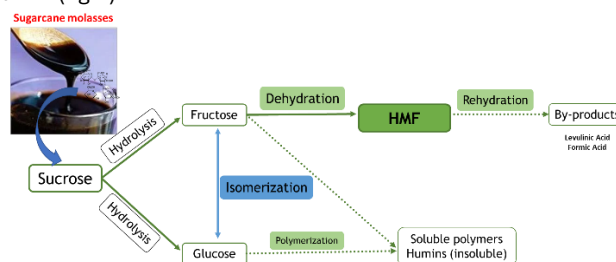


Fig 3. Reaction scheme for the production of HMF from sugarcane molasses and C6 sugars.

Due to the rapid expansion of fully developed technologies of first- and second-generation biofuels, a large volume of glycerol is available on the market. Thus, the valorisation of glycerol was considered the second objective of the present work. Glycerol esterification with acetic acid is an acid-catalyzed liquid-phase reaction leading to value-added glycerol derivatives, i.e., mono-, di- and tri-acetins, which are valuable fuel additives.

Current Development

The research was first focused on the intermediate reactions involved in the conversion of SCM to HMF (fig. 2). The dehydration of C6 sugars (fructose and glucose) was studied using various carbon xerogel (Cxs)-based catalysts in a Parr-type batch reactor. Phosphorous and oxygen functionalities were introduced onto Cxs' surfaces by hydrothermal functionalization and modified by post-treatments in a gas phase at elevated temperatures [2]. Phosphorylated Cxs were found to be effective solid acids in the dehydration of fructose. An excellent HMF yield of 73.3% was obtained in the green H₂O-CO₂ system. The yield of HMF was improved by higher concentrations of the oxygen functionalities on the surface of the catalyst.

Composite catalysts containing Lewis acid sites as Nb₂O₅ and phosphorylated CXs as Brønsted acid sites. were tested in dehydration of glucose [3]. It was found that Lewis acid sites are crucial for the selective isomerisation of glucose to fructose. The maximum yield of HMF obtained from glucose was 31%, and the rate-controlling step was the isomerisation of glucose to fructose. Thus, a catalyst with poor Brønsted acidity of Nb₂O₅ origin (Nb-OH) was preferable to achieve

moderate HMF yield with limited humin formation, when glucose was used as a feedstock. It was also shown that the type and amount of Brønsted acid sites from the carbon component affected the yield of HMF, and larger concentrations of P-O had a negative effect on the yield of HMF [3].

Subsequently, the dehydration of synthetic molasses (69.4 g/L of carbohydrates including sucrose, glucose, and fructose), and SCM was carried out using a series of starch-derived catalysts containing varied Brønsted acid sites (P, O, S functionalities) and bifunctional catalyst containing Brønsted acid sites and SnO₂ as Lewis sites. Due to the excessive production of insoluble humin in the one-pot conversion of sugar mixtures, the conversion of SCM was carried out in the microwave reactor. The study of the influence of the temperature on the one-pot process revealed that the conversion of sugars in SCM is favoured at elevated temperatures. However, the selectivity to HMF decreases at higher temperatures, as it is more likely to be transformed to humin (fig.2). Thus, higher temperatures effectively shortened the reaction time, but also hindered selectivity to HMF.

Two types of catalysts were compared in SCM valorisation to HMF, namely carbon with only Brønsted acid sites (i.e., sulfonic, oxygen, or phosphorous functionalities) and bifunctional catalyst combining Brønsted acid sites (i.e., phosphorous functionalities) with Lewis acid sites (SnO₂).

The highest yield of 26 % HMF was obtained from synthetic molasses at 190 °C by catalyst containing sulfonic groups. However, when SCM was used as a feedstock under the same reaction conditions, the HMF yield dropped to only 13%, which was attributed to the negative effect of impurities in SCM.

The decrease of the reaction temperature from 190 °C to 160 °C with extended reaction time and purification of SCM via simple centrifugation increased the HMF yield from 13% to 28.6%. The testing of catalysts with different active sites revealed that the HMF yield was proportional to the amount of SO₃H (fig.3). Bifunctional catalysts did not increase the yield compared to the blank experiment. On the other hand, phosphorylated hydrochar, which had the highest total acidity, increased the conversion of sugars and decreased the selectivity to HMF.

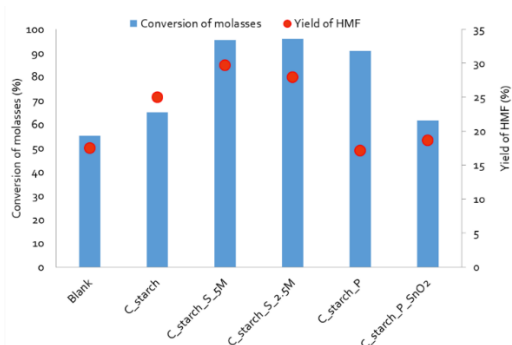


Fig 4. Catalytic results of tandem conversion of 10% SCM in water at 160 °C for 2.5 h.

In collaboration with AMU, environmentally benign solid acid catalysts were prepared from sugars or SCM, applying partial carbonisation or hydrothermal carbonisation and chemical activation [4]. The materials were applied in glycerol transesterification with ethyl acetate under different reaction conditions (fig. 4). All the prepared samples were found to effectively catalyze the reaction, producing a mixture of mono-, di- and triacetins (MA, DA, and TA, respectively); however, the efficient production of the target compounds, namely DA and TA, which are valuable biofuel additives, was found to be strongly dependent on the content of sulfonic groups on the

surface of these catalysts. A convenient way to obtain carbonaceous solid acid catalysts via one-step partial carbonization was shown, which offers promising alternatives to modified carbons produced by conventional multi-step techniques.

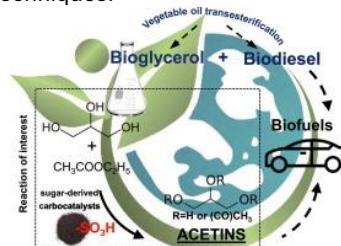


Fig 5. Valorisation of glycerol to acetins [4].

Future Work

The development of methods to convert industrial grade SCM to platform chemicals such as HMF could provide alternative revenue streams to the sugar industry with limited environment impact and decrease the amount of landfills. The use of industrial waste as feedstock contributes to reaching sustainable production patterns by replacing fossil sources with plant content, increasing processing efficiency by applying circular economy and limiting energy and material inputs. The collaboration with RAR concerning valorisation of SCM waste will be continued. Further steps will be focussed on increasing the yields of HMF obtained from SCM by using a biphasic solvent containing organic phase that will extract HMF from water, limiting its degradation. Different catalytic systems and solvent combinations will be explored to minimise the production of humin. Finally, one-pot synthesis of FDCA will be attempted by in-situ oxidation of HMF formed from sugars, without the purification step. Based on the groups' know-how in carbon based multifunctional catalysts, a novel solid acid will be developed containing additional transition metal active sites for oxidation of HMF.

Related Sustainable Development Goals



Outputs

Master Dissertations

Catarina Mafalda Gomes Monteiro Oliveira, One-Pot Catalytic Conversion of Sugarcane Molasses to 5-Hydroxymethylfurfural, MIEQ, FEUP, 2022
Bernardo B. Silva, Production and Functionalization of Carbon Materials From Sugar Cane Molasses For Application in Catalysis, MIEQ, FEUP, 2022

Márcia Verónica Nunes Barros, Valorisation of sugarcane molasses into biofuel and precursor of bioplastics, MIEQ, FEUP, 2023

Selected Publications

- [1] K. Morawa Eblagon et al., *Nanomaterials* 10 (2020)
- [2] K. Morawa Eblagon et al., *Fuel* 334 (2023)
- [3] K. Morawa Eblagon et al., *Catal.Today* 418 (2023)
- [4] A. Malaika et al., *Fuel* 304 (2021)

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Biomass Conversion into Fuels and Chemicals

Conversion of Biomass and Bio-Oils to Aviation Fuels and Chemicals

KEYWORDS: Lignocellulosic biomass / Bio-oils / One-pot process / Heterogeneous Catalysts/ Carbon materials / Aviation fuels

The transport sector has a great influence on the global dynamics of societies, directly contributing to the mobility of people, products and services, and this sector represents about one third of the total energy consumed in the world, most of this energy being almost exclusively from oil. Renewable fuels could have a significant impact on lowering greenhouse gas emissions and providing a long-term sustainable alternative to petroleum-derived fuels. Since lignocellulosic biomass and bio-oils are low-cost feedstocks that do not compete with food, they have drawn great attention as attractive alternatives to replace fossil feedstocks for the production of fuels. However, the catalytic upgrading of these residues in industry still remains a big challenge and the development of highly integrated systems that allow the direct conversion of wastes is essential to achieve that goal. So far, a complete palmitic acid conversion was achieved, with an outstanding hexadecane yield of 90% over a synthesized Co-Mo catalyst supported on HNO₃ oxidized carbon nanotubes (CNT_{ox}), which was similar to the catalytic performance obtained using the commercial Co-Mo/Al₂O₃ catalyst (89.4% hexadecane yield). Moreover, Co-Mo/CNT catalyst allowed to convert waste cooking oil into linear (13.8%) and branched (0.4%) hydrocarbons in the aviation fuel range, while Ni-Mo/CNT_{ox} provided a higher selectivity (81.2%) in the green diesel hydrocarbons range.

Introduction

The continued crude oil depletion, combined with the ever-growing need of renewable sources, highly motivates the search and development of advanced fuels. While natural gas and coal can be substituted by solar and wind for electricity production, petroleum can only be replaced by biomass since it is the only source of renewable carbon available on Earth. Biomass valorisation achieves an effect on CO₂ reduction because biomass grows utilizing CO₂ and sunlight through photosynthesis (Fig. 1). Considering the availability of forestry and agricultural feedstocks, aquatic plants and algae, as well as municipal and industrial wastes, there is a great worldwide potential for producing fuels and chemicals from biomass [1]. Therefore, converting sustainable lignocellulosic residues into fuels and high-value chemicals offers a promising approach to fulfil the pressing global task of carbon footprint reduction, helping to reduce the dependence on fossil resources.

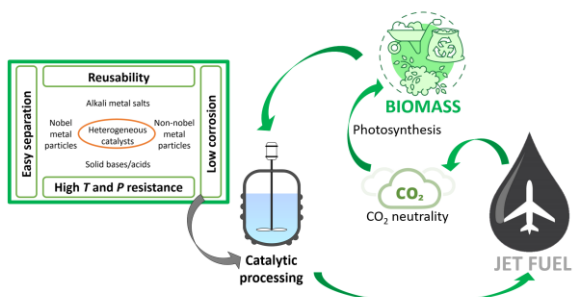


Fig 1. Schematic representation of the catalytic conversion of biomass to jet fuel.

Within the subject of sustainable drop-in fuels production, the field that shows both the greatest challenges and biggest opportunities is sustainable aviation fuel (SAF). Although the COVID-19 pandemic has affected the aviation sector's emissions, it is expected that pre-COVID levels will be rapidly reached and that the global demand for SAF will increase to more than double the current level by 2050. Sustainable fuels are fundamental for the transition to zero carbon as planned by the European Green Deal and the UN Sustainable Development Goals.

There are several methods for producing fuels from biomass, such as: i) hydrodeoxygenation (HDO), hydrocracking, and isomerization of lipids; ii) gasification-Fisher Tropsch synthesis-HDO, iii) biomass pyrolysis-bio-oil hydrocracking/ isomerization; and iv) depolymerization of biomass-platform chemicals synthesis-fuel precursor design and synthesis-HDO. Some processes were already developed at a commercial scale and the fuels were approved by ASTM D7566, but others, like fermentation and catalytic conversion to hydrocarbons, are still at the research stage. In fact, the catalytic route is a highly complex process involving deep chemical changes through selective oxygen removal steps (e.g., dehydration, decarboxylation, hydrogenolysis), followed by molecular-weight and structural adjustments (e.g., aldol condensation, oligomerization). Accordingly, to obtain high-energy-density fuels from bio-oils, an oxygen removal process is required, typically a catalytic hydrotreatment, commonly known as HDO. However, for the conversion of biomass-derived compounds, the employment of C-C coupling reactions is necessary to obtain products with higher carbon numbers that can be further transformed into jet fuel (C₈-C₁₆ hydrocarbons), since biomass compounds can only originate hydrocarbons with carbon number up to 6, which is shorter than aviation fuel.

Current Development

The work in the area of fuels started through a collaboration with LAQV-REQUIMTE, Faculty of Sciences of the University of Porto and Polytechnic Institute of Porto. This work focused on the production of ethyl levulinate (EL) fuel bioadditive from 5-hydroxymethylfurfural (HMF) using biochar catalysts, produced by hydrothermal carbonization of vineyard pruning wastes [2]. This efficient catalytic route to produce biofuel additives from HMF is an important step for the production of inexpensive, easy-to-prepare and innovative metal-free biochar-based catalyst. Full HMF conversion together with outstanding EL yields (over 84%) were achieved at 130°C and after 6 h over functionalized biochar (Fig. 2). These results offer a competitive alternative for the production of fuel additives using low-cost easily prepared biochar-based catalysts, all from lignocellulose resources, as an example to support a future exploitation of a potential biorefinery.



Fig 2. Schematic illustration of the conversion of HMF to EL over biochar catalysts produced from vineyard pruning wastes.

Moreover, the investigation of the one-pot conversion of oils to SAF was initiated, in which carbon range distribution varies from C_8 to C_{16} depending on the feedstock composition and refining process. Initially, the conversion of sunflower oil was evaluated using Co-Mo/ Al_2O_3 commercial catalysts without any solvent, and among the various products obtained were C_8 , C_{10} , C_{15} , C_{16} , C_{17} and C_{18} hydrocarbons. This study has been carried out in collaboration with 7 companies, 6 universities, 2 R&D institutes, 2 associations and TAP Air Portugal, though a financed mobilizing project – Move2LowC, with the aim of producing jet fuel from microalgae oil. Then, to move on to the conversion of microalgae oil, the study was started by studying one of its model compounds, palmitic acid. The influence of the different reaction parameters on the conversion of palmitic acid into alkanes, such as temperature, stirring rate, reaction time, H_2 pressure, amount of catalyst mass and substrate mass concentration was assessed using the commercial Co-Mo/ Al_2O_3 catalyst. The outcomes also demonstrated that the hydrodeoxygenation route was followed during the fatty acid's deoxygenation. After optimizing the process, new carbon-supported catalysts were synthesized and evaluated for the production of aviation fuel ranged hydrocarbons. A complete palmitic acid conversion was achieved, with a remarkable hexadecane yield of 90% over a synthesized Co-Mo catalyst supported on HNO_3 oxidized carbon nanotubes, which was similar to the catalytic performance obtained using the commercial catalyst (89.4% hexadecane yield) (Fig. 3) [3]. Furthermore, reproducibility tests were performed to validate the results, as well as recyclability studies, which showed a slight decrease in the hexadecane yield up to the fourth cycle with great stability in further successive runs.

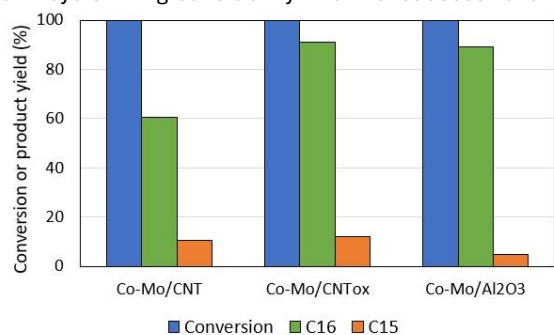


Fig 3. Palmitic acid conversion and products distribution. Reaction conditions: palmitic acid (0.50 g), n-decane (50 mL), Co-Mo/ Al_2O_3 (0.25 g), 350 °C, 30 bar H_2 , 150 rpm, 6 h.

More recently, a collaboration was established with Dr. José Luis Pinilla Ibarz's group at Instituto de Carboquímica, Zaragoza, Spain. The work aimed to evaluate the one-pot conversion of waste cooking oil into liquid fuels. For this purpose, bimetallic Co-Mo and Ni-Mo (2.5 wt.% of Co and Ni, and 10.5 wt.% of Mo) catalysts supported on multiwalled

carbon nanotubes (CNT) and oxidated CNT (CNT_{ox}) were tested to assess the deoxygenation reaction of the triglycerides containing in the oil into hydrocarbons. It was observed that the Co-Mo/CNT catalyst enhanced the selectivity to linear (13.8%) and branched (0.4%) hydrocarbons in the aviation fuel range, while Ni-Mo/ CNT_{ox} provided a higher selectivity (81.2%) in the green diesel hydrocarbons range.

Future Work

Concerning the conversion of bio-oils to SAF, the next steps will consist of the investigation of other model molecules (e.g., oleic acid) and the conversion of waste cooking oil. Furthermore, and taking advantage of this latter collaboration with Spain, another goal is to evaluate the catalysts in a continuous reactor, as well as to study other solvents that provide H_2 in situ to continue the collaborative work. In addition, the reaction mechanism will be studied to enable the improvement of the catalytic systems used in the sustainable deoxygenation of oils.

Furthermore, the first steps towards the conversion of lignocellulosic wastes to jet fuel are already being taken, since the predicted future demand will not only be fulfilled by these types of oleochemical/lipidic feedstocks like vegetable oils. In this field, various non-edible forestry, agricultural and urban residues are being considered for study. However, the employment of C-C coupling reactions is necessary to obtain products with higher carbon numbers that can be further converted to jet fuel (C_8 - C_{18} hydrocarbons). Despite the considerable number of steps required to convert lignocellulosic biomass residues into SAF, the present goal is to take advantage of the similar processing conditions of two or more steps (e.g., acid hydrolysis and dehydration), so they can be potentially combined in one single-reactor, minimizing the overall separate reactions and reactors needed. Therefore, an initial optimization is fundamental to reduce the overall number of reaction steps. However, it is important to note that each feedstock has different reaction characteristics (e.g., dehydration) in similar processing environments, so the development of a unified strategy for a wide range of feedstocks is a great challenge to overcome. Accordingly, preliminary studies will also be performed with the individual fractions (e.g., cellulose, hemicellulose) and model/intermediate compounds (e.g., glucose, fructose) to further understand the reaction pathways and explain the product portfolio. A proper study will also be executed on the change in product selectivity with time, productivity, and catalytic stability and regenerability, which have a vital importance on the determination of the techno-economical potential of the developed process.

Related Sustainable Development Goals



Outputs

Master Dissertations

Marta Noites Sacramento, Sustainable production of aviation fuels directly from biomass, MIEQ, FEUP, 2022

Selected Publications

- [1] L.S. Ribeiro, M.F.R. Pereira, Industrial & Engineering Chemistry Research (2023), under review.
- [2] A.F. Peixoto et al., Fuel 303, 121227 (2021)
- [3] K.K. Ferreira, L.S. Ribeiro, M.F.R. Pereira, Fuel (2023), under review.

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