|  |  |
| --- | --- |
| cetlogo ***CHEMICAL ENGINEERING TRANSACTIONS*** ***VOL. , 2023*** | A publication ofaidiclogo_grande |
| The Italian Associationof Chemical EngineeringOnline at www.cetjournal.it |
| Guest Editors: Sauro Pierucci, Jiří Jaromír KlemešCopyright © 2023, AIDIC Servizi S.r.l.**ISBN** 978-88-95608-98-3; **ISSN** 2283-9216 |

Catalytic Conversion Of Glucose and *Chlorella sp.* Into Furans in the Presence of Niobium Oxide

Elisa I. García-Lópeza, Serena Limab, Giuseppe Marcìb, Francesca Scargialib\*

aUniversità di Palermo, STEBICEF, Viale delle Scienze Ed. 16, 90128 Palermo, Italy

bUniversità di Palermo, Dipartimento di Ingegneria, Viale delle Scienze Ed. 6, 90128 Palermo, Italy

corresponding author: francesca.scargiali@unipa.it

A series of Nb2O5 solid catalysts have been prepared to be used for the catalytic dehydration of glucose and sugars from algae *Chlorella sp.* into added value furans. The glucose transformation gave rise to 5-hydroxymethylfurfural (5-HMF). *Chlorella sp.* was used in the same catalytic conditions to be valorised to furans. By preliminary studies we concluded that the algae aqueous suspension needed a previous treatment in the presence of SiO2 pellets to liberate the carbohydrates that in the catalytic reaction in the presence of Nb2O5 materials gave rise 5-HMF and furfural. The best operative conditions and Nb2O5 catalysts were individuated. The most performant Nb2O5 catalyst also showed an excellent reusability without deactivation. The selectivity to furans was related to the acidity of the solid used as catalyst.

* 1. Introduction

Exploring alternative and sustainable feedstocks has recently attracted substantial attention because of the shortage of fossil stocks. Biomass, available in large amounts, can be considered a resource for the chemical industry (Tuck et al., 2012). The development of economically viable and sustainable processes for the production of biomass-derived chemicals is an significant task (Ohara et al., 2010). 5-hydroxymethylfurfural (5-HMF) is one of the top-value added bio-based platform chemicals (Teong et al., 2014). Furans, such as 5-HMF and furfural, are sustainable substitutes for the petroleum-based building blocks used in production of fine chemicals and plastics (Mariscal et al. 2016).

The use of acidic metal oxides as heterogeneous catalysts to promote the biomass transformation to 5-HMF has been extensively reported (Xu et al, 2022). Many catalytic approaches have been pursued to obtain 5-HMF from fructose (Xu et al., 2020); alternatively, glucose, more abundant and cheaper, can be used, even though the synthesis of 5-HMF is more selective from ketohexoses that from aldohexoses (Mika et al., 2018).

The mechanism to obtain 5-HMF from glucose requires a first step of isomerization to fructose, followed by its dehydration to 5-HMF (Tanabe et al., 1995). During this process, some side reactions would occur, such as the self-condensation of 5-HMF, leading to the formation of soluble or insoluble oligomers/polymers known as humins. The rehydration of 5-HMF, forming levulinic and formic acids, would decrease the selectivity to 5-HMF (Ohara et al., 2010). Scheme 1 represent the possible pathways of the reaction.

Significant efforts have been made to explore robust heterogeneous catalysts for the isomerization of glucose to fructose. The most successful conditions demanded high temperatures and highly acidic environment, often in homogeneous regime; further strategies include the use of heterogeneous catalysts in organic or biphasic reaction medium. The use of a heterogeneous catalyst and water as solvent are the most desirable conditions. Many heterogeneous solid acid catalysts have been studied including resins, zeolites, niobic acid, zirconia and heteropolyacids among others, under different reaction conditions (Agarwal et al., 2018). Nb2O5 is abundant and cheap material exhibiting Lewis and Brønsted acid sites (Novak, 1999; Tanabe et al. 1995) so promising as catalyst in sugar valorisation reactions. It is generally accepted that the glucose to fructose isomerization is catalyzed by Lewis acids, while the dehydration reaction of fructose is typically activated a by Brønsted acids (Van Putten et al., 2013).



Scheme 1. Typical reaction scheme for HMF formation from fructose dehydration in acidic catalytic conditions

 The valorisation of biomass is much more challenging than the use of model carbohydrates because the decomposition behaviour of the feedstock is a complex process (Pagán-Torres et al., 2012). Microalgal biomass is quite attractive in this context and a systematic study of the valorisation of algal biomass substrates to obtain furans in the presence of niobium oxide using water as the solvent has not been already reported.

Microalgae are unicellular photosynthetic microorganisms capable of fixing CO2 in carbohydrates. The use of microalgae as biomass has several advantages as they grow faster than terrestrial plants, even in non-arable land and in wastewater, leading to its remediation (Lima et al., 2020). Microalgal biomass contains high value biocompounds (carotenoids, proteins and lipids) employed for drugs and cosmetics (Arena et al. 2021).

Microalgal biomass catalytic conversion to furans requires some steps: its degradation to carbohydrates, further hydrolysis of the obtained polysaccharides to hexoses, the successive isomerization to fructose and eventually the dehydration to furans, mainly 5-HMF and furfural (see Scheme 1). The use of an acidic oxide as heterogeneous photocatalyst in the last steps of the process is suitable because the Lewis acidic sites catalyse the isomerization of hexoses to fructose, whereas the Brønsted sites its dehydration to furans (Wang et al, 2016).

In this work, a set of home prepared Nb2O5 catalysts have been used for the valorisation of the carbohydrates contained in the microalgae *Chlorella sp*. to obtain higher added value products as 5-HMF and furfural. Glucose has been used as model substrate to study the feasibility of the process in the presence of the different Nb2O5 materials and optimise the reaction conditions for its conversion.

* 1. Experimental
		1. Preparation of the catalysts

A set of Nb2O5 catalysts by using NbCl5 as precursor were prepared. Niobic acid (Nb2O5·nH2O) nanoparticles were prepared by dissolving the precursor in ethanol and increasing the pH as reported by Testa et al. (2013). The obtained solid was filtered, washed and dried at 120 °C, and labelled as Nb2O5-T. Alternatively, NbCl5 was suspended in water and the resulting white precipitate aged under stirring for 3 h and then filtered, washed and dried at 120 °C. It was labelled as Nb2O5-E. A third material, labelled as Nb2O5-B, was synthesized as reported by Idress et al. (2019), where an aqueous solution of NbCl5 was treated with H2O2 and the niobium peroxo-complex solution autoclaved at 120 °C for 24 h giving rise to a powder that was filtered, washed and dried at 100 °C. The Nb2O5-B was also annealed at 300 or 500 °C for 2 h, resulting in solids labelled as Nb2O5-B-300 and Nb2O5-B-500. Two commercial Nb2O5 materials, provided by Sigma Aldrich and Companhia Brasileira de Metalurgia e Mineração (CBMM), labelled as Nb2O5-SA and HY-340, respectively, were also tested in the same reactions for the sake of comparison.

* + 1. Catalytic activity for glucose dehydration

A stainless-steel autoclave equipped with a 50 mL PTFE chamber was used as reactor. The autoclave was introduced into a thermostatic preheated synthetic oil bath placed on a hot magnetic stirrer. Typically, 24 mL of a 2.3 mM glucose aqueous solution containing the catalyst (1 g∙L-1) were introduced in the reactor. The operative parameters, as reaction time, temperature and catalysts mass ratio, were optimised. Once the oil reached the established temperature (180 °C), the reactor was immersed in the bath and the reaction started. When the reaction time was over, it was quickly cooled down in a cold water bath until room temperature. The suspension was filtered, and the aqueous solution analysed by HPLC Thermo Scientific Dionex Ultimate 3000 equipped with Diode Array and Refractive Index detectors and a REZEK ROA Organic acid H+ Phenomenex column. The performance of the Nb2O5 catalysts was evaluated in terms of conversion (X) of glucose, selectivity (S) to fructose and 5-HMF and yield (Y) to 5-HMF, calculated as follows:

$X=\frac{\left[glucose\right]\_{i}-\left[glucose\right]\_{f}}{\left[glucose\right]\_{i}}∙100$ (1)

$S\_{fructose}=\frac{\left[fructose\right]\_{f}}{\left[glucose\right]\_{i}-\left[glucose\right]\_{f}}∙100$ (2)

$S\_{5-HMF}=\frac{\left[5-HMF\right]\_{f}}{\left[glucose\right]\_{i}-\left[glucose\right]\_{f}}∙100$ (3)

$Y\_{5-HMF}=\frac{\left[5-HMF\right]\_{f}}{\left[glucose\right]\_{i}}∙100$ (4)

where [glucose]i and [glucose]f are the initial and final molar concentrations of glucose, respectively and [fructose]f and [5-HMF]f are the molar concentrations of fructose and 5-HMF, respectively.

**2.3. Algal growth and analysis of the carbohydrate content of the biomass**

Microalgae *Chlorella sp. Pozzillo* was isolated from Sicilian littoral and molecularly characterized (Lima et al., 2020). The strain was kept in liquid medium enriched with a commercial fertilizer. A pre-culture of the microalgae was set up. When cells were in late exponential phase, 500 mL of the cell suspension were used to inoculate the bubble-column photobioreactor with a volume of 5 L under a photon flux density of about 200 µmol m-2 s-1. The algae were cultivated for 15 days. After the batch cultivation, the biomass was harvested and the obtained biomass was frozen in liquid nitrogen and freeze-dried for 24 h in a bench lyophilizator (Lima et al., 2020). The NREL protocol was used for the quantification of total carbohydrates in the algae (Van Wychen et al., 2015). In brief, 20 mg of freeze-dried biomass were weighted in a glass tube and 250 μL of H2SO4 72 % wt added. The mixture was vortexed and kept at 30 °C for 1 h, hence 7 mL of water were added, and the glass tube tightly closed and placed in an autoclave at 121 °C for 1 h. After that, the suspension was filtered through 0.2 µm membranes and the obtained sugars (glucose and fructose) were analysed by HPLC.

**2.5. Heterogeneous catalytic activity: Hydrothermal conversion of Chlorella sp.**

Lyophilized *Chlorella sp* (40 mg) were dispersed in 24 mL of water and the suspension was placed in the same autoclave described before (section 2.2.). The catalytic experiments were performed both in homogeneous and heterogeneous regimes, either in HCl (0.7, 2.0 or 7.0 % wt) or Nb2O5 (1 g·L-1). Moreover, selected experiments were carried out in the further presence of SiO2 pellets (10 g·L-1 size: 0.2-0.5 mm). Some parameters, as reaction time, temperature, and catalysts/biomass mass ratio, were optimised.

Further experiments were performed in two stages. The first aimed at the extraction of sugars from the biomass, the second at the transformation of the sugars obtained into furans. In the first step, 40 mg of biomass in 24 mL of water and 240 mg of SiO2 pellets were placed in the autoclave and kept for 2 h at 140 or 180 °C. For selected runs, acetic acid was added to reach pH 4. The second step was performed in the presence of Nb2O5 at 180°C. The experiments were carried out at various reaction times. At the end of the reaction, the autoclave was cooled down and the suspension filtered and analysed by HPLC. The course of the reaction, both in homogeneous and heterogeneous conditions, was evaluated in terms of total yield (Y) to furans (5-HMF and furfural) from the sugars contained in the algae:

$Y=\frac{\left[5-HMF\right]\_{f} + \left[furfural\right]\_{f}}{\left[total sugar in biomass\right]}∙100$ (5)

where [5-HMF]f and [furfural]f are the concentrations of the products measured in solution at the end of the reaction, and [total sugar in biomass] the total concentration of sugars from the algae matrix quantified by the NREL protocol.

* 1. Results and discussion

**3.1. Catalytic dehydration of glucose**

Some preliminary runs were carried out to optimize the experimental conditions, concluding that the reaction should be carried out at 180°C for 1 h in the presence of 24 mL of 2.3 mM of glucose aqueous solution containing 1 g L-1 of Nb2O5 catalyst. The glucose conversion, the selectivity to fructose and 5-HMF and yield in 5-HMF in the presence of the various catalysts are summarized in Table 1.

*Table 1: Glucose conversion (X), selectivity towards fructose and 5-HMF (S) and yield (Y) towards 5-HMF, after 1 h of reaction at 180 °C in the presence of the Nb2O5 catalysts.*

|  |  |  |  |  |
| --- | --- | --- | --- | --- |
| Catalyst | XGlucose [%] | Sfructose [%] | S5-HMF [%] | Y5-HMF [%] |
| Nb2O5-T | 67 | 29 | 30 | 20 |
| Nb2O5-E | 65 | 12 | 32 | 21 |
| Nb2O5-B | 98 | 1 | 30 | 29 |
| Nb2O5-B-300 | 91 | 4 | 36 | 33 |
| Nb2O5-500 | 59 | 7 | 19 | 11 |
| Nb2O5-SA | 44 | 24 | 21 | 9 |
| HY-340 | 47 | 22 | 21 | 10 |
| Nb2O5-B-300\* | 75 | 18 | 35 | 26 |

*\*experiment carried out in the presence of 270 ppm of Chloride anions.*

A perusal of the results reported in Table 1 evidenced that the highest conversion of glucose was obtained in the presence of Nb2O5-B, whereas the highest selectivity and yield to 5-HMF with the Nb2O5-B-300 catalyst. A further run in the presence of Nb2O5-B-300 was performed in the same conditions but in the presence of ca. 270 ppm of chloride ions (NH4Cl), simulating the salt content of the algae dispersion. The presence of chlorides decreased the glucose conversion but the selectivity to 5-HMF remained constant, hence the yield to 5-HMF decreased. At the same time, the selectivity to fructose increased. These results suggest that the presence of chlorides not only reduce glucose conversion, but they are also responsible for reducing the formation of by-products different from fructose and 5-HMF.

**3.2. Catalytic valorization of *Chlorella sp.***

The carbohydrate content of the dried *Chlorella sp*, estimated by the NREL protocol, resulted ca.12.0%. This figure was used to determine the yield to furans obtained in all the catalytic reactions (see equation 5). A series of experiments, summarised in Table 2, were carried out to ascertain the best operative conditions.

Table 2: Total yield (Y) versus 5-HMF and furfural from sugars contained in algae for experiments carried out with Chlorella sp under different experimental conditions.

|  |  |  |  |  |  |  |  |
| --- | --- | --- | --- | --- | --- | --- | --- |
|  | ID | SiO2 | Reaction time [h] | Temperature [°C] | HCl [% wt] | Amount of Nb2O5[gcatalyst / gbiomass] | Yield [%] |
| Homogeneous | 1 | - | 6  | 120 | - | - | 0.0 |
| 2 | - | 2  | 140 | 7 | - | 7 |
| 3 | - | 3  | 140 | 7 | - | 6 |
| 4 | - | 6  | 140 | 7 | - | 10 |
| 5 | - | 16  | 140 | 7 | - | 4 |
| 6 | - | 2  | 160 | 7 | - | 6 |
| Presence of SiO2 pellets | 7 | Yes | 6  | 120 | - | - | 0.0 |
| 8 | Yes | 0.33 | 120 | 2 | - | 9 |
| 9 | Yes | 2 | 120 | 2 | - | 6 |
| 10 | Yes | 4 | 120 | 2 | - | 8 |
| 11 | Yes | 6 | 120 | 2 | - | 8 |
| 12 | Yes | 2 | 120 | 0.7 | - | 7 |
| Heterogeneous (Nb2O5-T) | 13 | - | 2  | 120 | - | 0.6 | 0.1 |
| 14 | - | 4  | 120 | - | 0.6 | 0.1 |
| 15 | Yes | 2 | 120 | - | 0.6 | 0.1 |
| 16 | Yes | 4 | 120 | - | 0.6 | 0.1 |
| 17 | Yes | 23 | 120 | - | 0.6 | 0.2 |
| 18 | Yes | 6 | 120 | - | 0.6 | 0.0 |
| 19 | Yes | 6 | 140 | - | 0.6 | 0.0 |
| 20 | Yes | 6 | 160 | - | 0.6 | 0.1 |
| 21 | Yes | 6 | 180 | - | 0.6 | 0.2 |

The microalgae biomass was catalytically treated under hydrothermal conditions in both homogeneous and heterogeneous regimes. All the experiments were carried out with 40 mg of *Chlorella sp*. in 24 mL of aqueous suspension. The absence of catalyst at 120 °C for 6 h resulted in no transformation of the algae (Table 2, entry 1), conversely, the presence of HCl (homogeneous catalyst), gave rise to modest yields in furans (Table 2, entries 2-6). Further experiments were performed by adding SIO2 pellets to the suspension to increase the mechanical damage of the cells, thus aiding the release of sugars into the solution. In any case, the yield to furans was very low (Table 2, entries 7-12). The heterogeneous conversion of *Chlorella sp* was also performed in the presence of the Nb2O5-T catalyst, both in the absence and in the presence of the SiO2 pellets (Table 2, entries 13 to 21). The presence of only Nb2O5 at 120°C for 2 or 4 h gave negligible results, probably due to the lack of release of sugars from the biomass. The additional presence of SiO2 pellets, together with Nb2O5, did not change the yield in furans. In any case, the yields were still very low even for long reaction times. It is likely that the difficult release of sugars in solution, as indirectly confirmed by some tests (Table 2, entries 18-21) at different temperatures, could be the cause of the low yields of furans.

Considering the very low yields obtained (Table 2), a different strategy was devised, and the algae transformation was performed in two steps. The first step aimed at the release of carbohydrates from the algae and the second at the catalytic conversion of carbohydrates into furans. In the first step, carried out for 2 h at 140°C, SiO2 pellets were added to the aqueous suspension of *Chlorella sp*. After the filtration, the solution underwent a second treatment, at 180°C for 1 h, in the presence of the various Nb2O5. The obtained yields in furans, reported in Figure 1 (A), resulted still very low. Consequently, an optimization of both stages was performed. The first one gave the maximum release of carbohydrates from the algae at 180°C for 2 hours in acetic acid (pH=4). The optimization of the second stage was focused on reaction time, and it was performed at 180 °C in the presence of Nb2O5-T. The maximum yield to furans was reached after 10 h of reaction, while for longer reaction times it decreased, probably due to polymerization (see Scheme 1). The results obtained under the best conditions at both stages, are reported in Figure 1 (B). The Nb2O5-T, -E, -B and HY-340 show similar performances, whereas Nb2O5-B-300 and Nb2O5-SA exhibited lower activities. The results can be attributed to the physicochemical features of the solids, indeed, the non-calcined solids, exhibited higher specific surface area and acidity than the calcined and commercial ones (Eblagon et al. 2020). An in-depth chemical-physical characterization is underway in order to correlate the features of each solid to the catalytic activity.



Figure 1. Yield towards 5-HMF and furfural for runs carried out in two stages (A) the first one in the presence of only SiO2 (2 h at 140°C), and the second in the presence of Nb2O5 (1 h at 180°C) and (B) the first one in the presence of SiO2 a pH 4 (2 h at 180°C), and the second in the presence of Nb2O5 (10 h at 180°C).

* 1. Conclusions

The current research demonstrates the feasibility to transform the carbohydrates content in microalgal biomass into furans. A set of home prepared Nb2O5 catalysts have been used for the valorisation of the carbohydrates contained in the *Chlorella sp*. to obtain higher added value products as 5-HMF and furfural. Glucose has been used as model substrate to study the behaviour of the different Nb2O5 materials and optimise the reaction conditions for its conversion to fructose and furtherly to 5-HMF. The *Chlorella sp.* was subjected to preliminary treatments in homogeneous or heterogeneous conditions with low yields of furans. Due to the fact that the microalgal cell wall is a complex structure and the releasing of the carbohydrates from its matrix is a challenging procedure the reaction was performed in two steps, the first to release the carbohydrates followed by the heterogeneous catalytic reaction in the presence of Nb2O5 to transform the carbohydrates to 5-HMF and furfural. The feasibility of the process by using *Chlorella sp*. as substrate in the presence of Nb2O5 in an eco-friendly catalytic approach was demonstrated.

**References**

Agarwal B., Kailasam K., Sangwan R.S., Elumalai S., 2018, Traversing the history of solid catalysts for heterogeneous synthesis of 5-hydroxymethylfurfural from carbohydrate sugars: A review, Renewable and Sustainable Energy Reviews 82, 2408-2425.

Arena R., Lima S., Villanova V., Moukri N., Curcuraci E., Messina C., Santulli A., Scargiali F., 2021, Cultivation and biochemical characterization of isolated Sicilian microalgal species in salt and temperature stress conditions, Algal Res. 59, 102430.

Eblagon K.M., Malaika A., Ptaszynska K., Pereira M.F.R., Figueiredo J.L., 2020, Impact of Thermal Treatment of Nb2O5 on Its Performance in Glucose Dehydration to 5-Hydroxymethylfurfural in Water, Nanomaterials 10, 1685;

Idrees F., Dillert R., Bahnemann D., Butt F.K., Tahir M., 2019, In-Situ Synthesis of Nb2O5/g-C3N4 Heterostructures as Highly Efficient Photocatalysts for Molecular H2 Evolution under Solar Illumination. Catalysts 9, 169.

Lima S., Villanova V., Grisafi F., Caputo G., Brucato A., Scargiali F., 2020, Autochthonous microalgae grown in municipal wastewaters as a tool for effectively removing nitrogen and phosphorous, J. Water Process Eng. 38, 101647.

Mariscal, R. Maireles-Torres, P. Ojeda, M., Sádaba I., López Granados, M., 2016, Furfural: a renewable and versatile platform molecule for the synthesis of chemicals and fuels. Energy Environ. Sci., 9, 1144-1189.

Mika L.T., Cséfalvay E., Németh Á.,2018, Catalytic Conversion of Carbohydrates to Initial Platform Chemicals: Chemistry and Sustainability, Chem. Rev. 118, 505–613.

Nakajima K., Hirata J., Kim M., Gupta N.K., Murayama T., Yoshida A., Hiyoshi N., Fukuoka A., Ueda W., 2018, Facile Formation of Lactic Acid from a Triose Sugar in Water over Niobium Oxide with a Deformed Orthorhombic Phase, ACS Catal. 8, 283-290.

Nowak I. Ziolek M., 1999, Niobium compounds: preparation, characterization, and application in heterogeneous catalysis, Chem. Rev. 99, 3603-3624.

Ohara M., Takagaki A., Nishimura S., Ebitani K., 2010, Syntheses of 5-hydroxymethylfurfural and levoglucosan by selective dehydration of glucose using solid acid and base catalysts, Appl. Catal. A Gen. 383, 149-155.

Pagán-Torres Y.J., Wang T., Gallo J.M.R., Shanks B.H., Dumesic J.A., 2012, Production of 5-Hydroxymethylfurfural from Glucose Using a Combination of Lewis and Brønsted Acid Catalysts in Water in a Biphasic Reactor with an Alkylphenol Solvent, ACS Catal. 2, 930-934.

Sumiya S., Oumi Y., Sadakane M., Sano T., 2009, Facile preparation of SBA-15-supported niobic acid (Nb2O5·nH2O) catalyst and its catalytic activity, App. Catal A 365, 261-267.

Tanabe K., Okazaki S., 1995, Various reactions catalyzed by niobium compounds and materials, App. Catal. A, 133, 191-218.

Teong S.P., Yi G., Zhang Y., 2014, Hydroxymethylfurfural production from bioresources: Past, present and future, Green Chem, 16, 2015-2026.

Testa M.L., La Parola V., Liotta L.F., Venezia A.M., 2013, Screening of different solid acid catalysts for glycerol acetylation, J. Mol. Catal. A 367, 69-76.

Tong, X., Ma Y., Li Y., 2010, Biomass into chemicals: Conversion of sugars to furan derivatives by catalytic processes, Appl. Catal. A Gen. 385, 1-13.

Tuck C.O., Pérez E.; Horváth I.T., Sheldon R.A., Poliakoff M., 2012, Valorization of Biomass: Deriving More Value from Waste, Science, 337, 695-699.

Van Putten R.J., Van Der Waal J.C., De Jong E., Rasrendra C.B., Heeres H.J., De Vries J.G., 2013, Hydroxymethylfurfural, a versatile platform chemical made from renewable resources, Chem. Rev. 113, 1499-1597.

Van Wychen S., Laurens L.M.L., 2015, Determination of Total Carbohydrates in Algal Biomass - Laboratory Analytical Procedure ( LAP ), Lab. Anal. Proced. 18. [www.nrel.gov/publications](http://www.nrel.gov/publications).

Wang J.J., Tan Z.C., Zhu C.C., Miao G., Kong L.Z., Sun Y.H., 2016, One-pot catalytic conversion of microalgae (Chlorococcum sp.) into 5-hydroxymethylfurfural over the commercial H-ZSM-5 zeolite, Green Chem. 18, 452–460.

Xu C., Paone E., Rodríguez-Padrón D., Luque R., Mauriello F., 2020, Recent catalytic routes for the preparation and the upgrading of biomass derived furfural and 5-hydroxymethylfurfural, Chem. Soc. Rev. 49, 4273–4306

Xu H., Li, X., Hu W., Lu L., Chen J., Zhu Y., Zhou H., Si C., 2022, Recent advances on solid acid catalyic systems for production of 5-Hydroxymethylfurfural from biomass derivatives, Fuel Process. Technol. 234, 107338.