

# **Light-driven transformation of biomass into chemicals using photocatalysts – vistas and challenges**

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## Abstract

Lignocellulosic biomass has become an important sustainable resource for fuels, chemicals and energy. It is an attractive source for alternative fuels and green chemicals because it is non-edible and widely available in the planet in huge volumes. The use of biomass as starting material to produce fuels and chemicals leads to closed carbon cycle and promotes circular economy. Although there are many thermo-chemical methods such as pyrolysis, liquefaction and gasification close at hand for processing lignocellulosic biomass and transforming the derived compounds into valuable chemicals and fuels, the photocatalytic method is more advantageous as it utilizes light and ambient conditions for reforming the said compounds. Appraisal of recent literature indicates a variety of photocatalytic systems involving different catalysts, reactors and conditions studied for this purpose. This article reviews the recent developments on the photocatalytic transformation of biomass and its derivatives into value-added chemicals. The nature of the biomass and derived molecules, nature of the photocatalysts, efficiency of the photocatalysts in terms of conversion and selectivity, influence of reaction conditions and light sources, effect of additives and mechanistic pathways are discussed. Importance has been given also to discuss the complementary technologies that could be coupled with photocatalysis for better conversion of biomass and biomass-derived molecules to value-added chemicals. A summary of these aspects, conclusions and future perspectives are given in the end.

**Keywords:** Photocatalysts; Biomass; Added-value chemicals; Cellulose; Lignin; Sugars; Alcohols

## Introduction

The ever-increasing consumption of fossil-fuels leads to a number of issues such as rising greenhouse gas emissions, worsening of global climate, exhaustion of fossil fuels, economic losses and environmental crisis. In order to address these negative consequences, alternative renewable- and sustainable-energy sources are being explored. Among the renewable resources, biomass is the only material containing carbon that can be converted into a variety of useful solid, liquid and gaseous products, and additionally into energy in the form of heat and electricity (Zuo et al., 2012). In this connection, the conversion of biomass and its derivatives into value-added chemicals and fuels has attracted the global interest, as it could diminish the mankind's dependence on fossil fuels (Chakthranont et al., 2020). The processing methods of biomass and their components include steam gasification, pyrolysis, supercritical and hydrothermal conversions, and catalytic, electrochemical, enzymatic, biological and photocatalytic degradation processes (Lekelefac and Czermak, 2016; Sheldon and Sheldon, 2014; Tekin et al., 2014; Yan et al., 2015). The choice of biomass as a resource for chemicals and fuels also stems partly from its availability, where the annual generation of biomass on land is reported to be approximately around 100 billion tons (Wang et al., 2015). Lignocellulosic biomass is an important renewable material for developing chemicals, fuels and other products as it is non-edible and available abundantly. In recent times, efforts have been put forth for the degradation of lignocellulosic materials and conversion of biomass-derived lignin and cellulose into added-value-chemical biofuels (Binder and Raines, 2009; Sheldon and Sheldon, 2014). **Fig. 1** depicts how biomass processing and conversion has accelerated inter-disciplinary research in different areas of science and technology. A major part of the research has been devoted to obtain chemicals and energy from biomass, as it draws the attention of both industry and academia due to the demand involved. The research has created a lot of new knowledge on bio-processing of biomass, environmental advantages and implications of biomass processing, industrial process development related to biomass

reformation, bio-refinery etc. The research on materials science aspects particularly materials chemistry related to biomass processing is limited but it is necessary to understand and develop new and advanced materials to transform biomass into value-added products. Recently, use of photocatalysts to reform biomass into chemicals and fuels has gained traction due to environmental friendliness of photocatalysis process. Accordingly, **Fig. 2** shows the simplified photobiorefinery concept that involves the photocatalytic conversion of different biomass-derived components such as cellulose, hemicelluloses and lignin into renewable chemicals.

As a result of intense research on photocatalytic materials, a wide range of photocatalysts has been developed during the last three decades. These catalytic materials opened up pathways to use the abundant natural sunlight for photocatalytic chemical conversions. Owing to their merits, these light-driven semiconductor materials are employed also in biomass reformation. In contrast to other energy intensive methods, photocatalysis is non-energy-intensive and it can transform biomass derivatives into value-added chemicals via photochemical redox reactions at ambient conditions utilizing *in situ* produced electron/hole pairs or superoxide anions or hydroxyl-radicals generated by the excitons through secondary reactions (**Fig. 3(a)**) (Colmenares and Luque, 2014). The potential of this emerging sustainable process in selective-conversion of biomass-derived chemicals has been highlighted in some of the recent articles (Granone et al., 2018; Li et al., 2016; Parrino et al., 2018) . **Fig. 3 (b)** illustrates the significant progress made in terms of research articles published on photocatalytic biomass conversion in the last 10 years. The surge in the number of publications in the recent years evidences the rising interest among the researchers on this topic and it appears that there is a positive trajectory leading to green future. In this connection, there are only a limited number of review reports available on the photocatalytic transformation of biomass and biomass-derived products into fuels and value-added chemicals(Colmenares et al., 2017; Colmenares and Luque,

2014; Granone et al., 2018; Li et al., 2016; Parrino et al., 2018) and within the available reviews many of them focused only on certain biomass like lignin.

Translating a lab scale photocatalytic reaction into a real industrial process is an essential and challenging task. The tutorial review by J. C. Colmenares et al. (Colmenares et al., 2017) reported on the photocatalytic conversion of lignin-inspired materials using micro fluidic reactors integrated with nanocatalysts. In this review, the authors highlighted the key challenges and opportunities stemming from combining the heterogeneous photocatalytic process and micro-flow chemistry to exploit their synergistic effect on the selective transformation of lignin-derived chemicals into high-value products and/or intermediates for the fine chemical industries. Parrino et al. (Parrino et al., 2018) critically scrutinized different parameters related to photocatalysts, explored chemical and engineering issues related to real applications of photocatalytic process alone or with combination of other technologies for the synthesis of high-value chemicals, and finally concluded that analyzing the efficiency of the photocatalytic process in a precious way is a challenging but essential task. In their article published in 2018, L. I. Granone et al. (Granone et al., 2018) discussed about mechanisms and emphasized strategies aimed at establishing technical applications of photocatalytic processes for transforming biomass into value-added molecules. Xiaoqing Liu et al. reviewed photocatalytic conversion of lignin, cellulose, cellulose derivatives and native lignocellulose and concluded that conversion of native lignocellulosic biomass is a highly challenging task (Xiaoqing Liu et al., 2019). Based on the reviews mentioned, it may be concluded that the development of a single, effective photocatalyst or a single process for the selective conversion of all biomass and biomass-derived chemicals into value-added chemicals is a highly challenging task. This is because of the fact biomass is a complex natural product and made up of combination of sturdy natural compounds, composition of which may vary depending on the source. For this reason, the photocatalytic conversion process cannot be generic and optimization of it for different types of biomass is a challenge. Further the

limitations associated with designing large scale photo-reactors and optimization of the associated engineering parameters and flow chemistry make scaling up of the photocatalytic process presently unrealistic. A better understanding of the nature biomass and photocatalysts, efficiency of the photocatalyst in terms of conversion and selectivity, influence of reaction conditions and light sources, effect of additives, mechanistic pathways and recyclability of the catalysts is necessary to address these challenges and to realize photocatalysis for industrial production of value-added chemicals. In this article, recent developments in conversion biomass and biomass derived compounds to different value-added chemicals using photocatalysts are briefed and critically discussed. A summary of different biomasses, biomass-derived molecules and photocatalysts studied for the production of value-added chemicals discussed in this article is presented in **Table 1**.

### **Nature of lignocellulosic biomass**

Lignocellulose is the main structural-constituent of plant matter and mostly non-edible. It is made up of three main molecules known as cellulose, hemicelluloses, and lignin (**Fig. 4**)(Wu et al., 2018). Cellulose is a crystalline, stable biopolymer made of glucoside units that is insoluble in most solvents and difficult to hydrolyze(Kumar and Gupta, 2008). Compared to cellulose, hemicelluloses is more easily hydrolyzed as it is amorphous, and composed of pentose sugars such as xylose and arabinose. Lignin is a biopolymer composed of randomly arranged phenyl propane units, *p*-coumaryl alcohol, coniferyl alcohol, and sinapyl alcohol(Nguyen et al., 2014; Sannigrahi et al., 2010). Even though the processing of complex lignocellulosic materials is one of the major hurdles in the commercial-scale production of biofuels and renewable chemicals, there are many underlying economic, environmental and social benefits. In this direction, different types of photocatalysts and reactors have been studied to breakdown and process lignocellulosic biomass (or its constituents), cellulose and lignin(Wu et al., 2018).

## **Direct biomass processing – Combining photocatalysis with other technologies**

Complete, direct-photocatalytic conversion of lignocellulosic biomass to high value products is difficult to be conceived because of its sturdy nature and limitations in process engineering aspects. However, the combination of photocatalysis with other technologies can be thought out to achieve the same. In the bioethanol production process, saccharification is a step in which complex carbohydrates are broken down to monosaccharide components. For saccharification of lignocellulosic biomass, as the lignin, hemicellulose and cellulose are strongly bound, dilute sulfuric acid (Sun et al., 2015, Martin et al., 2007), alkali (Klinke et al., 2002), and pressured hot water (Dien et al., 2006) were used for pretreatment. Recently it has been shown that photocatalysis can be used for the pretreatment of biomass in saccharification process targeting improved yield of EtOH. Napier and silver grass were subjected to photocatalytic pretreatment with  $\text{TiO}_2$  followed by enzymatic saccharification by Acremoyzimecellulase and then fermentation by *Saccharomyces cerevisiae* (Yasuda et al., 2011). The photocatalytic pretreatment done under UV light ( $\lambda = 360 \text{ nm}$ ) was significantly effective as it exceptionally reduced the time required for the completion of the biological reactions catalyzed by the cellulase and yeast yet did not interfere in the reactions. It was suggested that  $\text{TiO}_2$  pretreatment oxidizes the phenolic moiety present in the lignin part of the lignocellulose. As hemicellulose component of the biomass is present near the lignin part, lignin-hemicellulose bond seems to be cleaved during photocatalytic pretreatment there by helping the enzyme action.

In another example, the pretreatment of starch under visible in the presence of a 25%  $\text{TiO}_2$  loaded  $\text{TiO}_2/\text{Bi}_2\text{WO}_6$  nanocomposite catalyst broke starch into smaller molecules, which helped for further anaerobic digestion and ethanol fermentation (Shiamala et al., 2018). The heterojunction for between  $\text{TiO}_2$  and  $\text{Bi}_2\text{WO}_6$  was effective in making the catalyst both under visible light and UV-Vis

light. When the 25%  $\text{TiO}_2/\text{Bi}_2\text{WO}_6$  nanocomposite was treated with visible light, the photogenerated electrons formed at valance band of  $\text{Bi}_2\text{WO}_6$  are excited to conduction band of  $\text{Bi}_2\text{WO}_6$  and at the same time, electrons from the valance band of  $\text{TiO}_2$  migrate to valance band of  $\text{Bi}_2\text{WO}_6$ . This creates holes in the valance band of  $\text{TiO}_2$  which was harnessed for cleaving starch. Hence, it is clear that photocatalysis can be exploited for hydrolytic process and fractional acedogenesis of biomass in biofuel production processes. The photocatalytic pre-treatment of biomass can be envisaged from an environmentally conscious approach, as it eliminates the need of acid and alkali. Hence, the modern direct biomass conversion strategy could be combination of biological, chemical, and photocatalytic methods, utilizing their benefits and limitations to achieve sustainability. Emphasizing this modern strategy, mechanistic processes for the technological application of the photo-catalytic and chemical reactions have been proposed (Granone et al., 2018). It was further underscored in a work reported by Shwetharani and Balakrishna(Shwetharani and Balakrishna, 2016) wherein bio-oil extraction from microalgae (*Nannochloropsis oculata*algal) was carried out via photocatalysis using nano- $\text{TiO}_2$  as photocatalyst under sunlight. This technique gave 52.2% of lipid yield from the algal biomass and the bio-oil thus produced was subjected to transesterification reaction to obtain bio-fuel. It was proposed that the reactive oxygen species (ROS) produced during the light irradiation of the nano- $\text{TiO}_2$  attached to algae react with the cell walls. These reactions damage the cell wall and lipid part is detached from the cell wall and come out as algal oil. The negatively charged surface of algae favored the close attachment of positively charged nano- $\text{TiO}_2$  particles on the algal cell wall. This study opened up the possibility of production of renewable-biofuels without passing through energy consuming steps such as dewetting and drying. In our opinion, though there are some limited examples for the application of photocatalysts in combination with other technologies for direct processing of biomass to value-added products, more concrete studies with different biomasses required before the industrial realization.



## Photocatalytic transformation of cellulose and lignin

Though direct transformation of lignocellulosic biomass as such into value-added chemicals using photocatalysis as a sole method is not conceivable, cellulose can be directly transformed to high-value chemicals using a combination of photocatalyst and chemical agents. The crystalline cellulose is highly stable hence generally harsh conditions such as acids, alkali and high temperatures are necessary to break it down and produce value-added chemicals. However, under these harsh conditions it is difficult to achieve the selectivity of the desired value-added chemicals as the sugars and the intermediate products are labile under the mentioned conditions and undergo nonselective reactions. Hence, the use of the combination of photocatalyst and chemical agents is advantageous as there is possibility for cellulose degradation under milder conditions. It is expected that the chemical agents catalyze certain reactions and assist the photocatalysts to break down and convert the sturdy cellulose molecules to value-added chemicals. For example, hydrolyzing the glycosidic bonds of cellulose to get glucose, dehydration of glucose and cyclisation of the dehydration product are the steps involved to get 5-(hydroxymethyl)furfural (5-HMF) from cellulose. However the photocatalyst alone cannot facilitate these steps and hence additional acids or acid sites are required for efficient 5-HMF production (**Scheme 1**).

The use of Lewis acid,  $\text{ZnCl}_2$  along with  $\text{TiO}_2$  photocatalyst has been reported for the conversion of cellulose to get 5-(hydroxymethyl)furfural (5-HMF) (Fan et al., 2011). The conversion was performed in a cylindrical-photocatalytic corrugated-plate reactor coated with anatase- $\text{TiO}_2$  thin film. The corrugated-plate reactor design increased the exposed surface area of the coated  $\text{TiO}_2$  catalyst and helped to capture large number of photons. Cellulose was dissolved in concentrated  $\text{ZnCl}_2$  and then subjected to degradation in the reactor using UV light (254 nm, 21W UV lamp). The yield of 5-HMF in the presence of the  $\text{TiO}_2$  photocatalyst and  $\text{ZnCl}_2$  under the UV light was ten times higher than

hydrolyzing cellulose in the presence of  $\text{ZnCl}_2$  alone and eight times higher than the combination of  $\text{ZnCl}_2$  and UV light. As a Lewis acid,  $\text{ZnCl}_2$  can hydrolyze the glycosidic linkages in cellulose to form glucose molecules and catalyze the further dehydration reactions. The hydrolysis of cellulose in the presence of  $\text{ZnCl}_2$  happens to smaller extent at higher temperatures ( $200^\circ\text{C}$ ). However, in the presence of  $\text{ZnCl}_2$ ,  $\text{TiO}_2$  and UV light, the degradation of cellulose happens at  $50^\circ\text{C}$ . Further a different mechanism could be operative wherein,  $\text{TiO}_2$  generates active  $\bullet\text{OH}$  radicals in the presence of UV light and  $\text{ZnCl}_2$  which cleave cellulose in to glucose molecules and then  $\text{ZnCl}_2$  catalyze step-wise dehydration of the glucose molecules to give 5-HMF. In another example,  $\text{TiO}_2$  nanofibers supported on H-form of Y zeolites-decorated with Au-NPs was studied for breaking down cellulose (Wang et al., 2015). In this work, acid strength of the zeolite, localized surface plasmon resonance (LSPR) effect of Au-NPs, temperature and light intensity were found to impact the cellulose degradation. The complete conversion of cellulose and  $\sim 60\%$  yield of HMF were obtained at  $130^\circ\text{C}$  in 24h over the optimized catalyst. The study established that the acid strength of the zeolite is enhanced by LSPR effect due to polarized electric fields. From the above examples, the role of acids for photocatalytic cellulose conversion into HMF is evident. If acid sites are not present then HMF will not be obtained and cellulose degradation may resulted in intermediate products like disaccharides and glucose. Incidentally, as an evidence for this, Zhang et al.(Zhang et al., 2016) used  $\text{TiO}_2(\text{Pt})$  to convert cellulose into value-added chemicals and obtained glucose, cellobiose (a disaccharide) and formic acid in the presence of UV light irradiation. Since platinum was present as co-catalyst, it facilitated simultaneous cellulose oxidation and also water reduction to form hydrogen. No formation of HMF was obtained probably due to the absence of strong acid sites in the catalyst. Further by studying physically mixed cellulose and bare  $\text{TiO}_2$ , physically mixed cellulose and  $\text{TiO}_2(\text{Pt})$  and cellulose immobilized on the  $\text{TiO}_2(\text{Pt})$  surface, the authors suggested that immobilization of cellulose on the catalyst surface is crucial for its oxidation.

Lignin is a richly available renewable carbon source on earth next to cellulose. Lignin is also present in pulp, and paper-mill effluents, which is a major chemical oxygen demand (COD) component in the wastewater (Lora and Glasser, 2002). It is a potential, renewable non-fossil source of aromatic and cyclohexyl compounds (Delidovich and Palkovits, 2015). It can be a raw material for many important substances such as activated-carbon, vanillic-acid, vanillin, ion-exchange materials, dispersing agents, polymer fillers, and complexing agents. The scope for selective-decomposition of lignin and conversion of lignin-based compounds into added-value chemicals and simultaneous lignin containing wastewater treatment was summarized recently by Shao-Hai Li et al. (Li et al., 2016).

Technically, photocatalytic degradation of lignin is favorable due to the existence of many hydroxyl-groups in its structure. Depolymerization of lignin by breaking down the different linkages (**Scheme 2**) present in it is necessary to convert it into smaller molecules and value-added product. The  $\beta$ -O-4 linkages present in lignin account for 43 to 65% of all linkages and the main challenge in lignin depolymerization is to breakdown these abundant  $\beta$ -O-4 linkages. Often model compounds were studied instead of lignin obtained from biomass due to the ease of studying the mechanism. Further as lignin is a sturdy and complex molecule, multiple strategies were used to establish the catalyst systems for selective lignin depolymerization. In this connection, recently Nengchao Luo et al. (Nengchao Luo et al. 2016) (~~Wang et al., 2016~~) attempted direct cleavage of  $\beta$ -O-4 alcohols (as model compounds of lignin) via tandem oxidation and hydrogenolysis reactions in one-pot by switching between 455 and 365 nm light wavelengths using Pd/ZnIn<sub>2</sub>S<sub>4</sub> and TiO<sub>2</sub> catalysts. In this study, first selective photocatalytic oxidation of  $\alpha$ -C-OH groups of  $\beta$ -O-4 alcohols to  $\alpha$ -C=O was achieved using Pd/ZnIn<sub>2</sub>S<sub>4</sub> in the presence of O<sub>2</sub> and 455 nm light. After this reaction, switching over to 365 nm light in the presence of TiO<sub>2</sub>-NaOAc catalyst in ethanol lead to cleaving of C-O bonds neighboring to the  $\alpha$ -C=O bonds. Ethanol was found to act as hydrogen donor and the mechanisms of cleavage occurs via transfer hydrogenation. The

work further revealed that *in situ* formed  $Ti^{3+}$  ions on the catalyst surface rather than photogenerated electrons participate in C-O bond hydrogenolysis and cleavage. Instead, the electrons reduce surface  $Ti^{4+}$  sites to  $Ti^{3+}$ .

As far as conversion of lignin from real samples like pulp-effluent is concerned, the photocatalytic degradation of lignin derived from wheat-straw by Kraft-digestion has been studied using  $TiO_2$  and ZnO photocatalysts (Kansal et al., 2008). The comparative studies indicated that the supported ZnO could efficiently degrade the lignin present in pulp and paper-mill bleach effluents than  $TiO_2$  (Kansal et al., 2008). However, in contrast to this, other studies showed  $TiO_2$  is still an efficient catalyst for depolymerization and value addition of lignin. Raquel Prado et al.(Prado et al., 2013) studied the depolymerization of lignin present in two different samples obtained by different pulping methods (Organosolv and Bmim[MeSO<sub>4</sub>]) using  $TiO_2$  as heterogeneous photocatalyst. The main products of degradation were syringaldehyde, pyrocatechol and raspberry ketone. Degradation of lignin sulfonate obtained from a local paper plant by means of a circulating reactor was demonstrated by Lekelefac et al.(Lekelefac and Czermak, 2016). The reactor system design had  $TiO_2$  coated on sintered glass (150–250  $\mu m$  nominal pore size), packed in a 26-cm- long borosilicate tube. Different catalysts  $TiO_2$ -P25-SiO<sub>2</sub>+Pt,  $TiO_2$ -P25-SiO<sub>2</sub>, TiOSO<sub>4</sub>\_30.6 wt % and ZnO+ $TiO_2$ -P25-SiO were synthesized by sol-gel method. The order of the catalytic systems with respect to their reaction rates was the following:  $TiO_2$ -P25-SiO<sub>2</sub> + Pt ~  $TiO_2$ -P25-SiO<sub>2</sub> > ZnO +  $TiO_2$ -P25-SiO<sub>2</sub> > TiOSO<sub>4</sub>\_30.6 wt.%. The reactor design was effective in degrading relatively high concentrations of lignin sulfonate solutions (500 mg/L). The UV-vis spectroscopic study revealed that the cleavage of aliphatic side chains was faster than that of aromatics.

Achieving higher selectivity of the value-added products during lignin degradation/oxidation is a challenge because often the photocatalytic oxidation is non-selective and results in complete degradation

of the products into CO<sub>2</sub> and water. In this case, tuning the photocatalyst for higher selectivity of the desired products is necessary and such an example has been reported recently. TiO<sub>2</sub> modified with Bi and Pt was studied as a photocatalyst for the degradation of lignin (sodium ligninsulfonate) (Gong et al., 2017). Addition of these metals, modified the surface of TiO<sub>2</sub> and the Bi1%/Pt1%-TiO<sub>2</sub> catalyst exhibited the best performance for lignin conversion. Maximal conversion of sodium lignin sulfonate, 84.5%, and the highest yield of guaiacol, 22.7%, could be achieved using Bi1%/Pt1%-TiO<sub>2</sub> after 1 h of solar light irradiation; the maximum yield of vanillic acid, 3.5%, was observed after 1.5 h of oxidation. The effect of pH, light intensity and catalyst stability were also studied. The selective lignin oxidation due to Bi addition was attributed to higher production of O<sub>2</sub><sup>•-</sup>, and suppression of •OH on the Bi/Pt-TiO<sub>2</sub> catalyst. It is known that •OH is a non-selective radical because of its high redox potential (2.8 V vs SHE), which leads to the total oxidation of organic compounds. In contrast to this, O<sub>2</sub><sup>•-</sup> was expected to favor selective oxidation because of its favorable redox potential (0.89 V vs SHE). Nattida Srisasiwimon et al. (Srisasiwimon et al., 2018) established a method to improve lignin conversion into high value chemicals by means of a lignin-based carbon modified TiO<sub>2</sub> composite photocatalyst (TiO<sub>2</sub>/lignin). TiO<sub>2</sub>/lignin 1:0.5 sintered under nitrogen showed better photocatalytic activity than pristine-TiO<sub>2</sub> and gave the highest lignin conversion of 40.28% under UVA radiation and selectively yielded high value chemicals.

Lignin is a sturdy polymeric substance and hence, different methodologies/technologies are necessary to break it down and convert into value-added molecules. In this sense, a combination of photocatalytic and electrochemical processes for lignin degradation, where a Ta<sub>2</sub>O<sub>5</sub>-IrO<sub>2</sub> thin film as electro catalyst and TiO<sub>2</sub> nanotube arrays as photocatalyst, was proposed by Min Tian et al. (Min Tian et al., 2010) (~~Miyazaki et al., 2014~~). A Ti/TiO<sub>2</sub> nanotubes array and Ti/Ta<sub>2</sub>O<sub>5</sub>-IrO<sub>2</sub> electrode were connected and used as working electrode and Pt coil was used as counter electrode. Ag/AgCl was used

as reference electrode. The TiO<sub>2</sub> nanotube array was irradiated with 365 nm UV light. This photoelectrochemical strategy was very promising and could be a potential technology for the conversion of lignin into vanillin, vanillic acid, complexing agents and polymer fillers. In this combined system, when potential is applied, apart from promoting electrochemical oxidation on the electrocatalyst, the charge carrier recombination on the photocatalyst is also suppressed. Hence a strong synergy was observed during lignin degradation using the photocatalyst-electrocatalyst system. A combination of TiO<sub>2</sub> photocatalyst and a biocatalyst (laccase enzyme obtained from *Trametes versicolor*) was used to degrade lignin through single- and dual-step processes, which was demonstrated by Kamwilaisak and Wright (Kamwilaisak and Wright, 2012). Lignin degradation by TiO<sub>2</sub> and laccase alone was also studied and compared; increased lignin degradation was observed while using the combined TiO<sub>2</sub> and laccase systems. Furthermore, the combined action of biocatalytic and photocatalytic reactions was found to be better as a dual-stage process with photocatalytic treatment using TiO<sub>2</sub> first and enzymatic process with laccase second. Laccase needs more supply of oxygen for its action, so H<sub>2</sub>O<sub>2</sub> was also added. H<sub>2</sub>O<sub>2</sub> also played a significant role in improving the lignin degradation by TiO<sub>2</sub>. GC-MS analysis revealed that industrially important succinic and malonic acids are prominent compounds in the oxidation processes involving TiO<sub>2</sub>/H<sub>2</sub>O<sub>2</sub>. The dual-stage process increased the yields of fatty acids and carbohydrate significantly. A TiO<sub>2</sub>/polyethylene oxide (PEO)+methyl linoleate (ML) system for the degradation of herbaceous lignin and unsaturated polyester was proposed by Miyazaki et al (Miyazaki et al., 2014). According to the authors, methyl linoleate works as an initiator, and being photo-catalytically activated by TiO<sub>2</sub>/PEO, it has the ability of attacking the unsaturated polyester and lignin because of its hydrophobic structure. It was observed that TiO<sub>2</sub>/PEO alone did not work as the hydroxyl radicals produced by the TiO<sub>2</sub> photocatalyst could not penetrate the hydrophobic network. The <sup>1</sup>H-NMR characterization of chloroform extract showed that the

TiO<sub>2</sub>/polyethylene oxide + methyl linoleate photocatalyst system preferentially cleaved carbon–carbon bonds.

In summary, TiO<sub>2</sub> is the main photocatalyst studied for depolymerization/degradation/oxidation of cellulose and lignin. Selective photocatalytic cellulose conversion into value-added product like HMF requires acid catalysts along with the photocatalyst. In the absence of acid catalysts, the degradation of cellulose yields mainly disaccharides and glucose. Use of UV radiation facilitates faster lignin degradation, however, it should be considered with caution as it will also lead to mineralization. Tuning the TiO<sub>2</sub> catalyst by surface modification with metals, carbon or use of suitable reagents like PEO and methyl linoleate can be employed to improve lignin conversion and selectivity of the value-added products. Further combining photocatalysis with electro catalysis or enzyme catalysis may be fruitful for achieving better lignin conversion and higher value-added products selectivity.

### **Photocatalytic conversion of sugars to value-added chemicals**

Glucose, fructose, xylose and arabinose are the sugars that can be derived from polysaccharides such as starch, cellulose and hemicellulose present in biomass. Many value-added chemicals which are used in pharmaceutical, food, cosmetics detergent and polymers production can be obtained from these carbohydrates (Gallezot et al.2012). The selective oxidation of the anomeric and primary hydroxyl groups present in these free sugars is highly desirable as it will yield aldonic, uronic, and aldaric acids which are highly useful chemicals. For example, oxidation of glucose at C1 position will yield gluconic acid and oxidation of both C1 and C6 positions will lead to glucaric acid. These acids are important chemical feedstocks possessing many chiral centers useful in the production of pharmaceuticals, detergents, polymers, food additives and corrosion resistant products. Glucaric acid is recognized as one of the top 12 platform chemicals obtained from biomass and can be used as a feedstock for the

production of adipic acid (Boussie et al. 2016). Adipic acid is used for production of nylon and other polymers. Glucaric acid can also find applications in the production of polyesters and in the making of detergents due its chelating ability with cations. Another deep glucose oxidation product, formic acid is also important as it can be used as a source for production of hydrogen, a green fuel (Jin et al., 2017). The possible selective oxidation products that could be obtained from glucose are shown in **Scheme 3**. The selective oxidation of free sugars obtained from biomass to value-added products is an interesting research topic and a recent review discussed this selective oxidation and also production of hydrogen from sugars (Omri et al., 2018). The envisaged advantage of heterogeneous photocatalytic oxidation of sugars is that it offers high selectivity for aldonic acid/aldonate salts and quantitative yields in shorter reaction time (Omri et al., 2018). However, tuning the properties of the catalysts and optimization of different parameters is required to achieve the selective oxidation of sugars and also in general for other biomass derived compounds (Parrino et al., 2018).

TiO<sub>2</sub> which is relatively wide band gap ( $\approx 3.2$  eV) semiconductor, and normally active under UV light has been studied widely for oxidation of sugars. But the conventional TiO<sub>2</sub> P-25 photocatalyst is not selective towards glucose oxidation and it rather forms more of mineralization products, CO<sub>2</sub> and water than the expected products, gluconic acid, glucaric acid and arabitol (Colmenares et al., 2011). At the same time, TiO<sub>2</sub> (US) the catalyst prepared via ultrasound-modified sol-gel process effectively produced gluconic acid, glucaric acid and arabitol with 70% combined selectivity. (Colmenares et al 2011). The TiO<sub>2</sub> (US) was nanostructured and hence possessed high specific surface area compared to TiO<sub>2</sub> P25. It is expected that the catalytic activity and product distribution are influenced by surface area, crystal structure, surface hydroxylation and crystallinity of TiO<sub>2</sub> (Bellardita et al., 2016). It was observed that TiO<sub>2</sub> anatase phase is responsible for the formation of fructose since Lewis acid sites are more on TiO<sub>2</sub> anatase, which catalyze glucose isomerization whereas, rutile and brookite TiO<sub>2</sub> showed



better selectivity for selective glucose oxidation products under both aerobic and anaerobic reaction conditions (Bellardita et al., 2016). Many studies found bare TiO<sub>2</sub> as not effective for production of aldonic and aldaric acids and suggested the requirement of additional supports and catalyst modifications. Loading of TiO<sub>2</sub> photocatalyst on high surface area supports like activated carbon improved its ability to oxidize glucose in aqueous solutions (Kukh et al., 2019). In this connection, loading TiO<sub>2</sub> on zeolites was found to be a better strategy as it will increase the surface area of TiO<sub>2</sub> and at the same time delocalize the electrons produced by TiO<sub>2</sub> upon light irradiation. Colmenares and Magdziarz (2013) synthesized TiO<sub>2</sub>-supported on zeolite Y (TiO<sub>2</sub>/Ze) by a modified ultrasound-assisted sol-gel method for the selective oxidation of glucose. The synthesized TiO<sub>2</sub>/Zeolite photocatalyst was more selective towards glucaric/gluconic acid products (selectivity= 68.1% with 15.5% glucose conversion) in the presence of UV light illumination for 10 min in 50% H<sub>2</sub>O/50% acetonitrile as solvent. The TiO<sub>2</sub>/Ze photocatalyst was found to be better than TiO<sub>2</sub>/SiO<sub>2</sub> and bare TiO<sub>2</sub>-P25 and synthesized TiO<sub>2</sub> (US) catalysts. This activity difference was explained partly based on the repulsion experienced by the carboxylic acids from the negatively charged zeolite framework, this will prevent them from undergoing further oxidation by attaching to the active sites. However the authors did not present any possible influence of acid sites present in the zeolites on the catalytic activity.

Later, the same group (Colmenares et al., 2013) found that chromium modification of TiO<sub>2</sub>/zeolite can improve the combined selectivity of the desired products, glucaric and gluconic acids compared to the unmodified TiO<sub>2</sub>/Zeolite catalyst. Solvent composition (water+acetonitrile) and illumination times exerted a considerable effect on the activity/selectivity of the tested photocatalysts. A red-shift in the band energy gap energy was observed in the chromium doped catalyst compared to the neat TiO<sub>2</sub> catalyst, indicating its better visible light absorption property. XPS studies indicated a change in the chromium oxidation state, Cr (III) to Cr (VI) during the annealing step. The surface atomic ratio

of the chromium ions,  $\text{Cr}^{3+}:\text{Cr}^{6+}$  was found to be 59:41. However, the exact role of these chromium ions on improving the selectivity of the desired gluconic and glucaric acids was not explained in detail though it was mentioned that the Cr doping may change the acidic nature of the catalyst. A more detailed study of influence of acid sites on photocatalytic conversion of glucose and selectivity of the oxidation products was recently published (Laosiripojana, 2020). Ag, Cu and Ag-Cu loaded  $\text{TiO}_2$  supported on A zeolite (Type Y) (ZeY), was used for the selective photocatalytic oxidation of glucose under UV light irradiation (Laosiripojana, 2020). The influence of  $\text{TiO}_2$  loading (10, 20, 40, and 50 mol.%) and  $\text{SiO}_2/\text{Al}_2\text{O}_3$  ratio (10, 100, and 500) of the zeolite on conversion of glucose and selectivity of carboxylic acids was studied. 20%  $\text{TiO}_2/\text{ZeY}$  ( $\text{SiO}_2/\text{Al}_2\text{O}_3 = 100$ ) photocatalysts showed the highest glucose conversion (75%) and it formed oxidation products such as gluconic acid, arabinose, xylitol and formic acid with 9, 26, 4, and 35% yields, respectively. Higher selectivity of gluconic acid = 29% and formic acid = 32%, was obtained over lower  $\text{SiO}_2:\text{Al}_2\text{O}_3$  ratio zeolite ( $\text{SiO}_2:\text{Al}_2\text{O}_3 = 10$ ) than the higher  $\text{SiO}_2:\text{Al}_2\text{O}_3$  ratio zeolites studied. It is known that while increasing the  $\text{SiO}_2/\text{Al}_2\text{O}_3$  ratio, the number of acid sites decreases but acid strength increases. Hence, from these results it can be concluded that lesser the number of acid sites higher the glucose conversion but poorer the selectivity towards carboxylic acids. Among the metal loaded  $\text{TiO}_2$  (40%)/ZeY catalysts, both 1 wt% Ag-Cu and 1wt% Ag loading increased the conversion of glucose to 94.7%. 1 wt% Ag-Cu and 1wt% Ag loading on  $\text{TiO}_2$  (40%)/ZeY improved formic acid selectivity. But 1wt% Cu loading on  $\text{TiO}_2$  (40%)/ZeY catalyst favored arabinose selectivity. So it is clear that the nature of acid sites and metals present in the catalysts influence the photocatalytic glucose oxidation.

One more instance for the influence of acid sites on product distribution and selectivity could be found when  $\text{TiO}_2$  was modified with heteropoly acids. Bellardita et al.(Bellardita et al., 2015) functionalized  $\text{TiO}_2$  with Keggin heteropolyacid,  $\text{H}_3\text{PW}_{12}\text{O}_{40}$  (PW12) and home-made  $\text{K}_7\text{PW}_{11}\text{O}_{39}$

(PW11) and tested the prepared catalysts for photocatalytic glucose oxidation. While bare TiO<sub>2</sub> was tested, arabinose and erythrose were preferentially formed whereas fructose and gluconic acid were favored when PW12-TiO<sub>2</sub> composite was utilized as photocatalyst. But when PW11-TiO<sub>2</sub> composite was employed, formic acid was observed as the preferred product. The fructose formation, which was higher on PW12-TiO<sub>2</sub> composite, revealed that PW12 enacts its acid function, reducing the oxidizing ability of TiO<sub>2</sub>, but PW11 do not show any acid function and hence it enhanced the oxidizing ability of TiO<sub>2</sub> leading to the formation of formic acid. Further in PW11-TiO<sub>2</sub>, PW11 reduces electron-hole recombination by forming heteropoly-blue species facilitating the availability of the photogenerated charge carriers for redox reaction. A mechanism for the formation of different oxidation products involved was also proposed.

Selective oxidation of glucose in the presence of visible light or sunlight is highly desirable. However, conventional TiO<sub>2</sub> photocatalyst absorbs only UV light due to its relatively large band gap ( $\approx 3.2\text{eV}$ ). Hence suitable modification of TiO<sub>2</sub> is necessary to facilitate oxidation of glucose under visible light and sunlight. TiO<sub>2</sub> modified with silver nanoparticles (NPs) found to selectively oxidize glucose under visible light (Luigi D et al., 2016). Arabinose (>35%), formic acid (~30%) and gluconic acid (15–18%) were obtained with selectivity mentioned in the brackets when the Ag NPs loaded TiO<sub>2</sub> was tested as photocatalyst under visible light whereas, bare TiO<sub>2</sub> yielded erythrose and glyceraldehyde as oxidation products. The plasmonic Ag NPs loaded on TiO<sub>2</sub> makes it to absorb visible light and enhanced the conversion of glucose, improved the selectivity (>98%) towards the partial oxidation products and suppressed mineralization. On this catalyst system (Ag/TiO<sub>2</sub>), it was observed that the use of UVA light instead of visible light led to mineralization of the organics. The use of 50% H<sub>2</sub>O/50% acetonitrile solvent was found to be crucial to get the partial oxidation products because the use of water alone lead to negligible activity of the catalyst. XPS and TEM analysis indicated the presence of both

Ag and its oxides on the TiO<sub>2</sub> surface. The recycling of the Ag/TiO<sub>2</sub> photocatalyst was carried out and despite the change in morphology and chemical state of Ag, the glucose oxidation product distribution and conversion remained unaffected after multiple reuse.  $\alpha$ -scission combined with Ruff degradation were proposed by the authors for the partial oxidation of glucose on the Ag/TiO<sub>2</sub> catalysts. Generally, during photocatalytic reaction, glucose undergoes oxidation, however, Goe Kim et al. (Kim et al., 2015) showed that glucose may form ligand to metal charge transfer (LMCT) complex with TiO<sub>2</sub> (**Fig. 5(a)**) and induce visible light adsorption via a LMCT sensitization mechanism. Visible light cannot be absorbed by bare TiO<sub>2</sub> or glucose, but the TiO<sub>2</sub>-glucose structures absorb visible-light up to the range of 600 nm (**Fig. 5 (b)**). Not only glucose, also its derivatives (2-deoxy-d-glucose, glucosamine or 2-azido-2-deoxy-glucose) and other sugars (maltose, cellulose) exhibited the visible light absorption through LMCT-sensitization (Colmenares et al., 2013). The visible-light activity was significantly inhibited when the TiO<sub>2</sub> surface was fluorinated, because the surface fluorides inhibit the formation of the complex, which confirms the formation of the LMCT complex.

Apart from TiO<sub>2</sub> based photocatalyst catalysts, other photocatalyst were also investigated for the selective oxidation of glucose. Glucose oxidation was studied using a composite photocatalyst, ZnO/CoPzS<sub>8</sub> in water under simulated solar light irradiation in the absence of acid or base (Cheng et al., 2019). This composite photocatalyst, zinc oxide-supported cobalt thioporphyrzine (ZnO/CoPzS<sub>8</sub>), was prepared by immobilizing cobalt-tetra (2,3-bis)butylthio(maleonitrile)porphyrzine(CoPzS<sub>8</sub>) on ZnO (Cheng et al., 2019). The XPS characterization of the catalyst indicated the existence of interaction between CoPzS<sub>8</sub> and ZnO. Due to a synergistic effect, ZnO/CoPzS<sub>8</sub> showed enhanced catalytic performance compared to pure ZnO and CoPzS<sub>8</sub>. On both pure ZnO and ZnO/CoPzS<sub>8</sub>, upon oxidation, gluconic acid, arabinose, glycerol and formic acid were observed as oxidation products. However, on ZnO/CoPzS<sub>8</sub>, glucaric acid was also obtained along with the other products. This observation indicated

modification of the reaction pathway when CoPzS<sub>8</sub> was immobilized on ZnO. The presence of CoPzS<sub>8</sub> on the ZnO surface changed surface polarity of ZnO, which benefited the adsorption of terminal groups of glucose on the catalyst surface. Therefore, glucaric acid was selectively formed on the ZnO/CoPzS<sub>8</sub> photocatalyst. Rui Chen et al. (Chen et al., 2019) synthesized a supported biomimetic photocatalyst H-ZSM-5/FePz(SBu)<sub>8</sub>, where FePz(SBu)<sub>8</sub> = tetra(2,3-bis(butylthio)maleonitrile)porphyrine, and investigated glucose oxidation on the prepared catalyst in water under visible-light ( $\lambda \geq 420$  nm) using H<sub>2</sub>O<sub>2</sub> as oxidant. Gluconic acid, glucaric acid, formic acid, glycerol, and arabinose were formed upon glucose oxidation with H-ZSM-5/FePz(SBu)<sub>8</sub>, which showed higher conversion of glucose than the one obtained with FePz(SBu)<sub>8</sub>. Glucaric acid was found only when H-ZSM-5/FePz(SBu)<sub>8</sub> was used as the photocatalyst, indicating a synergy between H-ZSM-5 zeolite and FePz(SBu)<sub>8</sub>. The total selectivity for glucaric and gluconic acids reached to 45% at glucose conversion of ~35.8% (reaction time = 4 h, glucose concentration = 3 mmol L<sup>-1</sup>, H<sub>2</sub>O<sub>2</sub>:glucose ratio = 3.3:1) when H-ZSM-5/FePz(SBu)<sub>8</sub> was used as the catalyst.

From the above examples, it can be corroborated that based on the nature of the photocatalysts, supports, metal loading and surface modifications, the selective oxidation of glucose to the desired value-added products can be achieved. However, apart from the nature of the modified photocatalysts, reaction conditions and additives can also influence the product distribution during oxidation of glucose. Colmenares and Magdziarz (2013) suggested that the solvent system, 50% H<sub>2</sub>O/50% acetonitrile used by them played a significant role in improving the selectivity of gluconic and glucaric acids because the relatively basic acetonitrile will solvate carboxylic acids and prevent their further oxidation. This was supported by the observation that in 100% H<sub>2</sub>O, no carboxylic acid was formed. Also in some other reports, the significance of this solvent composition has been documented (Colmenares et al. 2013; Luigi D et al., 2016). This influence of H<sub>2</sub>O + acetonitrile solvent system on the oxidation of glucose

was attributed to a “shield effect” which prevents further oxidation of the carboxylic acid products (Colmenares et al. 2013). Since photocatalytic reactions involve active oxygen species, presence and absence of oxygen can influence the product distribution. The photo conversion of glucose under aerated and non-aerated conditions in the presence of Pt supported on different TiO<sub>2</sub> anatase, rutile and brookite powders in aqueous- medium was studied under 125 W medium-pressure mercury lamp emitting 365 nm light. (Bellardita et al., 2016). In the presence of air, the oxidation of glucose led to the formation of gluconic acid, arabinose, erythrose and formic acid and fructose was also observed as an isomerization product. Under anaerobic conditions, similar products that were formed in the presence of O<sub>2</sub> found, yet additionally, significant amount of H<sub>2</sub> was also produced. In glucose and xylose oxidation to formic acid, the presence of NaOH was found to be crucial. The nano TiO<sub>2</sub> photocatalyst showed almost complete conversion of glucose and 35% yield of formic acid at ambient temperature in 0.03M NaOH solution (Jin et al., 2017). Due to the presence of the base NaOH, the product of oxidation, formic acid was present in the solution as formate ion without being adhered to the catalyst surface. The hydroxyl ions trigger a unique “shield effect” that facilitates the adsorption of glucose and desorption of formic acid preventing the latter from further oxidation. Furthermore, the hydroxyl ions accelerated the utilization of photo-induced electrons (e<sup>-</sup>) and holes (h<sup>+</sup>) by forming active radicals required for oxidation of the sugars.

Utilizing the visible light absorption property of the TiO<sub>2</sub>-glucose complex, Luigi et al.(Colmenares et al., 2013) reported oxidation of glucose under visible light irradiation. TiO<sub>2</sub>-rutile, anatase and P25-TiO<sub>2</sub>were studied to assess their corresponding catalytic activity in the selective glucose photo-oxidation and P25 was found to be the most active catalyst. Under visible-light, TiO<sub>2</sub> catalyst was more selective towards gluconic acid with less mineralization towards CO<sub>2</sub> than with UVA

light. Furthermore, the Calcination of P25 at 500-600 °C resulted in rutile-rich that lead to improved activity.

In summary, minimizing mineralization of glucose and the oxidation products to selectively get value-added products such as gluconic, glucaric and formic acids is a challenge. The mechanistic routes by which glucose and fructose are converted into various products are given in **Scheme 4**. Titanium dioxide (TiO<sub>2</sub>) is the main photocatalyst studied for photocatalytic oxidation of glucose. From the existing reports, it is understood that modification of surface characteristics and tuning catalytic properties of TiO<sub>2</sub> is necessary to improve the selectivity towards the value-added oxidation products. The properties of the catalyst system can be modified by variety of ways by choosing a zeolite support with suitable acidity, loading metals such as Ag, Cu, Pt, nano-structuring the catalyst, making composite catalysts using materials like activated carbon, heteropoly acid and Fe or Co containing complexes. Using visible light to induce photocatalysis will also minimize the undesired products.

### **Photocatalytic oxidation of alcohols to value-added chemicals**

The transformation of biomass-derived alcohols into valuable chemicals is an important part of valorization of biomass chemicals. The oxidation of benzyl alcohol using photocatalysts has been studied by many researchers as it is a model compound for aromatic alcohols that are formed during lignin degradation. The photocatalytic transformation of biomass-alcohols can be conventionally performed in anaerobic or aerobic environments. Under aerobic environment, the photo-induced electrons in conduction band reduce the oxygen molecules to reactive species such as singlet-state molecular oxygen (<sup>1</sup>O<sub>2</sub>) and super-oxide radicals (O<sub>2</sub><sup>•-</sup>). These reactive species subsequently involve in the conversion of alcohols (**Fig. 6 (a)**). Similarly, holes (h<sup>+</sup>) in the valence band can also oxidize alcohols to the respective carbonyl-based compounds. On the other hand, in anaerobic environments,

photo-induced electrons will be largely available towards the reduction of protons to produce molecular hydrogen ( $H_2$ ), whereas the photo-induced holes will oxidize the alcohols, facilitating the simultaneous alcohol oxidation and  $H_2$  production as shown in **Fig. 6(b)**.

In this direction, the selective oxidation of benzyl alcohol to benzaldehyde in aqueous medium under visible-light irradiation using a Pt@CeO<sub>2</sub> nanocomposite having core-shell structure was demonstrated (Zhang et al., 2011). It is reported that the Pt sites trap/store the electrons and increase the charge carrier lifetime, thus enhancing the photocatalytic oxidation process. Benzyl alcohol adsorbed on the catalyst-surface reacts with holes and forms a radical cation. Further reaction of the radical cation with oxygen or superoxide radical gives rise to the formation of benzaldehyde. Since the interfacial-contact between the Pt and CeO<sub>2</sub> is favorable in core/shell Pt@CeO<sub>2</sub>, it showed better catalytic activity than yolk/shell Pt@CeO<sub>2</sub>. The hole potential of the core shell Pt@CeO<sub>2</sub> catalyst is +2.46 V vs. SHE and the anodic potential of benzyl alcohol is +0.85 V vs. SHE. As the latter is less positive than the former, the photocatalytic oxidation of benzyl alcohol is thermodynamically feasible. In another study, the Au/CeO<sub>2</sub>-TiO<sub>2</sub> nanotubes as photo-cathodes were used for the photoelectrochemical oxidation of biomass alcohols (benzyl alcohols) under visible light irradiation in O<sub>2</sub> atmosphere, where 98% conversion of benzyl alcohol and >99% selectivity of benzaldehyde were obtained at bias potential of -0.8 V under 8 h irradiation (Zhang et al., 2014). Interestingly, the simultaneous selective oxidation of benzyl alcohol and hydrogen production using Au/TiO<sub>2</sub> nanotube photonic crystals (Au/TiO<sub>2</sub> NTPC) as photoanode was demonstrated using a solar-driven photoelectrochemical cell (Song et al., 2017). The conversion of benzyl alcohol was as high as 84.68% and selectivity of benzaldehyde reached to 99%; meanwhile, the hydrogen production at the cathode was measured to be 143.83 mmol cm<sup>-2</sup>.

The oxidation of biomass-derived products, furfural-alcohol and 5-hydroxymethylfurfural (HMF) into aldehyde and acid is an important step in biomass valorization and quite a number of papers



have been published recently on this topic. The photocatalyst based on Ni/CdS nanosheets was demonstrated for the valorization of furfural alcohol and HMF to value-added products such as 2,5-diformylfuran, furoic acid and furandicarboxylic acid (aldehydes and acids) in aqueous medium under visible-light irradiation (Guanqun Han et al 2017). The transformation of HMF was remarkably lower than that of furfural-alcohol and this difference observed under the same reaction conditions indicates the influence of the aldehyde group in HMF on the oxidation of its alcohol group. This photocatalysis strategy enabled the production of aldehydes in neutral water and also under strong alkaline-conditions; the complete photocatalytic-transformation of furfural-alcohol and HMF to their corresponding carboxylates was also achieved.

The selective oxidation of ethanol, glucose, xylose, 2-furaldehyde, 5-hydroxymethyl-2-furfural, and furfural alcohol to their corresponding carboxyl compounds in air under ambient conditions was performed using Au-NPs supported on TiO<sub>2</sub> (Baowen Zhou, 2017). The oxidation reaction was performed in Na<sub>2</sub>CO<sub>3</sub> aqueous solution under both ultraviolet (UV) and visible-light. The visible-light-driven activity of the catalyst is mainly due to the surface plasmon resonance of Au-NPs, and the UV-light activity of the catalyst was correlated to band-gap photo-excitation of TiO<sub>2</sub>. Under UV light, Na<sub>2</sub>CO<sub>3</sub> acted as an inhibitor of reactive-oxygen-species, but under visible-light-induced oxidation, it behaved as an effective promoter. On the other hand, the metal-free g-C<sub>3</sub>N<sub>4</sub> based photocatalysts have also been reported for the selective oxidation of HMF to 2,5-diformylfuran under visible light irradiation (Zhang et al., 2017). Under high energy UV light, the catalyst led to over oxidation of HMF to furandicarboxylic acid. Furthermore, the heating process also favored the photo-oxidation, but decreased the selectivity of 2,5-diformylfuran due to further oxidation, where  $\cdot\text{O}_2^-$  was the dominant active species and it played an important role in the oxidation reaction. Similarly, the Nb<sub>2</sub>O<sub>5</sub> photocatalyst was demonstrated for the selective oxidation of HMF to 2,5-diformylfuran under visible light (Zhang et al.,

2017). The  $\text{Nb}_2\text{O}_5$  catalyst that calcined at  $800\text{ }^\circ\text{C}$  exhibited the best performance in the presence of  $\text{O}_2$ . It was proposed that the alcoholic hydroxyl group of HMF adsorbed on the  $\text{Nb}_2\text{O}_5$  catalyst and formed the alcoholate species, which also facilitated the band gap reduction in  $\text{Nb}_2\text{O}_5$  towards absorbing visible light photons. The experiments revealed that radical species such as  $\bullet\text{OH}$  and  $\bullet\text{O}_2^-$  were not the main active species for the reaction, but holes ( $\text{h}^+$ ) were found to be the dominant active species.

Further, the simultaneous photocatalytic-oxidation of HMF to 2,5-diformylfuran and water splitting was demonstrated using the interstitial P-doped  $\text{Zn}_x\text{Cd}_{1-x}\text{S}$  solid solutions with sulfur (S) rich vacancies system (Ye et al., 2018). Similarly, the Pt-supported graphitic-carbon nitride (Pt/g- $\text{C}_3\text{N}_4$ ) was used for the simultaneous photocatalytic reduction of HMF and water splitting under visible-light irradiation (Teoh et al., 2014). The Pt/g- $\text{C}_3\text{N}_4$  photocatalyst acted as a multifunctional and tandem catalyst, where it promoted the photocatalytic water splitting to produce hydrogen and favored the consecutive activation of the produced  $\text{H}_2$  for the reduction of HMF to DHMF.

It is known that the glycerol is a key biomass alcohol as it is a major by-product from the biodiesel industry. The photocatalytic aerobic selective oxidation of glycerol was demonstrated under visible-light irradiation using the sol-gel encapsulated, leach-proof, flower-like  $\text{Bi}_2\text{WO}_6$  microparticles incorporated into silica-based matrices ( $\text{SiO}_2$  xerogels) (Zhang et al., 2013). It is explained that the glycerol was preferentially oxidized at the secondary OH group, showing the remarkable encapsulation effect of the silica matrix on the photoactive  $\text{Bi}_2\text{WO}_6$  on the product selectivity. Similarly, the selective oxidation of glycerol to form hydroxyacetaldehyde (HAA) over  $\text{TiO}_2$ -photocatalyst in aqueous solution was demonstrated, where the product selectivity was found to be firmly dependent on the facets of  $\text{TiO}_2$  (Chong et al., 2014). The  $\text{TiO}_2$ -rutile with high percentage of  $\{110\}$  facets resulted in 90% selectivity of HAA, while anatase with  $\{001\}$  or  $\{101\}$  facets showed only 16 and 49% selectivity respectively. In addition to this, hydrogen was also produced during the reaction. The observed efficiency was attributed

to the two adjacent Ti–O• radicals on rutile {110} that lean to combine with each other to form surface peroxy-species and TiO-OTi, where it did not happen on anatase {001}. Theoretical studies showed that dissociated H<sub>2</sub>O had hydroxyl bound to a Ti<sub>5c</sub> site on anatase {001} facets, while the O ad-atom is bound to a Ti<sub>5c</sub> site on rutile {110} facets. The major reaction pathway of oxidation of glycerol with water is to generate hydroxyl-acetaldehyde, formic acid and H<sub>2</sub>, while the mild reaction is the direct dehydrogenation of glycerol to glyceraldehydes (GA). TiO<sub>2</sub>-supported-Nb<sub>2</sub>O<sub>5</sub> catalysts (Nb<sub>2</sub>O<sub>5</sub>/TiO<sub>2</sub>) with different loadings of Nb<sub>2</sub>O<sub>5</sub> between 0 and 5 mol.% were tested in the photocatalytic oxidation of 1-, 2-, 3-pentanol, and cyclohexanol (Furukawa et al., 2012). Although the Nb<sub>2</sub>O<sub>5</sub> loading decreased the alcohol conversion, the selectivity was found to be increased and the 3-mol% Nb<sub>2</sub>O<sub>5</sub>/TiO<sub>2</sub> catalyst demonstrated a maximum selectivity for the partial oxidation products.

A summary of photocatalyzed conversions of biomass-derived alcohols into various possible value-added chemicals/products is depicted in **Scheme 5**. Photocatalytic oxidation of alcohols, obtained from biomass, into value-added chemicals using oxygen or air under ambient, aqueous conditions is possible. The variety of alcohols obtained from different biomasses requires diverse photocatalyst systems and appropriate conditions for their effective conversion into value-added products. The important thing to note is that many of the reported photocatalysts can work in visible light, which is possible by proper selection of the semiconductors with suitable band gap and successful modifications of their surface and textural properties. Apart from the conventional TiO<sub>2</sub>, novel materials such as core/shell Pt@CeO<sub>2</sub>, g-C<sub>3</sub>N<sub>4</sub>, P-doped Zn<sub>x</sub>Cd<sub>1-x</sub>S, Nb<sub>2</sub>O<sub>5</sub>, Nb<sub>2</sub>O<sub>5</sub>/TiO<sub>2</sub>, Bi<sub>2</sub>WO<sub>6</sub>, Ni/CdS nanosheets have been so far studied for the selective conversion of alcohols into aldehydes and acids. It is known that the furandicarboxylic acid is a versatile molecule that can be a replacement for terephthalic acid used in the production of polyester, performs the conversion of HMF to 2,5-diformylfuran and a potential bio fuel

having higher energy content than bioethanol. These reports on the selective photocatalytic conversion of biomass-derived alcohols demonstrate the promising approach for the green future.

### **Photocatalytic conversion of vegetable oil**

Vegetable oils are important sources of compounds used as fuels. Biodiesel is mainly produced from vegetable oils. Various edible vegetable oils such as soybean oil, sunflower oil, cotton seed oil etc. can be used for the production of biodiesel. But due to the loss of food security involved in the use of edible oils, nonedible oils obtained from plants such as *Jatropha* are preferred for biodiesel production. Biodiesel is mainly prepared by alkali catalyzed transesterification of the fatty acid glycerol esters. However the excess presence of free fatty acids (FFAs) in the oils along with the fatty acid glycerol esters affect the catalytic production of biodiesel. Esterification of FFAs followed by transesterification of glycerol esters was found to be a suitable strategy to improve the biodiesel production. Recently it has been shown that photocatalytic esterification of FFAs present in *Jatropha* oil with methanol using ZnO/SiO<sub>2</sub> photocatalyst in the presence of UV light followed by transesterification of the glycerol esters using conventional NaOH produce a better quality biodiesel which meets international standards (Corro et al. 2013). The photocatalytic esterification seems to proceed via formation of CH<sub>3</sub>O• and R-COOH• radicals which are formed by reaction of methanol with photogenerated holes and the FFAs with photogenerated electrons respectively. In a very recent work, photocatalytic decarboxylation of fatty acids obtained from soybean and tall oils were converted to alkanes using hydrogenated Pt/TiO<sub>2</sub> photocatalyst under 365 nm UV light (Huang et al. 2020). The fatty acids studied were in the range of C<sub>12</sub>-C<sub>18</sub> so that they produce diesel range alkanes during the photocatalytic decarboxylation. The reaction proceeds via production of alkyl radicals after decarboxylation of fatty acids. These alkyl radicals are highly susceptible for uncontrolled polymerization reactions. However, dissociation of H<sub>2</sub> gas on the reduced Pt/TiO<sub>2</sub> surface produce surface hydrogen species which terminate the alkyl radicals

thus improving the yield of alkanes. This is an important finding because it provides an opportunity to produce diesel fuel from bio-based fatty acid feed stocks.

### **Summary, conclusion and future perspectives**

The quest for finding sustainable ways to produce green energy and chemicals has made the researchers to ponder one of the largest available sustainable resources on this planet, the biomass. Non-edible, lignocellulosic biomass is a highly suitable renewable source for producing green energy and chemicals as it is made up of carbon and available in plenty. The photocatalytic transformation of biomass and its derivative chemicals is a green process as it is usually performed under ambient conditions and aqueous solvents under UV or visible light irradiation. Variety of biomass or biomass-derived materials ranging from raw biomass to cellulose, lignin, sugars and alcohols have been studied to produce valuable chemicals and chemical intermediates.

Complete conversion of lignocellulosic biomass to high value products using photocatalysis alone is difficult to be conceived because of the sturdy nature of biomass and limitations in process engineering aspects. Hence, a combination of photocatalysis with other technologies can be thought out to achieve the same. Photocatalysis has been used for the pretreatment of biomass before it is enzymatically degraded to get bioethanol. The photocatalytic pre-treatment of biomass can be envisaged from an environmentally conscious approach, as it eliminates the need of acid and alkali. However, there are only limited examples for the application of photocatalysts in combination with other technologies for direct processing of biomass to value-added products, and more concrete studies with different biomasses required before the industrial realization.

Cellulose and lignin can be transformed to high-value chemicals via photocatalysis in combination with other chemical agents or methodologies. TiO<sub>2</sub> is the main photocatalyst studied for

depolymerization/degradation/oxidation of cellulose and lignin. The value-added products generally obtained from cellulose are HMF, glucose and formic acid. Selective photocatalytic cellulose conversion into HMF requires acid catalysts as the photocatalyst alone cannot catalyze dehydration and cyclization steps. Depolymerization of lignin by breaking down the different linkages present in it is necessary to convert it into smaller molecules and get value-added products. Syringaldehyde, pyrocatechol, raspberry ketone vanillin, vanillic acid and Guaiacol are some of the value-added products obtained from photocatalytic lignin depolymerization. Use of UV radiation facilitates faster lignin degradation, however, it should be considered with caution as it will also facilitate complete mineralization. Tuning the properties of  $\text{TiO}_2$  catalyst by surface modification with metals or carbon or adding suitable reagents like PEO and methyl linoleate can be employed to improve lignin conversion and selectivity of the products. The suppression of non-selective radical such as  $\cdot\text{OH}$  and producing more selective oxidizing agent such as  $\text{O}_2^{\cdot-}$  by modifying the  $\text{TiO}_2$  catalyst with Bi looks promising. Further combining photocatalysis with electrocatalysis or enzyme catalysis will be fruitful for achieving better lignin conversion and higher value-added products selectivity.

The selective glucose oxidation to gluconic, glucaric and glycolic acid is desirable because these carboxylic acids are important building-blocks for pharmaceutical, food and perfumery chemicals. Converting glucose to formic acid is also desired as it is a source for hydrogen fuel. Minimizing mineralization of glucose and selectively getting these value-added products is a challenge. Titanium dioxide ( $\text{TiO}_2$ ) is the main photocatalyst studied for photocatalytic oxidation of glucose. From the existing reports, it is understood that modification of surface characteristics and tuning catalytic properties of  $\text{TiO}_2$  is necessary to improve the selectivity towards the value-added oxidation products. The properties of the catalyst system can be modified by variety of ways by choosing a support with suitable acidity, loading metals such as Ag, Cu, Pt, nano-structuring the catalyst, and making composite

catalysts using materials like activated carbon, heteropoly acid and Fe or Co containing complexes. Using visible light instead of UV light to induce photocatalysis will also minimize the undesired products.

The selective photocatalytic oxidation of alcohols obtained from biomass to value-added chemicals using oxygen or air under ambient, aqueous conditions is feasible. The variety of alcohols obtained from different biomasses means diverse photocatalysts and conditions required for converting them into value-added products. Apart from conventional  $\text{TiO}_2$ , novel materials such as core/shell  $\text{Pt@CeO}_2$ ,  $g\text{-C}_3\text{N}_4$ , P-doped  $\text{Zn}_x\text{Cd}_{1-x}\text{S}$ ,  $\text{Nb}_2\text{O}_5$ ,  $\text{Nb}_2\text{O}_5/\text{TiO}_2$ ,  $\text{Bi}_2\text{WO}_6$ , Ni/CdS nanosheets have been studied for selective conversion of alcohols to aldehydes and acids. The studies emphasized on the requirement of proper selection of the semiconductor photocatalysts and modifications of their surface and textural properties, and energetics for selective oxidation of alcohols. The selective conversion of biomass derived HMF into furandicarboxylic acid, a molecule which is a replacement for terephthalic acid used in the production of polyester, the conversion of HMF to 2,5-diformylfuran, a potential biofuel having higher energy content than bioethanol, the transformation of free fatty acid containing vegetable oils to biodiesel and the conversion of fatty acids into diesel range of alkanes using photocatalysts show the promise photocatalysis show for the green future.

In a nutshell, the main challenge in the photocatalytic-transformation of biomass and biomass-derived chemicals is to prevent the complete mineralization of the molecules in to  $\text{CO}_2$  and  $\text{H}_2\text{O}$  and to achieve selective oxidation to get the desired valuable products. This challenge has been addressed by suitably modifying the photocatalysts, tuning the reaction conditions, addition of suitable chemical agents and coupling photocatalysis with complementary technologies such as electrocatalysis, enzyme catalysis, acid catalysis etc. It is noteworthy that many listed photocatalysts are recyclable and can work in visible light/sunlight, indicating the sustainability of the photocatalytic process. However it is unlikely

that photocatalysis be a unique solution for transformation of biomass and biomass-derived molecules into valuable chemicals. The development of a single, effective photocatalyst system for the selective conversion of biomass and biomass-derived chemicals into value-added chemicals is a challenge. This is because of the fact, biomass is a complex natural product and made up of combination of chemical compounds having different properties. So, the modern biomass processing aimed to produce value-added chemicals should essentially be a combination of photocatalytic, enzymatic, chemical and electrochemical technologies, so that their benefits are utilized and their limitations are compensated to achieve sustainability.

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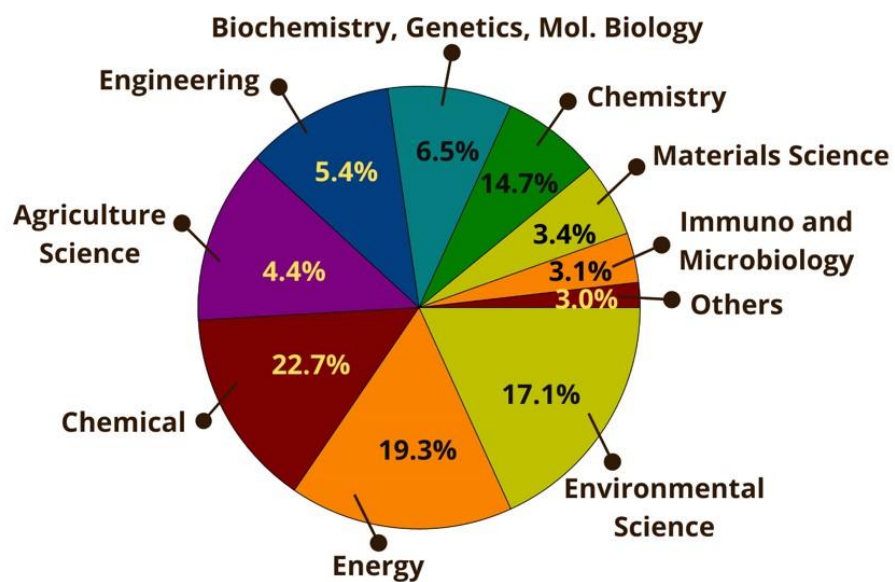


Figure 1. Percentages of articles published from 2010 to 2020 on “biomass conversion to chemicals” under different categories of research areas; Source: Scopus (data collected by May 2020).

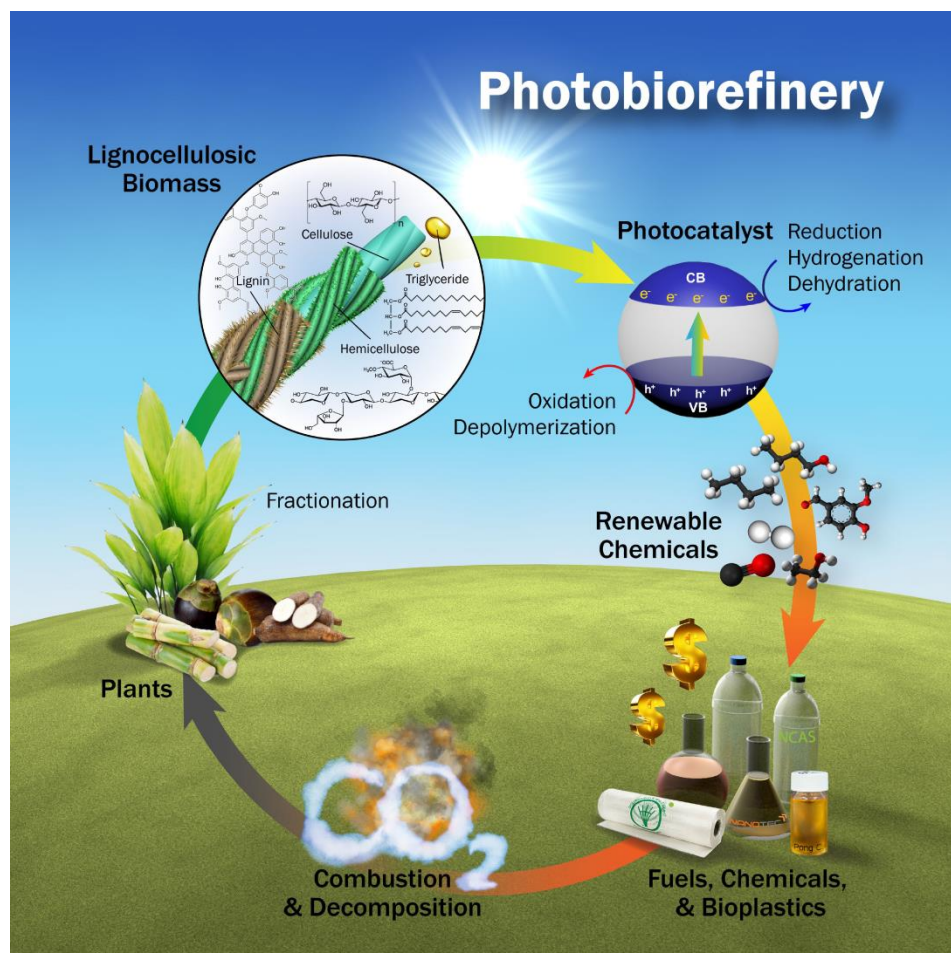
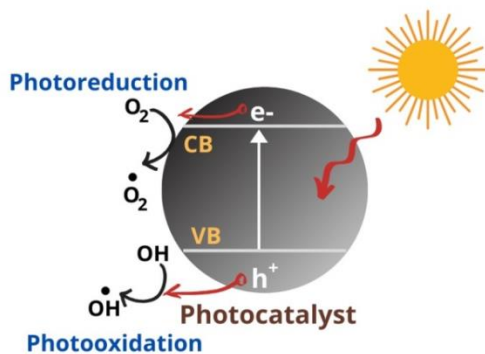


Figure 2. Photobiorefinery concept for the conversion of biomass into sustainable chemicals

(a)



(b)

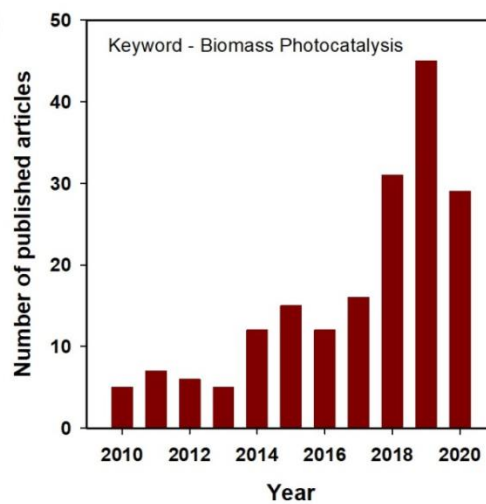


Figure 3. (a) Photo-activation of a semiconductor and primary reactions occurring on its surface, (b) number of published articles on photocatalysis-based biomass reformation between 2010 and 2020. Source: Scopus, data collected in May 2020.

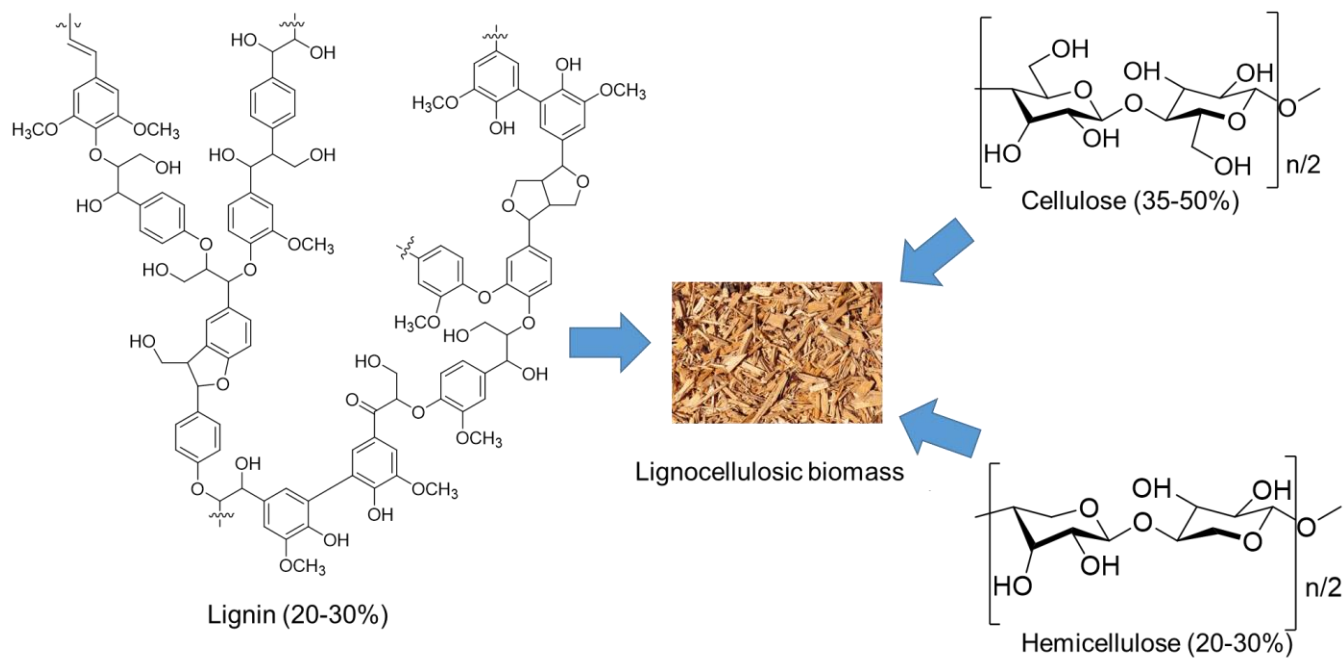


Figure 4. Main components making lignocellulosic biomass

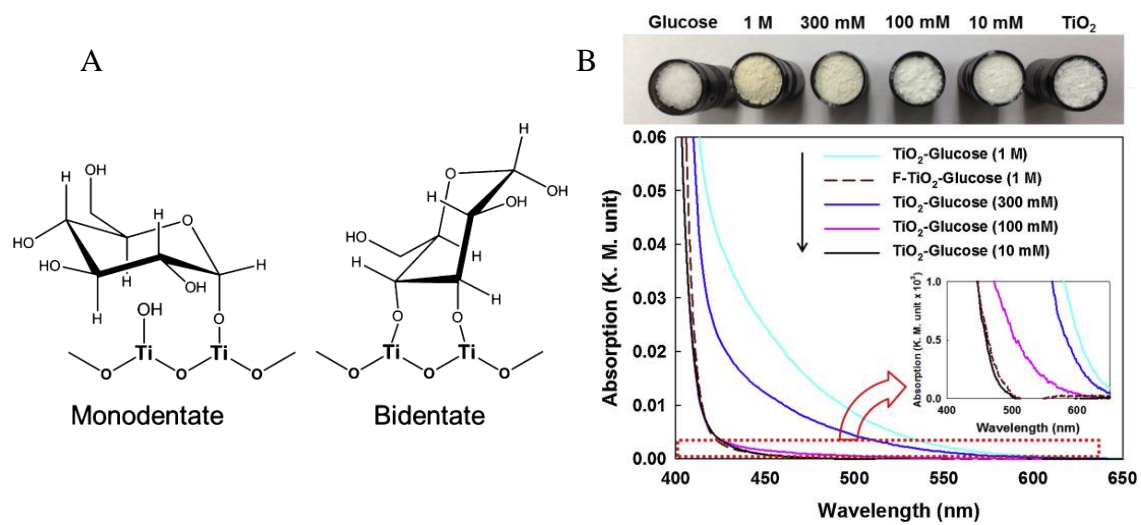


Figure 5. (a) Coordination structures of  $\text{TiO}_2$ -glucose complex. (b) Diffuse reflectance UV-visible spectra (DR-UVS) of  $\text{TiO}_2$ -glucose powders. Reproduced after modification from (Kim et al., 2015).

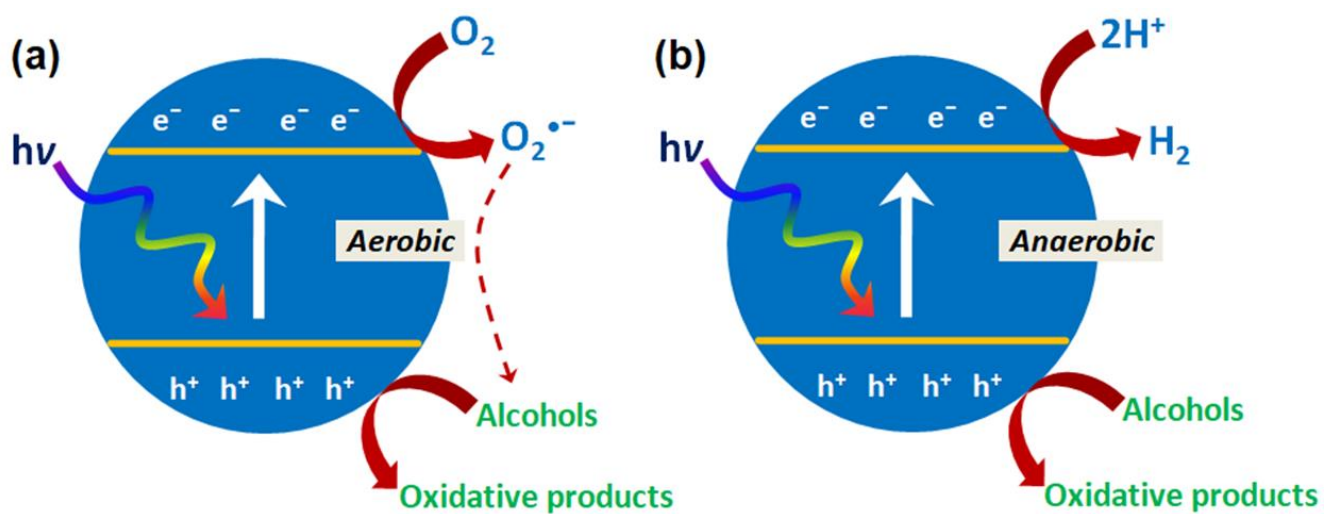
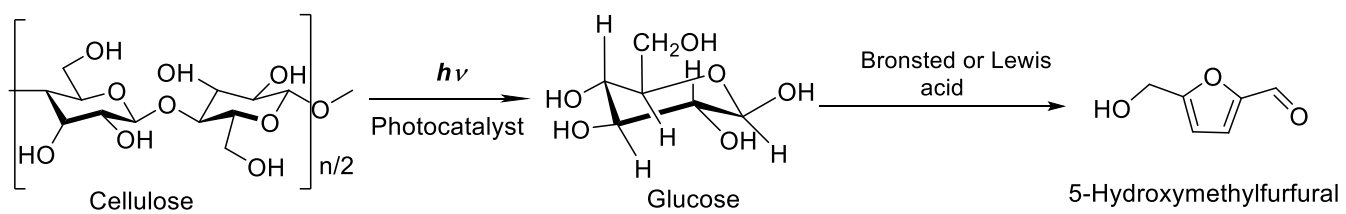


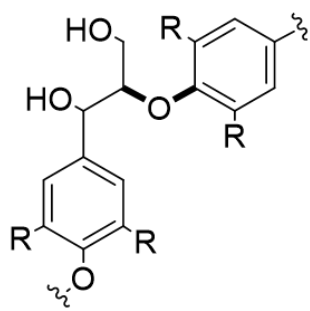
Figure 6 Mechanism for photocatalytic conversion of biomass-derived alcohol under (a) aerobic and (b) anaerobic environments



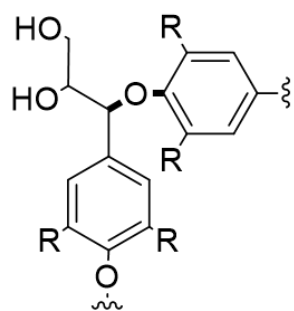
Scheme 1. Role of acids in photocatalytic conversion of cellulose to 5-hydroxymethylfurfural

Scheme 2. Different linkages present in lignin

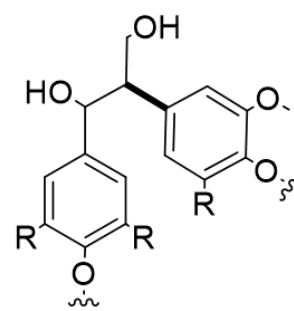




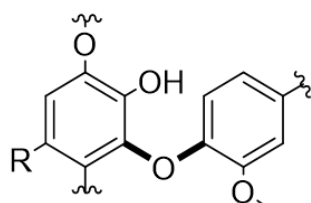
$\beta$ -O-4



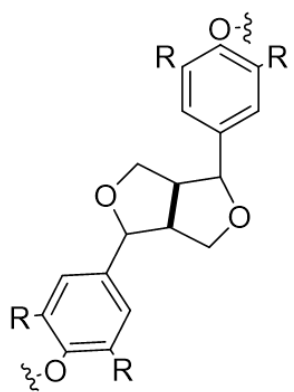
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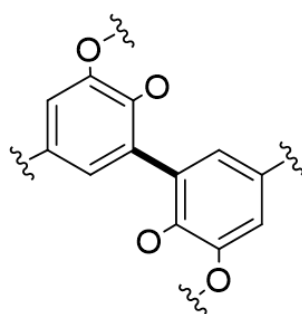
$\beta$ -1



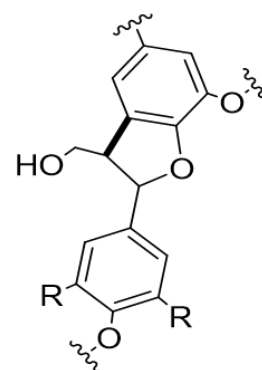
4-O-5



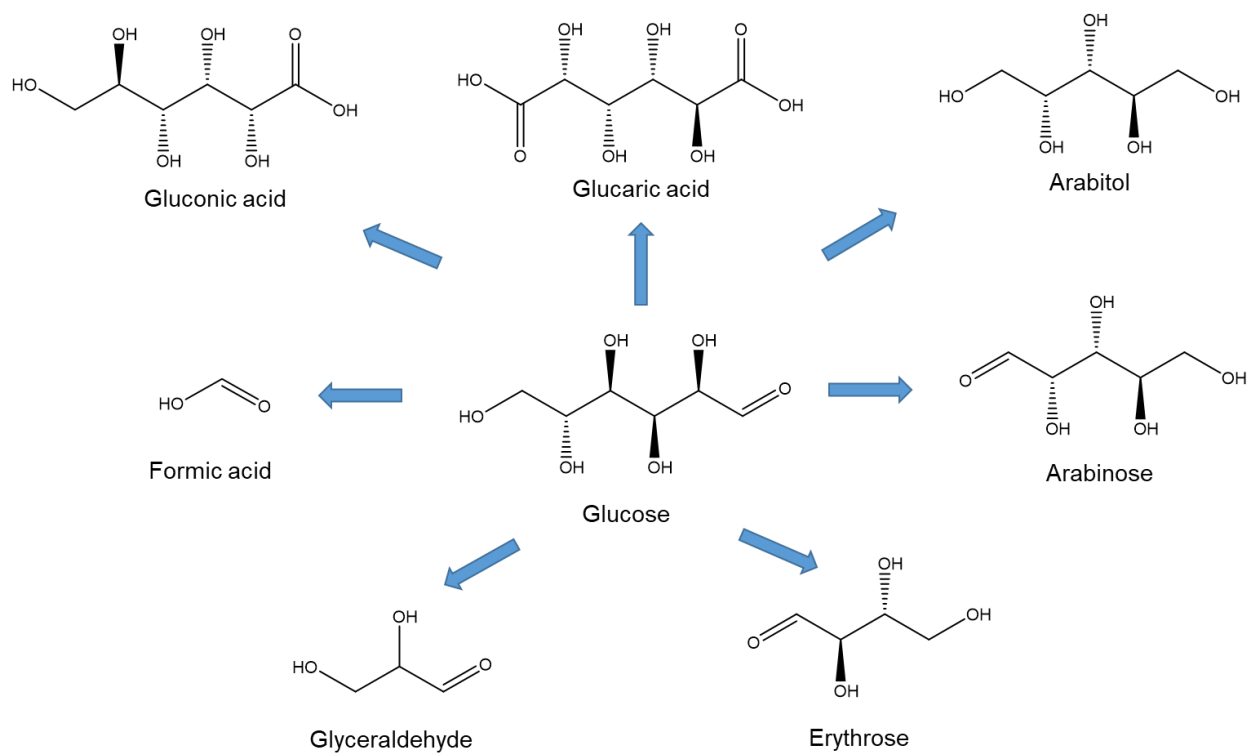
$\beta$ - $\beta$



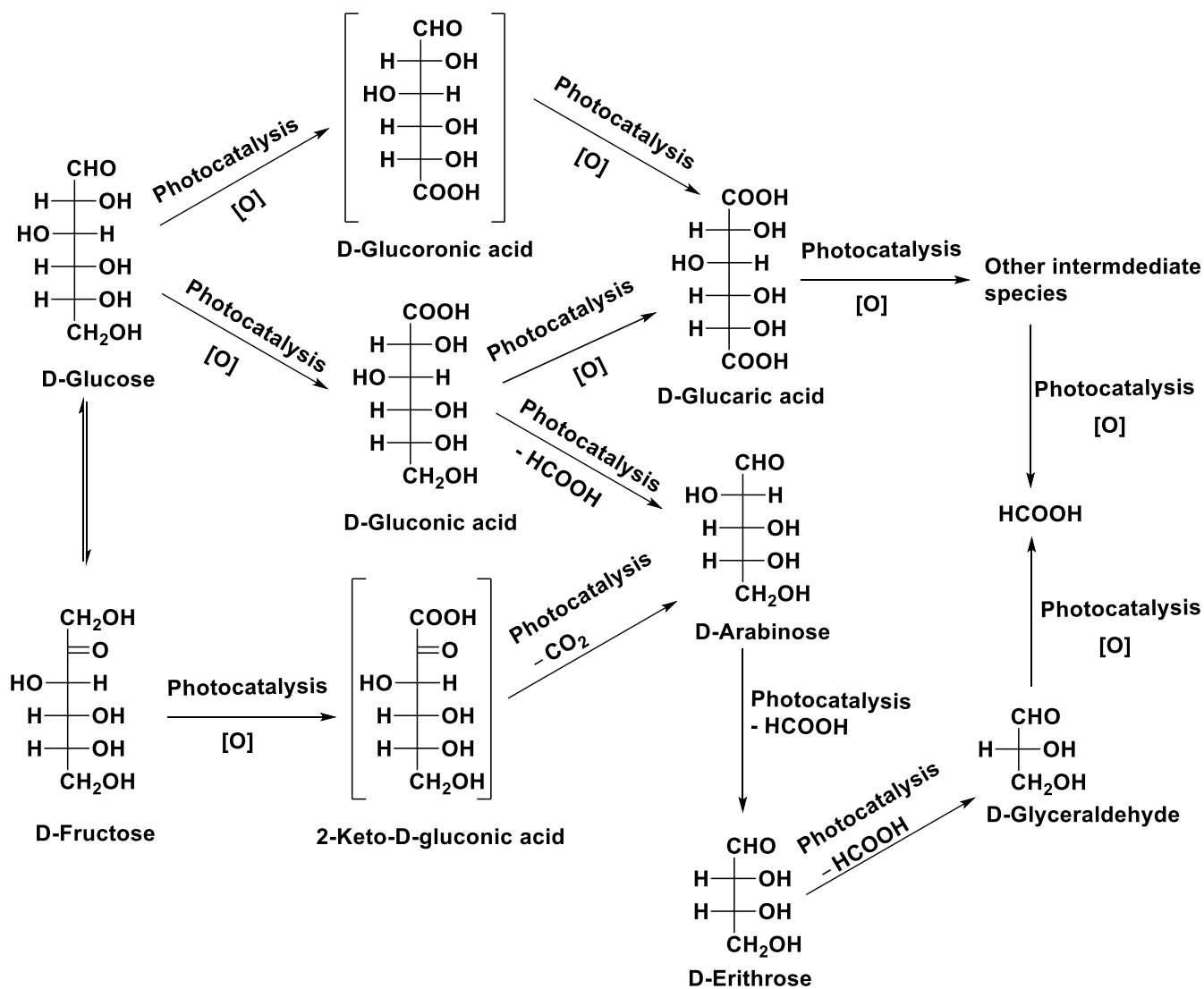
5-5



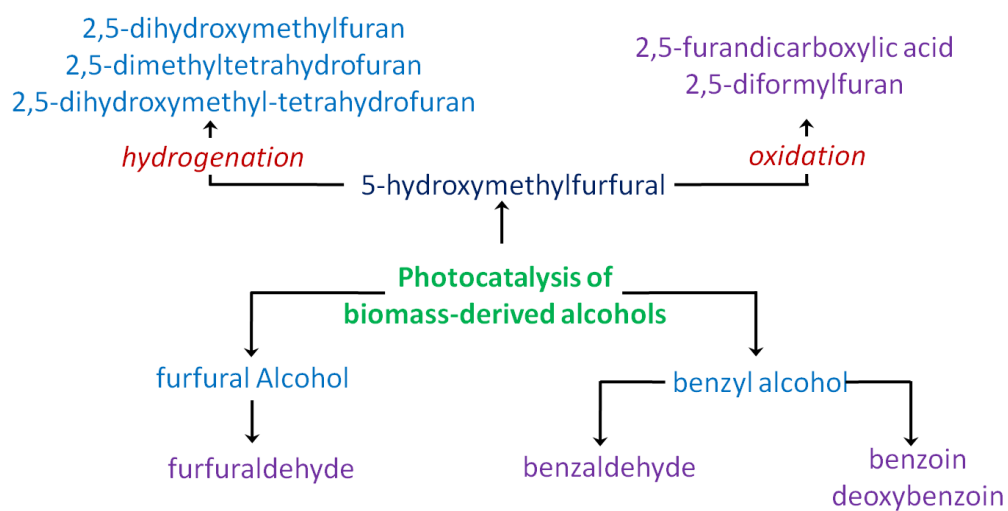
$\beta$ -5



Scheme 3. The expected value-added products obtained upon selective photocatalytic oxidation of glucose



Scheme 4. Mechanistic routes involved in photocatalytic oxidation of glucose and fructose



Scheme 5. Photocatalyzed conversions of biomass-derived alcohols into various possible value-added chemicals/products

Table 1. Summary of biomass, biomass-derived molecules, photocatalysts and value-added products

<b>Biomass/Biomass derived molecule</b>	<b>Photocatalyst and Light System</b>	<b>Reaction Conditions</b>	<b>Product (s) (Conversion/Yield/selectivity)</b>	<b>Reference</b>
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Cellulose	CrBr <sub>3</sub> , LiBr Visible light	Solvent : DMA Additive : NaBr	Conversion 92% Yield -93%	Joseph et al. (2009) J. AM. CHEM. SOC. 2009, 131, 1979–1985(Ref. 8)
Cellulose	TiO <sub>2</sub> nano fiber/Zeolite + Au NPs Visible light – intensity 0.7 W cm <sup>-2</sup>	Solvent : DMA Additive : NaBr	Conversion -36% Yield - 60%	Lina Wang et al.(2015) <a href="https://doi.org/10.1039/C5RA16616K">https://doi.org/10.1039/C5RA16616K</a> <i>RSC Adv.</i> , 2015,5, 85242-85247(Ref. 7)
Lignin (β-O-4 alcohol)	Pd/ZnIn <sub>2</sub> S <sub>4</sub> (Cu(OAC) <sub>2</sub> )  Particular wave length 455 nm and 365 nm light	Solvent : MeCN and MeOH Additive : TEMPO	Conversion -94% Yield -95%	Min Wang et al.(2016) DOI: 10.1021/acscatal.6b02049 <i>ACS Catal.</i> 2016, 6, 6086 – 6090 (Ref. 26)
Lignin	TiO <sub>2</sub> /Carbon form  UV-light	Solvent : water and acetonitrile	Conversion - 40.28%	<i>ACS Sustainable Chem. Eng.</i> 2018, 6, 11, 13968–13976

Hemicellulose	TiO <sub>2</sub> Heterogeneous photocatalyst UV Light irradiation 300W UV lamp	Solvent : Block liquor	Lignin 95%	R. Prado et al. (2013) Chemosphere 91 (2013) 1355–1361(Ref. 28)
Cellulose	TiO <sub>2</sub> UV Light irradiation UV lamp (21 W, wavelength 254 nm)	Solvent : ZnCl <sub>2</sub> solution	Yield-9%	Hongxian Fan et al.(2011) DOI 10.1002/jctb.2632(Ref. 22)
Cellulose	Cellulose +TiO <sub>2</sub> UV or solar light	Solvent : Water	Yield CO <sub>2</sub> -83.5% H <sub>2</sub> -91.7%	Guan Zhang , et al.(2015) DOI 10.1039/c5cc09075j(Ref. 21)
Potato Starch	TiO <sub>2</sub> – Bi <sub>2</sub> WO <sub>6</sub> Visible light UV filtered sunlight irradiation	Solvent : Starch Solution	Conversion 99.99%	L. Shiamala, et al.(2018) DOI 10.1016/j.jece.2018.04.065 (Ref. 19)
Glucose	Magnesium–aluminium hydrotalcites (HTs) UV/solar light	Solvent : 10 wt.% aqueous solution of glucose additive : Na <sub>2</sub> CO <sub>3</sub>	Selectivity- 30% Yield-89%	Irina Delidovich et al.(2015) DOI 10.1039/c5cc09075j(Ref. 25)

Algal biomass	TiO <sub>2</sub> Solar light (990 W/m <sup>2</sup> )	Solvent : Water	Yield-52.2%	R. Shwetharani, et al. (2016) DOI 10.1039/c5cc09075j(Ref. 20)
Glucose	TiO <sub>2</sub> dosage to zeolite (TiO <sub>2</sub> /ZeY) UV irradiation	Solvent : Water and acetonitrile	Conversion Glucose- 96.9%  Selectivity Gluconic acid-5.91%, Arabinose-20.49%, Xylitol- 12.93%, and Formic acid- 59.73%	Kamonchanok Roongraung. et al. (2020) DOI 10.3390/catal10040423
Glucose	H-ZSM- 5/FePz(SBu) <sub>8</sub> visible light ( 420 nm) xenon lamp  Reaction :cylindrical Pyrex vessel  Light intensity : 1.70 W cm <sup>-2</sup>	Solvent : aqueous glucose	Conversion-95 %  Selectivity-17 % Yield-NA Photocatalytic degradation- 11.5%	Chen, et al. (2020) DOI : 10.1016/j.jcat.2019.04.0 44(Ref. 42)
Glucose	TiO <sub>2</sub> -supported Ag visible light 300 W Xe Oriel Lamp	Solvent : Water	Selectivity-98% Yield-NA Conversion -100 %	Luigi Da Vi et al. (2016) DOI : 10.1002/cctc.201600775 (Ref. 37)



Glucose	TiO <sub>2</sub>	Solvent : Water  Additive : NaOH	Selectivity-14.2 Yield-35 % Conversion Photocatalytic degradation  84%	Binbin Jin et al. (2017) DOI : 10.1021/acsschemeng. 7b00364(Ref. 38)
Lignin	TiO <sub>2</sub> /ZnO  UV light (30 W UV lamp – intensity  35 W/m <sup>2</sup> )  Reactor design: doubled wall reaction vessels	Solvent : lignin solution	Selectivity Yield Conversion - 86.3%	S.K. Kansal et al.(2008) (Ref. 27) (2008) DOI 10.1039/c5cc09098j
Glucose	H-ZSM-5/FePz (SBU) <sub>8</sub>  visible light( Xe lamp )  reactor :Pyrex vessel	Solvent : aqueous  Glucose  Additive : H <sub>2</sub> O <sub>2</sub>	Selectivity-44.7% Yield-72% Conversion - NA	Rui Chen, et al.(2019) (Ref. 43) Journal of Catalysis 374 (2019) 297–305
Benzyl alcohol	Pt/CeO <sub>2</sub>  Visible light  300 W Xe arc lamp  reactor :Pyrex bottle	Solvent : benzotrifluorid e	Selectivity-47% Yield-37% Conversion – 98%	Nan Zhang et al.(2011) (Ref. 45) J. Mater. Chem., 2011, 21, 8152–8158

Benzyl alcohol	Au/CeO <sub>2</sub> -TiO <sub>2</sub> Visible light 300 W Xe arc lamp 100 mWcm <sup>-2</sup>	Solvent : benzotrifluoride	Selectivity-99% Yield-NA Conversion -99 %	Yajun Zhang et al.(2014) ( <b>Ref. 46</b> ) Green Chem., 2014, 16, 386
Ethanol	Pt/TiO <sub>2</sub> Ultraviolet (UV) and visible (Xe lamp) Reactor : quartz window Light intensity : 0.3 W/cm <sup>2</sup>	Solvent : water Additive : Na <sub>2</sub> CO <sub>3</sub>	Selectivity-99 % Yield-99 % Conversion -100 %	Z. Zhang, et al.(2016) ( <b>Ref. 48</b> ) Green Chem., 2016, DOI: 10.1039/C6GC03022J
Furfural	Ni/CdS Visible light	Solvent : Water	Selectivity-NA Yield-90 % Conversion -90 %	Guanqun Han et al.(2017) ( <b>Ref. 49</b> ) J. Am. Chem. Soc. 2017, 139, 15584-15587
Glycerol	TiO <sub>2</sub> UV-Visible light (Xe lamp)	Solvent : Water	Selectivity-NA Yield-NA Conversion -71.2 %	Ruifeng Chong et al.,(2014) ( <b>Ref. 50</b> ) Chem. Commun., 2014, 50, 165
5-Hydroxymethylfurfural	Nb <sub>2</sub> O <sub>5</sub> UV-Visible and Visible light (Xe lamp)	Solvent : Water Acetonitrile Benzotrifluoride	Selectivity- 90 % Yield- 99 % Conversion -40 %	Huili Zhang et al.,(2017) ( <b>Ref. 51</b> ) ACS Sustainable Chem. Eng. 2017, 5, 3517 –3523
5-Hydroxymethylfurfural	P-doped ZnxCd1-xS LED light source	Solvent : Water	Selectivity- 65 % Yield- NA Conversion -91 %	Fang Ye, et al.,(2017) ( <b>Ref. 52</b> ) <a href="https://doi.org/10.1016/j.apcatb.2018.03.060">https://doi.org/10.1016/j.apcatb.2018.03.060</a>

Aromatic benzyl alcohol/ aromatic amines	Pd/CeO <sub>2</sub> visible light irradiation (300 W Xe arc lamp)	Solvent : Water Additive : Na <sub>2</sub> SO <sub>4</sub>	Selectivity- 99 % Yield- NA Conversion -NA	Fang Ye, et al.,(2017) <b>(Ref. 54)</b> dx.doi.org/10.1021/sc400116k
Ethyl Alcohol	TiO <sub>2</sub> / Nb <sub>2</sub> O <sub>5</sub> UV- light (Hg lamp)	Solvent : No	Selectivity- NA Yield- NA	Furukawa, et al.,(2011) <b>(Ref. 55)</b> dx.doi.org/10.1021/cs2005554
Ethyl Alcohol	Au/TiO <sub>2</sub> (surface Plasmon resonance) UV and visible light irradiation	Solvent : Water Additive : Na <sub>2</sub> CO <sub>3</sub>	Conversion -13% Selectivity- 95% Yield- 99%	B. Zhou et al.,(2016) <i>Green Chem.</i> , 2016, DOI: 10.1039/C6GC03022J <b>(Ref.48)</b>