Short review on heteropoly acid based catalyst for valorization of biomass waste into valuable chemicals

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Abstract. Depletion of fossil fuels resources has triggered more research on finding potential alternative sources that are more sustainable such as biomass waste. However, deconstruction of the complex biomass waste into desired products is too challenging and usually require a strong catalyst with a great hydrolysing property. Common acids such as sulphuric acid, hydrochloric acid and nitric acid were the most studies for biomass conversion. These liquid acids catalysts suffer low recovery and recyclability that can be overcome by a solid acid catalyst. Heteropoly acid (HPA) catalyst is the preferred choice to replace these common acid catalysts as it is known to have a strong Bronsted acid site with an oxidizing property that allows this catalyst to hydrolyse and oxidize in one-step reaction. Furthermore, heteropoly acid (HPA) catalyst can be modified into heterogenous type of catalyst by solidifying HPA to increase the surface area and recyclability. Future work of this research is necessary to improvise the previous method of the catalyst preparation and to suppress the by-products after the catalytic process. In this review, we summarize the use of HPA catalyst in the complex reaction process of biomass conversion to valuable chemical products.

Keywords: Heteropoly acid, heterogenous catalyst, biomass waste

1. Introduction

The key ingredients for industrial chemical production are petroleum-derived feedstocks that come from fossil fuel with the growth in demand for valuable chemicals, the industry greatly relies on the use of fossil fuels. However, the usage of fossil fuel in chemical industries is responsible for 5.5% CO₂ and 7% of greenhouse gasses emission. This emission includes process emissions during chemical transformation [1]. Increasing demand for chemical industries will cause a serious threat not only to the environment but to public health [2]. In this regard, biomass wastes are the alternative supply to greener route for chemical productions. Besides, abundant of natural resources are underutilized and usually dispose of by dumping and open burning which create additional environmental problems [3]. Hence, biomass wastes are a promising source as compared to non-renewable fossil fuel that will soon be exhausted [4].

Today, growth in the global chemical industry subsequently drive the market to utilize biomass waste as a feedstock to replace fossil fuels [6]. Biomass waste is the most abundant natural source composed by an organic substance that derived directly or indirectly from the photosynthesis process. In biomass utilization, cellulose is the major component of lignocellulosic biomass that effectively converted into various value-added chemicals [5]. Conversion of lignocellulosic biomass into chemicals will starts by breaking down cellulose into its constituents such as hexose and pentose. Efficient utilization of
renewable and inedible biomass waste meets the principles of green chemistry and create a sustainable green chemical [5]. Biomass can be classified as forestry waste, animal and human residues, aquatic biomass and municipal solid waste. The chemical composition of each biomass sources is different from one another. For example, plant origin waste consists of cellulose, hemicellulose and lignin while animal waste is rich in protein [6]. Table 1.1 show the possibility of converting raw biomass into value-added chemicals.

Table 1. Possible value-added chemicals converted from raw biomass.

| Raw Biomass  | Component of Biomass | Chemical Product(s) | References |
|--------------|----------------------|---------------------|------------|
| Corncob      | Hemicellulose        | Xylitol             | [7]        |
| Pinus Radiata| Lignin               | Formic acid         | [8]        |
| Sugarcane    | Cellulose            | Formic acid and acetic acid | [9] |
| Bagasse      | Hemicellulose        | Xylitol             | [10]       |
| Beech wood   | Hemicellulose        | Levulinic acid      | [11]       |
| Rice husk    | Cellulose            | Levulinic acid, furfural, formic acid and lactic acid | [12] |
| Sugarcane bagasse | Hemicellulose | Levulinic acid      | [13]       |
| Rice straw   | Hemicellulose and cellulose | Levulinic acid | [13] |
| Cotton straw |                      |                     |            |
| Barley straw |                      |                     |            |
| Paddy straw  |                      |                     |            |
| Rice husk    | Cellulose, hemicellulose and lignin | 5-hydroxymethyl furfural and furfural | [14] |
| Soy bean peel|                      |                     |            |

However, the harsh condition is needed to induce depolymerization of lignocellulosic. The reaction involves high temperature and pressure, corrosive acid or alkali that require an improvement strategy. Therefore, mild, selective and greener process should have replaced the previous method in order to provide a green route valorization of biomass by introducing heterogeneous catalyst, water-based and environmental-friendly oxidant [15]. A study reported that common methods for valorization of biomass are direct combustion, thermochemical conversion and bio-chemical transformation [16]. For thermochemical conversion, three techniques that commonly use include pyrolysis, liquefaction and gasification. All of these techniques lead to the production of bio-oils, chemicals and syngas. Furthermore, they also reported that liquefaction involves chemical reforming process of organic matters which combine the use of high hydrogen partial pressure and catalyst to improve the selectivity and quality of the products. Meanwhile, gasification is considered a cost-effective technique because gasification allows different types of biomass to be valorized. The product of gasification such as bio-syngas can be used as raw material for Fischer Tropsch Synthesis to produce green diesel and high value-added chemicals.

Therefore, increasing research efforts had been done on the usage of catalyst for biomass conversion to improve the reaction rate for the reaction to proceed effectively. Another point to emphasize is low reactivity of cellulose requires a highly reactive catalyst to access and break down the glycosidic bonds in cellulose [17]. Therefore, the suggested catalysts used for valorization of biomass for chemical productions are acid catalyst, base catalyst or photocatalyst. These catalysts have different characteristics that enable them to depolymerize lignocellulosic biomass optimally. Heteropoly acid (HPA) catalyst is one of the interests focus nowadays since this catalyst possesses Bronsted acidity and oxidizing property that works as a bifunctional catalyst such as phosphomolybdic acid [18]. According
to their finding, phosphomolybdic acid not only possesses acidic properties but also provides an oxidative catalytic system that able to degrade lignin completely with a high yield of aromatic oil. Another study found that conversion of cellulose into 5-hydroxymethylfurfural by a stable type of HPA able to maintain the same yield after a few runs [19]. Therefore, HPA does not only has good stability after being reused but HPA also contains high acidity that allows its effectiveness during cellulose conversion [20]. Thus, an effort has been made to write up a short review that mainly focuses on breaking down biomass waste using HPA based catalyst.

2. Acid and base catalyse depolymerization of lignocellulosic

Acid catalysis is defined as a reaction in which the acid catalyst donates a proton to the targeted species [21]. The liquid acids that are commonly used in acid hydrolysis include HCl, HNO₃ and H₂SO₄. However, recent studies have been focusing on the usage of solid acids compared to liquid acids for cellulose hydrolysis since the solid acids give better product separation, reusability and recovery of catalyst. Hence, a comparable Brønsted acid solid catalyst as the common liquid acids had gathered a lot of attention include acidic ionic liquid [22], metal oxides such as layered niobium oxide that possess Bronsted acid site [23] and heteropoly acid catalyst [24]. There are many functions of acid catalyst that several can be used for depolymerization of cellulose [25]. An investigation was made on acid hydrolysis of cellulose into levulinic acid in which cellulose initially break down into lower molecular weight fragments by the cleavage of β-(1-4)-glycosidic bond of cellulose. Then, lower molecular weight fragments such as glucose will decomposed into hydroxymethylfurfural and further converted into formic acid [26].

Another study was done to observed variety of solid acid catalyst ranging from crystalline to amorphous structure to understand the efficiency of structure towards lignin conversion [27]. From their observation, well defined structure catalyst such as zeolite is unstable because zeolite undergoes structure alterations under high temperature compared to SiO₂-Al₂O₃ that are more amorphous but have strong Bronsted acid site. An organic electrolytes solution which is 1-butyl-3-methylimidazole chloride solution with the presence of different mineral acids such as HCl, H₂SO₄ and H₃PO₄ was experimented to catalyze the hydrolysis of cellulose [28]. From the investigations, authors reported that the high acidity of H₂SO₄ mineral acid in aqueous solution contribute to a high acidity in organic electrolyte solutions that effectively enhance the cellulose hydrolysis.

Meanwhile, base catalyzed depolymerization by Bronsted or Lewis base usually present in liquid solvent such as water. The proton withdrawal occurred due to the electron donor such as HO⁻ that interact with the reactant. Furthermore, hydrothermal base lignin depolymerization relies mostly on Bronsted base alter the electronic structure of phenolics and other aromatic subunits which causes shift and destabilizes other linkages. Therefore, this will cause bond cleavage in lignin and lead to depolymerization [29][30][31]. To date, depolymerization of cellulose by base catalyst effectively cleave aryl-alkyl (β-O-4) in lignin but base catalyzed reaction requires high temperature which is around 340 °C [32]. Examples of base catalyst used by previous researchers include Pt-Mg-Al hydrotalcite as metal/base catalyst [33], ZrO₂-based catalysts [34], TiO₂ [35][36] and alkali-metal substituted zeolite catalyst [37].

3. Heteropoly Acid Catalyst

The general formula of keggin type heteropoly acid (HPA) is [XM₁₂O₄₀]ₙ, where X is the heteroatom and M is the transition metal. Figure 1 shows the chemical structure of HPA. HPA catalyst belongs to polyoxometalates (POMs) class in which consist of transition metal-oxygen-anion clusters that contain p or d block elements. Polyoxometalates (POMs) consist of cations and polyamions clusters in which oxometal polyhedral of transition metal at their high oxidation state and heteroatom are the basic construction units of POMs [38]. The primary structure of HPA is the heteropolyanions that linked to each other creating secondary structure of solid HPA. The structure of HPA must consist of tetrahedron (XO₄) where X is the heteroatom surrounded by 12 edges and corner-sharing metal oxygen octahedra (MO₆) [39][40]. HPA is defined based on its ionic clusters with general formula [X₃M₉O₃₅] in which
M is metal typically molybdenum, vanadium and phosphorus and X is the heteroatom usually silicon or phosphorus. HPA contains protons that made up the counter ions of HPAs [41]. At the surface of heteropolyanions, there are abundance of O₂ that can donate electron which make HPA as soft base. Meanwhile, the metal ions in HPA have unoccupied orbital that accept electrons which at the same time make HPA as Lewis acid. Therefore, their strong ability to accept and withdraw electrons indicate their available redox nature [38].

![Figure 1. Chemical structure of HPA](image)

HPA catalyst is known to be a promising catalyst due to its strong Bronsted acidity and together with the oxidizing property that allows HPA to be widely used in acid catalyzed oxidation reaction [42][43][44][45][46]. HPA exhibit stronger acidity approach compared to typical acids such as H₂SO₄, HNO₃ and HCl [18][40]. This type of catalyst also known for having a high proton mobility and stability [47] because in catalytic reaction HPAs play important role as proton donor that exhibit high catalytic activity [48]. HPA is reported to have good oxidation properties to cleave cellulose, lignin and model substrates under mild conditions [49]. Broader research areas of HPAs for the conversion of cellulose involve hydrolysis, alcoholysis, hydrolysis-hydrogenation, hydrolysis-oxygenation reaction [50]. Another advantage of HPAs is highly soluble in water which makes this catalyst greatly efficient to break down biomass in water [51]. While in water, HPA will dissociates protons and increase the amount of freely available H⁺ to interact with the oxygen atom in ether linkage of cellulose [52]. HPA then will continue to break the rigid structure of cellulose by attacking the intermolecular and intramolecular bonds in the structure of cellulose [53][42].

**Table 2.** shows the ability of HPAs to convert different types of lignocellulosic biomass into desire product.

| Heteropoly Acid Catalyst | Substrate | Product | Reaction Involved | References |
|--------------------------|-----------|---------|------------------|------------|
| K₄[PVW₁₁O₄₀] - KPWV₁ and K₆[PV₃W₆O₄₀] - KPWV₃ | Cellulose | Glucose | Hydrolysis | [37] |
| H₄PMO₁₁VO₄₀ and Cs₄PMO₁₁VO₄₀ | Methacrolein | Methacrylic acid | Oxidation | [54] |
| H₄SiW₁₂O₄₀, H₃PW₁₂O₄, SiO₂- H₄SiW₁₂O₄₀ and SiO₂-H₃PW₁₂O₄ | Cellulose | Lactic acid | Hydrolysis | [55] |
| H₄SiW₁₂O₄₀, H₃PW₁₂O₄ and H₃WO₄ | Cellulose | Glucose | Hydrolysis | [42] |
| Cs₃HSiW₁₂O₄₀ | Cellulose | Sorbitol | Hydrolysis-hydrogenation | [56] |
Another study reported that most of the previous studies were focusing more on strong Bronsted HPA and Lewis acidity. This characteristic was observed in HPAs catalyst and much attention has been drawn to study the environmental route for biomass fractionation [58]. These two important characteristics can be observed in HPAs catalyst and much attention has been drawn to study the environmental route for cellulose conversion. An investigation was done on different types of HPAs as bifunctional catalyst which are Cs₃H₀.₅PMO₁₁VO₄₀, Cs₅H₀.₅PW₁₁VO₄₀, Cs₅H₀.₅SiW₁₁VO₄₀ and Cs₄H₀.₅PMo₁₁VO₄₀ in one pot hydrolysis-oxidation of starch into formic acid [56]. The results showed strong acidity of catalyst provides a route for hydrolysis reaction while vanadium ions contribute in the oxidation process.

Another finding synthesized Mo-V-P HPA that possess both acidic and oxidizing properties and yielded 66% formic acid from cellulose under mild temperature [46]. During the reaction, cellulose was hydrolyzed to glucose by the acidic sites of HPA and proceed with oxidation in which vanadium is reduced from V⁵⁺ to V⁴⁺ to oxidize glucose into formic acid. However, there are a few types of modified HPA display a bifunctional catalyst by having a synergy Bronsted and Lewis acidity. This characteristic was observed in a research [59] using amino functionalized ionic liquid-supported polyoxometalates and sequential hydrogen transfer between the catalyst and glucose which leads to the dehydration of glucose into hydroxymethylfurfural. Besides that, a bifunctional molybdenum-based polyoxometalates supported on titanium was studied for conversion of lignin derived compound into alkylated phenols [60]. The pairing between Bronsted and Lewis acid for this catalyst enhance the catalytic reaction.

5. Homogenous HPA Catalyst

HPA catalyst is a versatile catalyst that can be used as homogenous, heterogenous or biphasic catalyst system. These catalytic systems showed great effectivenss in degrading lignocellulosic biomass but the limiting factor of homogenous catalyst is the difficulty for recovery since HPA is expensive compared to conventional acid catalysts [51]. However, from the investigation phosphotungstic acid (H₃PW₁₂O₄₀) can be reused again after extraction using diethyl ether. This extraction method is cheaper for recovery compared to filtration using mesoporous ceramic membrane [61]. Moreover, diethyl ether can also be used for separation and reusable of homogenous HPA [62]. The efficiency of HPW for production of glucose from cellulose under hydrothermal conditions was tested. Results of the investigation showed that the glucose yield is 50% with 90% selectivity at 453 K. The solubility of HPW in water and its high Bronsted acidity allows large dissociation of H⁺ during cellulose conversion which causes interaction between protons from HPW and oxygen atom from ether linkage of the cellulose.

Meanwhile, a study reported that silicotungstic acid as bifunctional catalyst is due to the presence of Bronsted and Lewis acidities that can enhance the depolymerization of solid cellulose into methyl levulinate [63]. This catalyst can be reused for 5 times and the yield of each cellulose conversion have no significance different. Another study who investigated four different types of homogenous HPAs such as Keggin, Wells-Dawson, Anderson and Lindqvist for oxidation of cellulose into formic acid observed that Lindqvist gave better selectivity of formic acid compared to other types of HPAs [64]. Another study reported that most of the previous studies were focusing more on strong Bronsted HPA catalyst which are 12-tungstoboric acid, silicotungstic acid and phosphotungstic acid for fractionation of cellulose to glucose, but these two catalysts have low selectivity towards glucose [65]. Hence, the
efficient HPA for cellulose conversion into glucose is 12-tungstoboric acid (H$_3$BW$_{12}$O$_{40}$) catalyst. From these 3 different HPAs that have been studied, they concluded that the sequence of the reactivity is as followed H$_3$BW$_{12}$O$_{40}$> H$_4$SiW$_{12}$O$_{40}$>H$_3$PW$_{12}$O$_{40}$.

Another study was done to understand the relation of different anion charge in H$_3$PMO$_{12}$O$_{40}$ towards fatty acid yield from hydrolysis of macauba oil [39]. Higher charge of anion in H$_3$PMO$_{12}$O$_{40}$ favors hydrolysis reaction because more soluble and strong oxidizing property. An investigation on three different HPAs which are silicotungstic acid (H$_4$SiW$_{12}$O$_{40}$), phosphotungstic acid (H$_3$PW$_{12}$O$_{40}$) and phosphomolybdic acid (H$_3$PMO$_{12}$O$_{40}$) for hydrolysis of cellulose into glucose observed that tungsten-based HPA yield more glucose but low selectivity because H$_3$PW$_{12}$O$_{40}$ have stronger acidity which hydrolyze all cellulose [52]. Meanwhile, molybdenum based HPAs produce better selectivity because of their moderate acidity and oxygen activation abilities. In another experiment, two different HPAs which are H$_3$PMO$_{12}$O$_{40}$ and H$_3$PW$_{12}$O$_{40}$ for valorization of lignin [51]. From the observation, H$_3$PMO$_{12}$O$_{40}$ yield higher carboxylic acids which attributed to its superior potential compared to H$_3$PW$_{12}$O$_{40}$. Although H$_3$PW$_{12}$O$_{40}$ showed remarkable yield at preheating period but at the end over-oxidation occur because of the acid strength. Thus, both acidity and oxidizing property should be balance in breaking down cellulose.

Another research on three different tungsten based HPAs which are H$_3$PW$_{12}$O$_{40}$, H$_4$SiW$_{12}$O$_{40}$ and H$_2$WO$_4$ for cellulose hydrolysis to glucose in homogenous system [42]. H$_2$PW$_{12}$O$_{40}$ showed the highest yield and selectivity of glucose because of strong Bronsted acidity that allows H$_3$PW$_{12}$O$_{40}$ to liberate high concentration of protons in water. A comparison was made in another study to understand the effectiveness between H$_3$PMO$_{12}$O$_{40}$ and H$_2$SO$_4$ to yield higher total organic carbon and from the observation H$_3$PMO$_{12}$O$_{40}$ yield better because H$_3$PMO$_{12}$O$_{40}$ is more soluble in water to break down cellulose in water medium [66].

6. Heterogenous HPA Catalyst

A pure form of HPA usually a homogenous catalyst that is efficient in the catalytic reaction due to high solubility in water and organic solvents. However, homogenous catalyst generally suffers low recovery, low surface area and difficult to separate from the reaction medium [67]. Heterogenous HPA is the suggested solution and the proses requires solidification for better recovery and recyclability [68]. Moreover, heterogenous HPAs in solid form are water tolerant and stable in reactions involving water such as hydrolysis, oxidation and esterification [69]. There are few proposed methods to solidify HPAs such as introduction of large inorganic cations, encapsulation by metal organic framework and impregnation with support material [70][52][68]. Incorporation of inorganic cations include substitution of cations with suitable size, amount, charge and hydrophobicity that result ionic interaction with HPA [69]. Common cations used to heterogenized HPAs are Cs$^+$, Ag$^+$, Sn$^{2+}$, Zn$^{2+}$, Mn$^{2+}$, Co$^{2+}$ and Cu$^{2+}$.

For example, a study has observed a high percentage yield of lactic acid (~93%) produced from glycerol conversion using silver-exchanged phosphomolybdic acid [71]. Their analysis showed that silver-exchanged phosphomolybdic acid is a promising catalyst for the reaction due to the strong Lewis acid property, high redox potential and water tolerant. Previous studies reported that the success of HPA for hydrolysis of cellulose is due to its strong acidity. A finding was done to compare 2 types of HPAs which are K$_3$[PVW$_{12}$O$_{40}$]-KPVW$_1$ and K$_3$[PV$_3$W$_9$O$_{40}$]-KPVW$_3$ for hydrolysis of cellulose into glucose to understand the effect of redox properties in metal ions of HPA by replacing tungsten atom to vanadium atom [41]. A previous finding was done to understand the ability of CePW$_{12}$O$_{40}$XH$_2$O to degrade lignin in the presence of isopropanol as a solvent. Almost 73.4% of lignin was degraded into monomers thru cleavage of C-C and C-O bonds followed by dehydration, dealkylation and demethoxyxlylation reaction of monomeric reaction [72].

Meanwhile, heterogenized of HPA by metal-organic framework also has attracted attention among researchers due to their unique combination of properties such as high surface area, crystalline structures and tunable pore size [67]. An example of a reported study on heterogenous silicotungstic acid (HSiW) encapsulated UiO-66 metal-organic frameworks showed efficient one-pot esterification of lauric acid to produce biodiesel which achieves 80% conversion and stable after 6 times of catalytic reaction [73].
Meanwhile, a metal organic framework supported phosphomolybdic acid catalyst was investigated for conversion of biomass-derived levulinic acid into ethyl levulinate using [74]. The metal support was synthesized using 1,3,5-benzenetricarboxylic acid and copper nitrate that provides Lewis acid site and enhance the esterification reaction.

Besides that, impregnation of HPA on support material may also provide better properties of pure HPA. Common support material that has been investigated by previous researchers include silica [75], zirconia [76], activated carbon [20] and bentonite [48]. Support play important role to provide better stability, efficiency and high dispersion of active sites for catalytic reaction. An example, HPA can be supported on inert solid matrices such as silica for easy separation from hydrolysate [52]. 5-hydroxymethylfurfural production from glucose was obtained using 2 different types of HPAs which are phosphotungstic acid (H₃PW₁₂O₄₀) and phosphomolybdic acid (H₃PMO₁₂O₄₀) on niobium (V) oxide (Nb₂O₅) and aluminium oxide (Al₂O₃) [19]. The result showed that H₃PW₁₂O₄₀/ Nb₂O₅ gave the highest yield (40.8%) and can be recycled four times without reducing yield due to the presence of Lewis and Bronsted acid sites on Nb₂O₅. They also stated that low yield of product observed for H₃PW₁₂O₄₀/ Al₂O₃ is due to only Lewis sites existed on the Al₂O₃ surface.

Meanwhile, HPW supported on activated carbon was also studied to determine the total percentage of reducing sugars by comparing with non-supported HPW [20]. The BET analysis showed supported HPW possess higher acidity compared to un-supported HPW. Besides, activated charcoal also possesses high surface area that improves the catalytic reaction. Another study examine the effectiveness of carbon foam supported HPW for cellulose conversion into glucose [73]. The product yield is 58.47% with cellulose conversion of 65.47%. The carbon foam consists of oxygen-containing functional groups that increase the affinity between cellulose and catalyst by forming a hydrogen bond with free hydroxyl groups of cellulose. Furthermore, carbon foam supported HPW is also rich with active sites that contribute to the disruption of β-1,4-glycosidic bonds of cellulose.

7. Conclusion
Several modified and unmodified heteropoly acid catalysts have been outlined in this review as a promising catalyst for valorization of biomass. The reason here is because HPAs is a bifunctional catalyst having both acid and redox site that can accomplish the conversion of biomass into valuable chemical products. Besides the preparation of the HPAs, the lignocellulosic types and the conditions of the conversion reactions also plays a crucial role in achieving a higher yield of the targeted product. Furthermore, Heterogenous HPAs based catalyst offers better properties compare to homogenous type especially in regeneration, recyclability and selectivity. However, some biomass conversion using heterogenous HPAs still obtained the undesirable products due to overoxidation of the product and sometimes the catalyst prepared is less acidic compared to the homogenous type. Thus, future works should be focused more on modifying the catalyst functionality by having a catalyst that has multiple functions in order to cater each of the limitations and fit for biomass conversion that usually involves a complex of reactions.

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