Cellulose conversion into renewable chemicals and fuels over supported metal catalysts

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Abstract. Nowadays, the development of biomass as an alternative energy source has been explored for the production of energy, chemicals and transportation fuels. Cellulose is an abundant, low-cost and renewable energy source that can be transformed into solid, liquid and gas products by pyrolysis. Sustainable, low cost and efficient catalysts are needed for catalytic cellulose conversion by pyrolysis. Among heterogeneous catalysts, supported metal catalysts have been extensively studied which demonstrated distinct reactivity and/or selectivity in a variety of chemical reactions. This paper reviews and provides a summary of the cellulose conversion by supported metal catalysts into value added chemicals and fuels. Emphases will be put on the reaction mechanism and key factors that exert effect on the catalytic performance.

1. Introduction

The diminishing of fossil fuel resources has initiated more researchers to use renewable resource for the production of energy, chemicals, and transportation fuels [1]. Lignocellulose composed of 30–55 wt% of cellulose, 25–30 wt% of lignin and 25–30 wt% of hemicellulose [2]. Being the most abundant and low cost renewable energy source, the usage of cellulose become more popular to produce chemicals and fuels. It consists of glucose units that are linked by β-1,4-glycosidic bonds with the intermolecular and intramolecular hydrogen-bond networks [3]. Even though large amount of cellulose are synthesized through photosynthesis of plants (800,000 billion metric tons), merely 0.2 billion metric tons is being used as feedstock in pharmaceuticals, paper, and food industry [4]. Thus, new advances has been created to limit the underused cellulose that is squandered each year.

Nowadays, the cellulose conversion into valuable chemicals and fuels has attracted worldwide interest [5]. Generally, the potential chemicals and fuels can be produced by different chemical processes. There are two routes for conversion of cellulose, which are chemo-catalytic through glucose by hydrolysis of cellulose and direct or one-pass catalytic process in the presence of a multifunctional catalyst. Recent research has paid much attention to the latter routes in order to enhance the conversion of cellulose. The typical processes can be categorized as gasification, pyrolysis, liquefaction and combustion. The latter method is the most direct and easiest process to convert organic matter to heat, carbon dioxide and water by adding an oxidant. Meanwhile, the gasification method involves the heating process and using an oxidant to produce syngas, which contains a mixture of carbon monoxide and hydrogen. Compared to combustion, gasification has
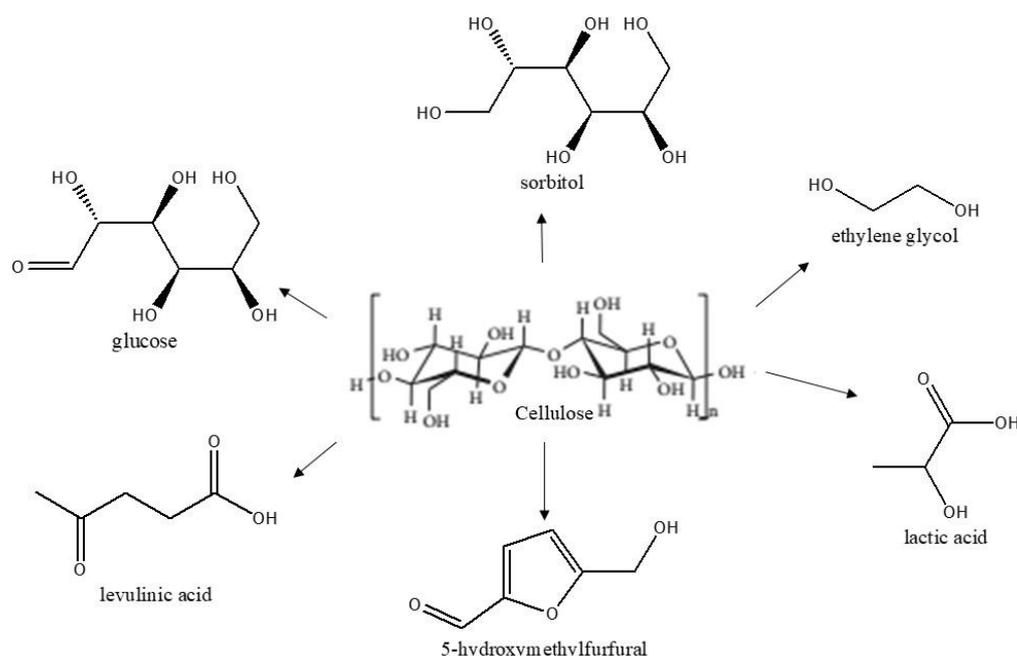
many advantages, which include converting the low-value material into electricity and vehicle fuels. However, gasification process requires complex and more expensive technologies compared to conventional petrochemical processes.

Pyrolysis is a thermal heating in an inert atmosphere, which produces the char, gas, and a liquid composed of a mixture of hundreds of oxygenated organic compounds. These unsaturated compounds cause low stability under storage conditions, which prompts their need to be upgraded. Currently, catalytic treatment has been the focus of many researchers to produce a liquid fuel. Therefore, it is necessary to design selective catalysts and optimize upgrading process in order to maximize the yield of high value added chemicals and minimize the formation of undesired compounds. In addition, the application of cellulose conversion in the chemical industry was hindered as a result the low reactivity of cellulose, accompanied by poor solubility in solvents and stable chemical structure. Based on those facts, the cellulose conversion by heterogeneous catalysis plays important role for the production of a chemicals and fuels such as hydroxymethylfurfural (HMF), glucose and sorbitol for further bio-refinery procedures. It offer advantages in terms of easy separation, reusability and anticorrosion with the ability to provide practical conveniences in a continuous system. Another merit of heterogeneous catalysts is their stability to severe reaction environments; some can withstand temperatures as high as 1300 °C and pressure up to 350 bar.
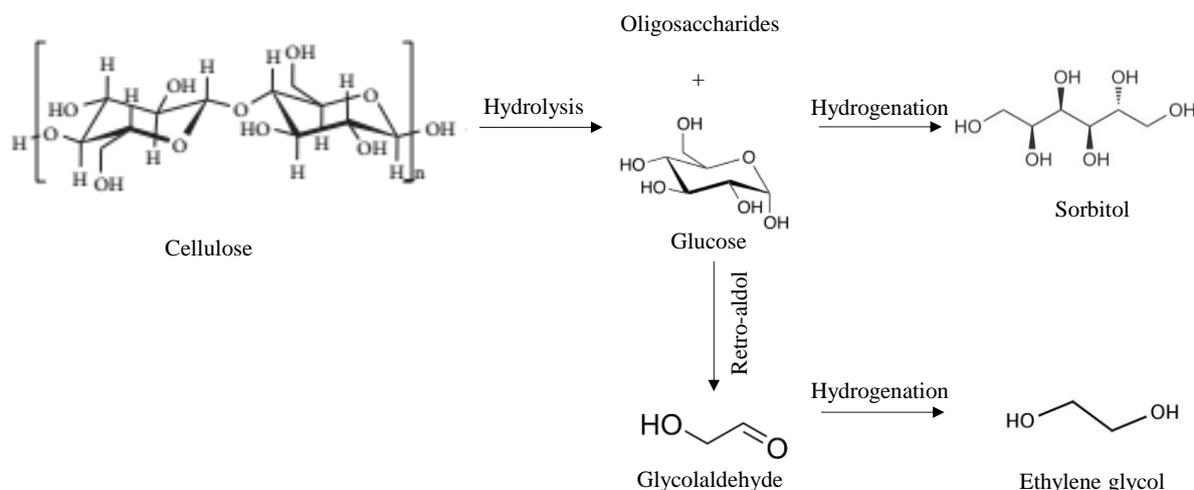
2. Catalytic Conversion of Cellulose to Renewable Chemicals

Lately, many researchers have focused on heterogeneous catalysis for cellulose conversion into valuable chemicals, particularly glucose, polyols, 5-hydroxy-methylfurfural (5-HMF), lactic acid and levulinic acid (Scheme 1) [6]. Different catalysts and reaction temperatures varies the major product from glucose to polyols. Glucose as the primary product when the reaction temperature below 423 K, meanwhile under pressurized hydrogen gas (H_2) and hydrogenation catalyst (supported ruthenium (Ru), platinum (Pt), iridium (Ir) and etc) were led to sorbitol production. For catalyst function, the acid site that originate from acidic groups can enhance the production of glucose by cleavage the C-C bonds. Similarly, basic catalyst such as calcium oxide also can act as C-C bond cleavage agent, however, the isomerization of glucose to fructose resulting in glycerol rather than polyols as the major product. Based on those facts, this review can stimulate a more profound comprehension with respect to the current catalytic conversion of cellulose into platform chemicals in the biorefinery.

Scheme 1. Catalytic conversion of cellulose into key platform chemicals.

2.1. Glucose

The production of glucose has become more attractive in catalysis study and fuel industry due to its broad applications. Glucose is a versatile chemical to produce value added products such as bioethanol, 5-HMF, and biodegradable plastics. Heterogeneous catalysts have been developed under aqueous conditions. Hara and co-workers obtained 64% of water-soluble oligosaccharides (β-1,4-glucan) and 4% of glucose yield with 68% cellulose conversion at 373 K for 3 h using sulfonated carbonaceous materials [7]. The higher production of β-1,4-glucan may be due to the faster hydrolysis process as consequent of the higher adsorption capacity of β-1,4-glucan by phenolic hydroxyl groups. Simultaneously, the hydrogen bonding was formed as a consequence of the cleavage of glycosidic bonds by the sulfonic groups.

Supported metal catalysts have also been widely used for the hydrolysis of cellulose. The metal site promoted the hydrolysis of cellulose via heterolytic dissociation of hydrogen gas (H_2) as well as hydrogenation of glucose. Currently, mesoporous carbon materials (CMKs) as the catalyst support showed the excellent properties which enhanced the production of glucose. Fukuoka *et al.* successfully prepared the CMK supported Ru catalyst (Ru/CMK) for conversion of cellulose to glucose which gave the glucose and oligosaccharide yield were 34% and 5%, respectively [8]. Compared to bare CMK, only 21% yield of glucose and 22% yield of oligosaccharide were obtained in the hydrolysis process. This result showed that synergystic effect of CMK and Ru in the production of glucose, in which CMK played role in the conversion cellulose into oligosaccharides, meanwhile Ru was able to convert oligosaccharides into glucose (Scheme 2). By increasing Ru loading to 10 wt%, the yield of glucose was raised up to 31%. The Ru species with high valent can be proposed as a catalyst for hydrolysis due to its higher dispersion on CMK.

Scheme 2. Conversion of cellulose into glucose via soluble oligomers.

2.2. Polyols

The cellulose conversion into chemicals is important to the improvement of a sustainable society. In particular, the catalytic cellulose conversion to polyols is a significant part of biorefinery, which has pulled in more enthusiasm to fulfil vitality needs. In this section, the latest developments in the catalysis of cellulose conversion into ethylene glycol (EG) and sorbitol have been focused, which they are widely utilized in the food industry, beauty care products and pharmaceutical production [9]. Scheme 3 shows the cellulose transformation into sorbitol and EG by hydrogenation process of glucose and glycolaldehyde, respectively. Firstly, cellulose is hydrolysed to glucose, which can be directly hydrogenated to sorbitol or break its C-C bond to glycolaldehyde (GA) that is subsequently hydrogenated to EG.

Scheme 3. Conversion of cellulose into sorbitol and ethylene glycol.

2.2.1. Ethylene glycol (EG). EG is an essential chemical, which is mainly used as a raw material for the production of polyester fibers and anti-freeze [9]. There are multi reactions involved in the production of EG such as of hydration, cracking and epoxidation in petroleum-based ethylene. The EG production by a viable process is essential to be accomplished due to its significance in chemical industry. Therefore, the cellulose was used as the starting material to produce EG. Numerous types of reactions are involved in cellulose transformation into EG such as hydrogenation, hydrolysis, condensation of retro-aldol, cracking, dehydration, decarbonylation, and hydration. About twenty compounds can be produced as the intermediate products as well as byproducts [10].

Table 1. EG yields from the conversion of cellulose by different catalyst.

Catalyst	Temperature (K), Pressure (MPa)	EG Yield (%)	Conversion of cellulose (%)	Ref
Ni-W/SBA-15	518, 6	75	100	[11]
Ru-W/CNT	478, 5	41	100	[13]
3Al-15W-3Ni	503, 4	76	100	[14]
Ni-W/CNF	518, 6	34	95	[15]
Ru/WO$_3$	513, 4	76	100	[16]

Table 1 shows the EG yields from the conversion of cellulose by different catalyst. The yield of EG about 75% was achieved with tungsten (W)-based bimetallic catalyst such as nickel (Ni)-W supported on SBA-15 (Ni-W/SBA-15), however the SBA-15 structure collapsed and catalyst could not be reused [11]. Thus, the higher resistance to acid and base attacking of carbon as a support is preferred under hydrothermal conditions [12]. Other than that, Ribeiro *et al*. reported that the production of EG from cellulose by Ru and W supported on multi-walled carbon nanotubes gave the higher yield about 41 % compared than the Ru and W monometallic catalysts which about 35 % at 5 MPa of H$_2$ and 478 K for 5h [13]. This was due to the synergistic effect of the W and Ru component, due to their close interaction of active sites for hydrogenation and retro aldol condensation reaction.

Hamdy *et al*. reported that the selective hydrogenolysis of cellulose into EG via hydrothermal and sol-gel process by 3Al-15W-3Ni catalyst gave a 100 % of cellulose conversion with 76% yield of EG under 4 MPa of H$_2$ pressure for 90 min at 503 K [14]. The presence of tri-metallic sites enhanced the production of EG, in which Al^{3+} acidic active species promote the hydrolysis of cellulose into glucose. The oxygen vacancies in the partially reduced WO$_{3-x}$ adsorb the oxygen of glucose, which assist in the

fast formation of glycolaldehyde [14]. Finally, glycolaldehyde was reduced to EG over the nanoparticles of metallic Ni.

Yang *et al*. synthesized a carbon nanofiber (CNF) supported bimetallic (Ni-W/CNF) catalyst gave 95% of cellulose conversion and 34% of EG yield under 6 MPa of H_2 pressure at 518 K for 2 h [15]. The higher catalytic activity most probably due to the excellent accessibility and uniform dispersion of metal species. Other than that, the W species acts as C-C cleavage agent before the intermediate glycolaldehyde hydrogenated onto EG by the catalysis of Ni. Next, Li *et al*. also found that effective hydrogenolysis for the cellulose conversion to EG by Ru supported on tungsten oxide (Ru/WO_3), leading to higher yield of EG about 76% with 100% cellulose conversion at 513 K for 2 h under 4 MPa of H_2 pressure [16]. This results increased due to the enhanced active site of W^{5+} as a Lewis base by addition of Ru species, thereby enhancing the retro-aldol condensation reaction of glucose by etching of H^+ for the hydrogenolysis of cellulose to EG (Scheme 4).
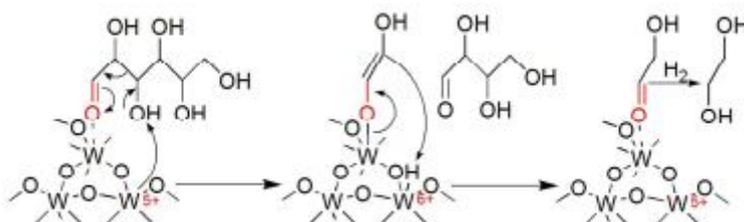
Scheme 4. W^{5+} species for retro-aldol condensation reaction in the production of EG. Adapted from [16].

2.2.2. Sorbitol. Sorbitol is the most valuable bio-based chemicals that can be used in food, textiles and pharmaceuticals and as starting material in synthesis of chemicals and fuels such as isosorbide, alkane and glycols [17]. There are two steps involves in the production of sorbitol which are hydrolysis of cellulose to glucose and then hydrogenation of glucose to sorbitol by acid and metal site, respectively [18]. Thus, the acid site, metal site and H^+ played the vital role in production of sorbitol. Recently, supported transition metals were used for the cellulose conversion to sorbitol. For example, the production of sorbitol was achieved by using Ni based catalyst, attributed to its low cost and high activity. However, they have shown low stability in the reaction medium [19]. Alternatively, various catalyst including Ru have shown as active catalyst for this reaction (Table 2).

Table 2. Sorbitol yields from the conversion of cellulose by different catalyst.

| Catalyst	Temperature (K), Pressure (MPa)	Sorbitol Yield (%)	Conversion of cellulose (%)	Ref
$Ru/NbOPO_4$	443, 4	69.1	90	[20]
Ru/SiO_2-SO_3H	423, 4	61.2	90.5	[21]
$Ru/CCD-SO_3H$	453, 4	85.5	100	[22]
Ru/MCM-48	393, 2.5	89.6	100	[23]

Xi *et al*. prepared a novel mesoporous niobium phosphate-supported bifunctional Ru catalyst ($Ru/NbOPO_4$), which showed excellent performance with 69.1% of sorbitol yield after 24 h at 333 K and 4 MPa H_2 [20]. This can be attributed to the high acid amount, mesoporosity as well as synergy effect between $NbOPO_4$ for cellulose hydrolysis and Ru nanoparticle for hydrogenation. The yield of sorbitol about 61.2% was achieved with sulfonic acid-functionalized silica-supported Ru catalyst (Ru/SiO_2-SO_3H) for the hydrolytic and hydrogenation of cellulose to sorbitol after 10 h at 423 K and 4

MPa H_2 [21]. Similar study was done by Li *et al.*, using SO_3-H which was supported on carbonized cassava dregs (CCD) and gave the sorbitol yield of 85.5% and 100% of cellulose conversion at 453 K and 4 MPa H_2 for 10 h [22]. The SO_3H sites and Ru hydrogenation sites of the catalyst played an important role in hydrolytic hydrogenation of cellulose. Romero *et al.*, prepared a bifunctional catalyst using MCM-48 as the support and Ru as the metal phase. MCM-48 provides a high surface area acid structure with good diffusional properties for the hydrolytic step, while Ru acts as the active phase for the hydrogenation of D-Glucose. This catalyst showed the good yield of sorbitol about 89.56% with 100% cellulose conversion at 393 K and 2.5 MPa H_2 [23].

2.2.3. Hydroxymethylfurfural (5-HMF). 5-HMF is an important platform chemical to fuels and plastics since it has been a target in the biorefinery [24]. A 5-HMF yield of 53.3% was achieved over niobia/carbon catalyst (Nb/C) at 443 K for 8 h, accompanied with 24.5% glucose [24]. The appropriate Brønsted (BAS) or Lewis acid sites (LAS) was favoured the cellulose conversion to 5-HMF (Scheme 5). The LAS plays the important role in the isomerization of glucose to fructose. Other than that, similar study also showed that the Lewis acidic catalyst such as aluminium chloride and phosphoric acid (H_3PO_4) as Brønsted acidic catalyst were used for the production of 5-HMF from cellulose, leading to the highest yield of 5-HMF about 49.42% at 453 K for 2 h in a single-phase reaction system of water and 1,2-dimethoxyethane (Scheme 6) [25]. The H_3PO_4 acts as Bronsted acid to provide hydrogen ions for the hydrolysis and dehydration reactions. Other than that, an effective catalytic activity of novel bifunctional catalytic system, $CrCl_3/[R_4N]ReO_4$ gave the yield of 5-HMF about 49.3% was achieved at 423 K for 30 min. Compared to the single $CrCl_3$ catalyst, the bifunctional catalytic system of the catalyst exhibited superior catalytic performance. This may be due to the synergistic effect of both role of LAS and BAS [26].
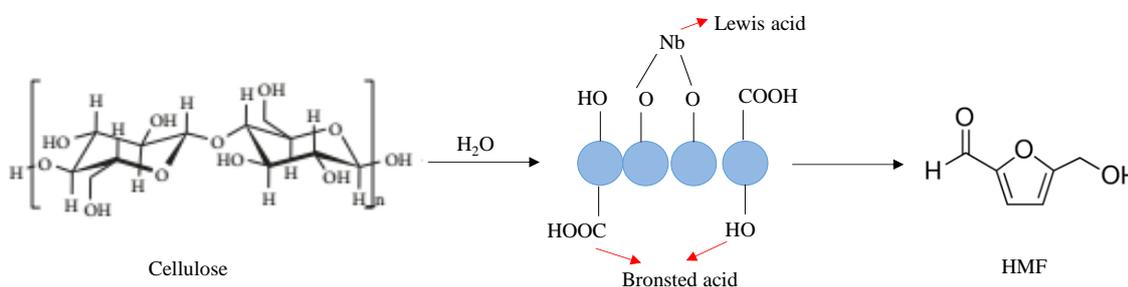
Scheme 5. Conversion of cellulose into HMF.
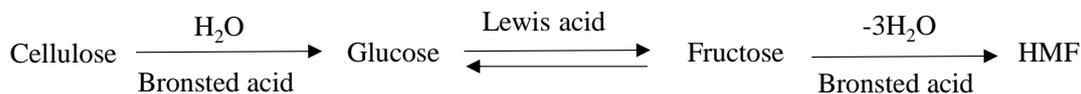
Scheme 6. Cellulose conversion to HMF catalysed by Lewis acid and Bronsted acid.

2.3 Levulinic acid
Levulinic acid (LA) is a versatile platform molecule, which can be transformed to various high-value chemicals. Thus, the conversion of cellulose into LA has been more focused by most researchers. Generally, the Bronsted or Lewis acids was used for production of LA. Xiang and co-workers reported that cellulose conversion into LA using hierarchically porous ETS-10-supported Ni catalyst (Ni-HMETS-10) in aqueous solution, led the highest yield of LA (91.0%) with complete conversion of

cellulose (100%). This reaction was achieved under 6 MPa of H_2 pressure at 473 for 6 h. The synergistic effect of LAS and hierarchical porous structures of ETS-10 in a H_2 atmosphere play the main role in

order to improve the production of LA [27]. Moderate Lewis acidic centers of the catalyst enabled the activation of the reaction substrates as well as intermediates, subsequently leading to the higher catalytic activity. Additionally, the incorporation of Ni has played a positive role in conversion growth, which proves to be a quite delightful and feasible strategy to take place of those widely used noble metals with promising activity.

2.4 Lactic acid

Lactic acid (LA) is an important platform chemical for the production of biodegradable plastics and starting materials for the pharmaceutical, chemical and industry [29]. The catalytic transformation of cellulose into lactic acid has become more interest in recent years. In order to achieve an effective of cellulose conversion into lactic acid, the activation of C–O and C–C bonds as well as multifunctional catalysts are mostly required, in which the latter requirement can combine various reactions comprising of hydrolysis, isomerization as well as retro-aldol condensation. Table 3 shows the catalyst used for conversion of cellulose into LA. The exceptional catalytic testing of the tin-modified niobium (SnO_2/Nb_2O_5) for the isomerization of triose sugars to LA, leading 98.7% of LA yield at 443 K after 4 h [29]. Basically, the promising yield of LA achieved from the conversion of dihydroxyacetone (DHA) in water in the presence of BAS as well as LAS (Scheme 7). As known, $Nb_2O_5.nH_2O$ has both strong BAS and LAS, which responsible for the dehydration of DHA to pyruvic aldehyde (PA), and the subsequent isomerization reaction of PA to LA occurred at the Nb and Sn sites. The strong interaction between these two sites makes the Sn/Nb_2O_5 catalysts suitable for the conversion of DHA to LA.
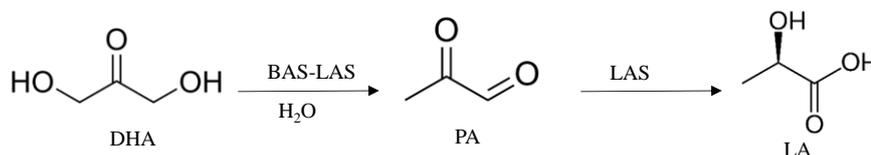
Scheme 7. Conversion of DHA in water into LA.

The isomerization of glucose over Pb–Sn-beta zeolite, that was prepared via ion exchange, led to 52% of LA yield [30]. Two steps are involved in this reaction, where firstly, the isomerization reaction of glucose took place in order to produce the fructose, and then followed by fructose condensation process to form the C_3 intermediates via retro-aldol reaction. Other than that, the catalyst also exhibited greater catalytic performance for both dehydration and isomerization of DHA and PA. In addition, this catalyst also inhibit the production of HMF. The effective usage of sugars as the starting material for production of lactic acid was achieved by sulfonated Sn-doped KIT-6 (Sn-KIT-6-Pr-SO_3H) catalyst in aqueous phase [31]. The catalyst showed high efficiency in lactic acid production (66.2 %) with cellulose conversion of 88.9%. Compare to Amberlyst15, HUSY catalyst, those catalysts exhibited superior performance in the production of LA.

| Catalyst	Temperature (K), Pressure (MPa)	Lactic acid Yield (%)	Conversion of cellulose (%)	Ref
SnO_2/Nb_2O_5	433, 5	98.7	95	[29]
Pb–Sn-beta zeolite	463, 5	52	99	[30]
sulfonated Sn-doped KIT-6	483, 5	16.2	88.9	[31]

Table 3. Lactic acid yields from the conversion of cellulose by different catalyst.

3. Catalytic Conversion of Cellulose to Fuels

The depletion of fossil resources and increasing energy demand has initiated researchers to explore the usage of renewable biomass resources for production of transportation fuels. Some researches regarding conversion of cellulose into aliphatic and aromatic hydrocarbon were reported.

3.1 Aliphatic hydrocarbon

Direct cellulose conversion into fuels has been considered as most prospective ways for the production of transportation fuels. The production of aliphatic hydrocarbon (C_5 and C_6 alkanes) from conversion of cellulose is better owing to its low boiling point and hydrophobicity as well as low energy consumption for their separation. Scheme 8 shows the reaction pathway of C_3 and C_4 hydrocarbons formation of cellulose. The intermediate products such as 5-HMF, levulinic acid and pentanoic acid were formed during the cracking reaction of glucose into C_4 hydrocarbons. Table 4 shows the summary of catalyst used for conversion of cellulose into aliphatic hydrocarbon.
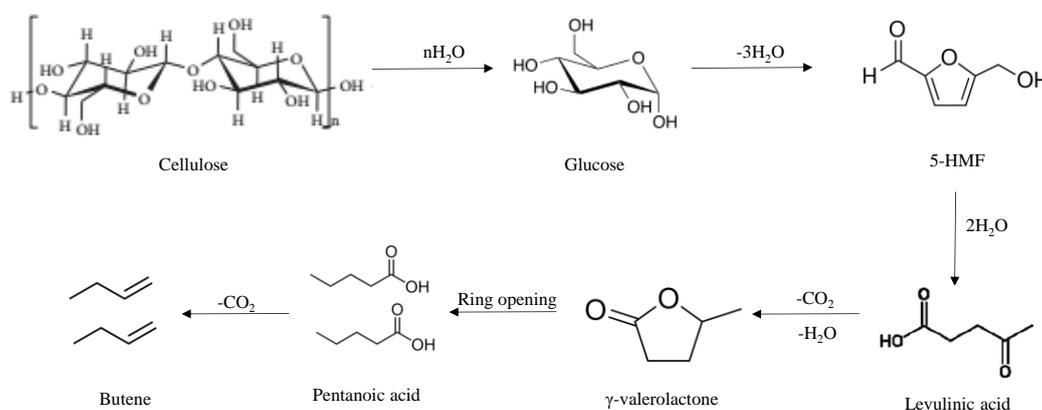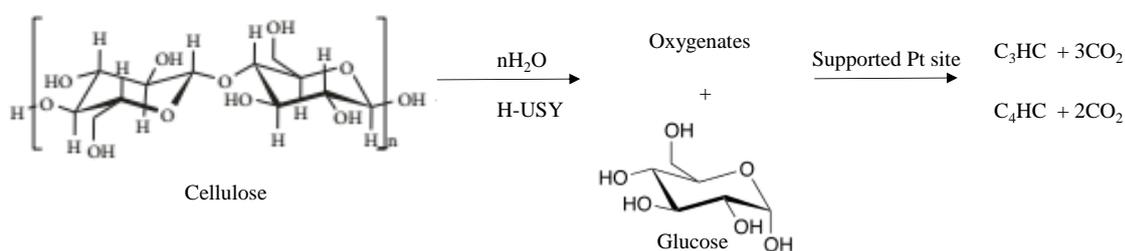

**Scheme 8.** Reaction pathway of C_3 and C_4 hydrocarbon formation from cellulose.

Reportedly, cellulose can be transformed into hydrocarbons using heterogeneous solid catalysts. The platinum supported on beta zeolite (Pt/H-beta) was used in one-pot cellulose conversion in aqueous solution with low selectivity of C_{5+} hydrocarbons about 11.2%, and higher C_3 and C_4 hydrocarbon production is about 46.8% at 443 K [32]. The Pt site and acid site in beta zeolite were the significant means for enhanced the production of hydrocarbon. A large pore system and effective acidity also contributed to the effective C_3 and C_4 hydrocarbons. Ogo *et al*. also reported one pot direct catalytic conversion of cellulose using platinum supported on USY zeolite (Pt/H-USY) catalyst at low temperature (443 K) that gave the 65.6 % of C_3 and C_4 hydrocarbons [33]. The results suggested that the acid site of H-USY zeolite solubilizes the cellulose; meanwhile Pt site cracked the glucose into hydrocarbons (Scheme 9).

Table 4. Aliphatic hydrocarbon yields from the conversion of cellulose by different catalyst.

Catalyst	Temperature (K), Pressure (MPa)	Product (% Yield)	Conversion of cellulose (%)	Ref
Pt/H-beta	443, 0	C_3-C_4 (46.8)	10	[32]
Pt/H-USY	443, 0	C_3-C_4 (65.6)	19.4	[33]
Pt/HZSM-5	673, 6.5	C_2-C_9 (89)	-	[34]
Ir–ReO$_x$/SiO$_2$+HZSM-5	463, 6	C_6 (83)	98	[35]
TSARu/C	493, 5	C_6 (82)	100	[36]
LiTaMoO$_6$/Ru/C	503, 6	C_6 (82)	-	[37]
BPO$_4$/Ru/C	403, 6	C_5-C_6 (70.6)	100	[38]

Scheme 9. Reaction pathway of hydrocarbon formation from cellulose over Pt/H-USY.

The Pt/HZSM-5 showed the yield of C_2-C_9 alkanes of about 89% when using the pretreated cellulose at 673 K with 6.5 MPa of H_2 atmosphere [34]. The pretreated cellulose in alcohol was lowering the molecular weight of cellulose with producing the intermediates products such as monosaccharide and disaccharide. Besides the pretreatment of cellulose, the reaction systems also influence the catalytic conversion of cellulose. The combination of metal-acid catalysts such as iridium-rhenium supported on silicon dioxide mixed with ZSM-5 zeolite (Ir–ReO$_x$/SiO$_2$+HZSM-5) or tungstosilicic acid (TSA) modified Ru/C catalysts was performed in biphasic reaction systems such as organic and water and exhibited higher yield of hexanes [35, 36]. The former catalyst performed in n-dodecane and water under 6 MPa of H_2. The HZSM-5 enhanced the hydrolysis of cellulose, meanwhile Ir–ReO$_x$/SiO$_2$ catalyst promotes the hydrogenation and hydrogenolysis of C-O bond, which gave the higher yield of n-hexane (C_6 paraffin) is about 83% at 463 K (Scheme 10). Other than that, the cellulose was directly transformed into n-hexane (82%) over Ru/C catalysts with H_2 pressure of 5.0 MPa at 493 K for 5 h [36].
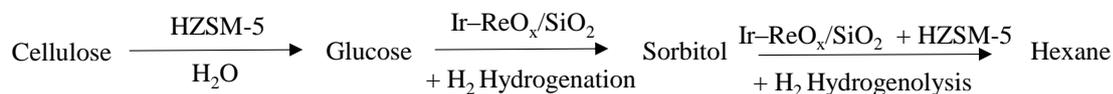

Scheme 10. Reaction pathway for conversion of cellulose over Ir–ReO$_x$/SiO$_2$+HZSM-5.

Compared to biphasic system or organic phase, the mono-phasic aqueous system is necessary to explore in order to make the catalytic conversion of cellulose into hexane more economical and environmentally friendly. Liu *et al*. has prepared a three-catalyst system, lithium tantalum molybdenum oxide (LiTaMoO$_6$) which is combined with Ru/C to transform cellulose into liquid alkanes in phosphoric acid (PA) solution giving a high yield (82%) [37]. The PA solution was used for the hydrolysis of cellulose, removal of oxygen as well as ring opening reaction. Other than that, the combining of boron phosphate with Ru/C catalyst in aqueous solution was used for C_5 and C_6 alkanes

production (gasoline-range hydrocarbons) from cellulose and exhibited higher yield (70.6%) [38]. The presence of boric acid plays important effect on the formation of hexane from sorbitol, in which reduced the formation rate of isosorbite (intermediate products of sorbitol). Hence, the production of liquid hydrocarbon can be improved significantly.

3.2 Aromatic hydrocarbon

Monoaromatic compounds, especially benzene, toluene and xylene (BTX), are versatile chemicals in the petroleum industry, which are used as gasoline additives. They also used as solvents and raw materials for preparation of chemical products such as rubber, plastics, and fiber. The general pathway of aromatic production from oxygenated compounds is illustrated in Scheme 11. Table 5 shows the summarized aromatics hydrocarbon yields from the conversion of cellulose by different catalyst. Rezaie *et al*. reported that the combining of HZSM-5 with dealuminated HY showed higher yields of aromatic hydrocarbon (27%) compared to the individual HZSM-5 (20%) and HY (9%) at 798 K [39]. The formation of coke was lower when using the combination catalyst, HZSM-5 with dealuminated HY, may be due to the larger pore of HY, which is as consequence of dealumination process, hence allow the diffusion of larger molecules into zeolite. Other than that, high density of acid sites located in the small space in HZSM-5 pores also caused the lower coke formation. Thus, it can be concluded that the synergistic effect between pore structure and acidity play important roles in minimizing the formation of coke and maximize the production of desired products.
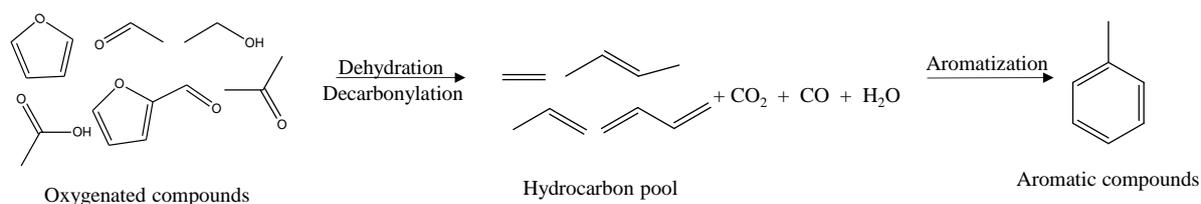
Scheme 11. General pathway towards aromatic hydrocarbon from oxygenated compounds.

Table 5. Aromatics hydrocarbon yields from the conversion of cellulose by different catalyst.

Catalyst	Temperature (K), Pressure (MPa)	BTX Product (% Yield)	Ref
HZSM-5 with dealuminated HY	773, 1	27	[39]
Ga/HZSM-5	773, -	53.7	[40]
Na_2CO_3- HZSM-5	573, -	38.2	[41]
Zn/HZSM-5	773,-	71.8	[42]
Ni/HF-HZSM-5	773, -	44.9	[43]

In viewpoint of the above requirement, metal modified and treated by alkali are the most approached methods by most researchers in order to improve the catalytic performance of zeolites, especially HZSM-5. The generation of more mesopore by alkaline treatment, can cause the large molecules more accessible into the zeolite. Differently, the micropore structure and acid sites are well preserved when using the alkali for desilication process. Dai *et al*. reported that the hierarchical HZSM-5 was prepared by desilication using 0.3 M sodium hydroxide (NaOH) solution. This catalyst showed the best catalytic performance, that gave 51.16 wt% of aromatic hydrocarbons as well as increases the BTX selectivity [40]. Qiao *et al*., also treated the HZSM-5 zeolites with three different types of alkali, which are NaOH, sodium carbonate (Na_2CO_3) and tetrapropylammonium hydroxide (TPAOH) [41]. Among them, the highest yields of aromatic hydrocarbon (38.2%) was achieved by using the Na_2CO_3-treated HZSM-5. This treatment increases the acidity of catalyst as well as having the micro and mesopore structure, which can produced the lower coke.

Metal modification also influence in improving the yield of aromatic hydrocarbon. Zheng *et al.*, successfully synthesized the metal loaded HZSM-5 (M-HZSM-5), in which using the Zn, Ga, Ni, Co, Mg and Cu [42]. Among them, Zn-HZSM-5 exhibited the highest yield of toluene and xylenes (71.84%), meanwhile Ni-HZSM-5 produced the higher contents of benzene (29.16%). This is because modification with Zn led to the increase of Lewis acid and promoted the reaction process. The Zn has an ability in dehydrogenation and aromatization which can promote the intermediate product of the pyrolysis to form aromatic hydrocarbons. Other than that, Fe and Ga was also used for conversion of cellulose. This metal modification gave the different effect on aromatics production in which, Fe-HZSM-5 exhibited higher production of BTX (58.13 %), while Ga-HZSM-5 enhanced the production of both BTX (53.70%) and alkylbenzenes [40]. Besides, the highest light aromatic yield (44.9%) was obtained by nickel/hydrogen fluoride modified HZSM-5 (Ni/HF-HZSM-5) [43]. The Ni acted as acceptors of electrons and promote the production of olefin oligomerization, particularly ethylene oligomerization. In addition, Ni induced the secondary cracking reactions to dehydrogenate and deoxidize.

4. Conclusion

The conversion of cellulose into renewable chemicals and fuels is one of the hot topics in green and sustainable chemistry. Various types of supported metal catalysts can be designed for the cellulose conversion. In this review, supported Ru and Ni was acted as active sites that promoted the hydrolysis of cellulose via heterolytic dissociation of H_2 as well as hydrogenation of glucose to produce renewable chemicals such as ethylene glycol, sorbitol, 5-hydroxymethylfurfural, levulinic acid and lactic acid. The Pt and Ir catalysts promote the hydrogenation and hydrogenolysis of C-O bond to produce the aliphatic hydrocarbon. Meanwhile, the transition metal such as Zn and Ni have an ability in dehydrogenation and aromatization, which can promote the aromatic hydrocarbons.

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