



Chemo-catalytic synthesis of C6 sugars from plant-derived carbohydrates: A technical assessment on solid catalysis

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Considering the wide applications of C6 sugars, several methodologies have been developed through chemo-catalysis from plant-derived biomass wastes. This review critically overviewed the existing industrial processes as well latest advancement in this area. Further, influence of catalyst properties in each developed processes, reaction kinetics, mechanism and plausible focus of the topic are technically assessed.

Keywords: Biomass waste, carbohydrate, C6 sugar, hydrolysis, isomerization, solid catalyst.

1. Introduction

It is well-known that since the industrial revolution happened in 18th century, fossil feedstocks became the prime source of chemicals and energy. As of today, many other options are available for the energy resource but for chemical synthesis yet, we are mainly dependent on fossil feedstocks. However with some dominant issues like – limited availability, price fluctuation in increasing trend and non-uniform global distribution, certainly restricts its application in chemical synthesis. Global warming due to rise in carbon dioxide level is a major environmental concern for the use of fossil feedstocks. At this stage, renewable and copiously available biomass (composite of C, H, O and N) waste has shown a potentiality to be utilized as feedstock for many chemical syntheses due to its high carbon concentration. Precisely, processing of biomass in bio-refinery under suitable conditions can lead to the formation of important platform chemicals as well as fine chemicals.

An overview of current research trend suggests that plant-derived biomass either in edible form or in non-edible form is mostly processed in chemical conversion pathway for chemical production^{1,2}. Fruits, crops, crop wastes, woods etc. have the major composition of free sugar monomers (C6: glucose, mannose, galactose, fructose etc., C5: xylose, arabinose

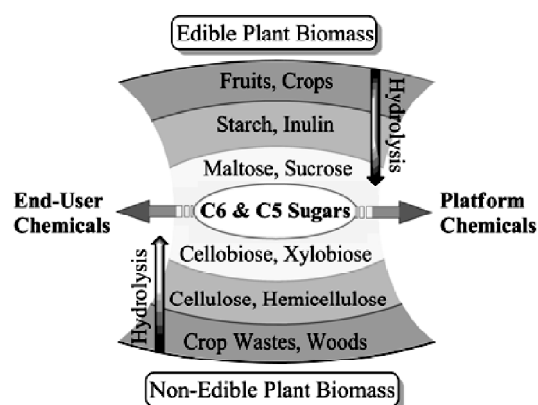


Fig. 1. Illustration for sugar synthesis pathways and applications of sugars.

etc.), sugar dimers (maltose: dimer of α -D-glucose, sucrose: dimer of α -D-glucose and β -D-fructose, cellobiose: dimer of β -D-glucose), sugar polymers (starch: polymer of α -D-glucose, cellulose: polymer of β -D-glucose, inulin: polymer of β -D-fructose, hemicellulose: copolymer of C5 and C6 sugars) and aromatic polymers (lignin). Hydrolysis of ether linkages (glycosidic linkages) in sugar dimers and polymers leads to formation of sugar monomers, which can be further used as end-user chemicals (fine chemicals, pharmaceuticals, cosmetics etc.) and platform chemicals (for synthesis of sugar

alcohols, sugar acids, other sugar derivatives, 5-hydroxymethylfurfural, furfural etc.) (Fig. 1)³⁻⁶. Accordingly, many industries and academic research have shown interest for sugar monomer production from plant biomass. However, in this review, we have focused on the developed methodologies for C6 sugar production.

2. Glances on current industrial processes for C6 sugar production

Most of the industries with C6 sugar production unit were established long back and use mineral acids as catalyst. A pioneer of work was reported in 1819, which is the first process for concentrated sulfuric acid catalyzed conversion of linen (textile) into glucose⁷. Accordingly, the first commercialized plant (Scholler process) was set-up in Germany based on cellulose hydrolysis into sugars in 1931⁸. Scholler process adopted two steps wherein firstly, wood wastes hydrolyzed into mainly oligomers in presence of diluted sulfuric acid (0.5 wt%) at 170°C and in the subsequent step, those oligomers were transformed into sugar monomers via fermentation reaction. The similar processing methodology viz. dilute acid hydrolysis and fermentation for conversion of waste biomass into sugars was also implemented for designing many other industrial plants in Russia in 1935-1945⁹. In 1948, a commercial plant was set-up in Japan (Hokkaido process) for sugar production using concentrated sulfuric acid and it was demonstrated that using a membrane, concentrated acid can be separated from produced sugar; which eventually reduces the risk of sugar degradation¹⁰. Using this technique an 80% recovery of concentrated sulfuric acid was validated. In recent time, BC International Corporation (BCI), USA started transformation of crop wastes (rice husk, corn stover, bagasse etc.) into sugars using sulfuric acid and its subsequent fermentation to ethanol using microorganisms¹¹. The concentrated acid hydrolysis of cellulosic material leads to the degradation of C5 sugars which declines the reaction rate of C6 sugar formation. Consequently, the method developed by Arkenol Inc., USA uses stepwise hydrolysis of cellulosic materials (cellulose + hemicellulose + lignin) into sugars wherein, in the first step, diluted sulfuric acid (20–30%) is used for hydrolysis of hemicellulose part into C5 sugars and then remaining biomass consisting cellulose and lignin is subjected to concentrated sulfuric acid (ca. 70%) hydrolysis to produce C6 sugars¹².

3. Kinetic and mechanistic approaches for sugar synthesis

Particularly, it is advantageous to study the kinetic parameter of a reaction to understand its deeper insights. Accordingly, many research groups have shown effort to investigate the kinetics of sugar synthesis reaction. The activation energy for dilute sulfuric acid hydrolysis reaction of maltose and cellobiose was calculated as 132–137 kJ/mol^{13,14}. It was also found that the hydrolysis reaction rate is proportional to the reaction temperature. In yet another report, activation energy value for cellobiose hydrolysis reaction was reported as 110±29.6 kJ/mol and 114±9.3 kJ/mol, respectively using sulfuric acid and maleic acid¹⁵. Conversely, a higher activation energy barrier (172–180 kJ/mol) was reported for cellulose hydrolysis to glucose due to rigid crystalline structure of cellulose^{16–18}. Actually, cellulose hydrolysis follows first order reaction kinetics, which is associated to the crystallinity of cellulose, acid concentration, reaction temperature etc.^{19,20}. It should be noted that upon mineral acid treatment to cellulose, glucose is formed as a primary hydrolysis product along with some secondary (degradation) products viz. 5-hydroxymethylfurfural (HMF) via dehydration reaction, formic and levulinic acid via rehydration reaction, humins via re-polymerization or condensation reaction etc. That means there is always conflict between the formation and degradation of glucose (C6 sugar). Some research groups have been investigated the kinetics of these two reactions (glucose formation and glucose degradation) with various substrates in presence of sulfuric acid and found that the rate of cellulose hydrolysis into glucose is always higher (filter paper: 1.22×10¹⁹ /min, Douglas Fir: 1.73×10¹⁹ /min, Solka Floc: 1.22×10¹⁹ /min and municipal solid waste: 1.16×10¹⁹ /min) than the rate of glucose degradation reactions (filter paper: 3.79×10¹⁴ /min, Douglas Fir: 2.38×10¹⁴ /min, Solka Floc: 3.79×10¹⁴ /min and municipal solid waste: 4.13×10¹⁵ /min)^{16–18}. However, due to lower activation energy barrier (137–142 kJ/mol) of glucose degradation reactions, the formation of degradation products is always possible.

From the understanding of kinetic analysis of cellulose acid hydrolysis into glucose, the mechanistic pathway of the reaction was proposed. The Brønsted acid catalyzed hydrolysis of cellulose occurs in the following pathways – (i) protonation to glycosidic oxygen, (ii) break down of ether (C-O) linkage and formation of carbocation, (iii) neutralization of

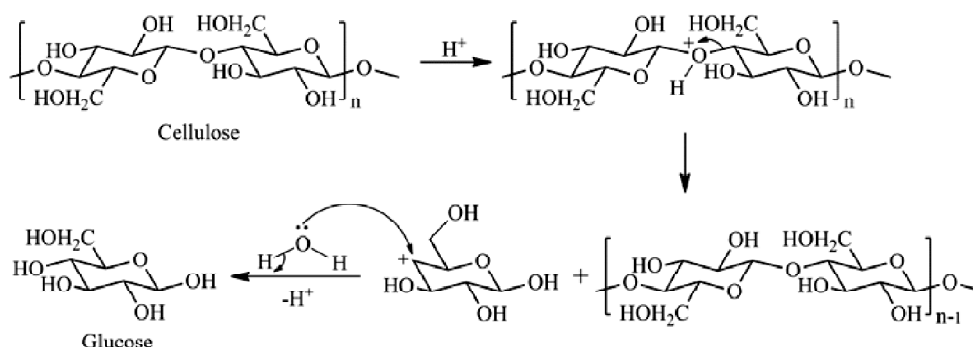


Fig. 2. Reaction pathway of Brønsted acid catalyzed cellulose hydrolysis into glucose.

carbocation by water molecule and release of proton. The mechanistic pathway for cellulose acid hydrolysis to glucose is represented in Fig. 2.

4. Sugar synthesis using solid catalysts

Handling of mineral acids for C6 sugar production are unsafe (corrosiveness, health hazard *etc.*), eco-unfriendly (large amount acid neutralization waste disposal, hazard to aquatic life *etc.*) and uneconomical (reactor corrosion, acid recovery problem, acid-sugar separation problem *etc.*). Accordingly, design of suitable heterogeneous (solid) catalyst

is desirable to cover-up those issues. Herein, systematic discussion is presented on the effect of applied solid catalysts for laboratory scale sugar synthesis.

4.1. Sugars from di- and poly-saccharides

C6 sugar monomers (glucose and fructose) are formed by the action of acid catalyzed hydrolysis of sugar dimers (maltose, sucrose and cellobiose) and sugar polymers (starch, inulin and cellulose). The summary of all the developed methods using solid acid catalysts is represented in Table 1.

Table 1. Summary of solid acid catalysed methods for sugar synthesis from di- and poly-saccharides

Sr. no.	Substrate	Catalyst	T (°C)	t (h)	Conv. (%)	Product yield (%)		Ref.
						Glucose	Fructose	
1.	Sucrose	Amberlyst-15	80	4	88	88	87	21
2.	Sucrose	Nafion-silica	80	4	28	28	26	21
3.	Sucrose	Amberlyst-15	80	3	–	78	–	22
4.	Sucrose	Nafion NR-50	80	3	–	42	–	22
5.	Sucrose	Nafion SAC-13	80	3	–	29	–	22
6.	Sucrose	Amberlite A120	80	4	92	82	–	23
7.	Sucrose	Amberlite 200	80	4	99	98	–	23
8.	Sucrose	FSM-16-SO ₃ H	80	4	90	90	89	21
9.	Sucrose	Ph-HMM-one pot	80	4	81	81	80	21
10.	Sucrose	Ph-HMM-graft	80	4	83	83	82	21
11.	Sucrose	Et-HMM-one pot	80	4	90	90	90	21
12.	Sucrose	Et-HMM-graft	80	4	86	86	82	21
13.	Sucrose	Nb ₂ O ₅ -PO ₄	80	4	80	–	~62	23
14.	Sucrose	HTiNbO ₅	80	3	–	~42	~42	22
15.	Sucrose	HNbMoO ₆	80	1	100	~100	~100	22
16.	Sucrose	Nb ₃ W ₇ oxide	80	1	–	65	–	45
17.	Sucrose	HY (Si/Al = 15)	85	2	~100	–	~100	51
18.	Maltose	Hβ (Si/Al = 50)	130	24	85	80	–	24

Table-1 (contd.)

19.	Maltose	H β (Si/Al = 12.5)	130	24	45	43	–	24
20.	Maltose	HMOR (Si/Al = 12)	130	24	70	66	–	24
21.	Maltose	HMOR (Si/Al = 7)	130	24	60	56	–	24
22.	Maltose	HY (Si/Al = 15)	150	2	~90	~83	–	51
23.	Cellobiose	Amberlyst-15	90	24	62	61	–	25
24.	Cellobiose	CoFe ₂ O ₄ -SiO ₂ -SO ₃ H	175	1	~80	50	<1	46
25.	Cellobiose	HY (Si/Al = 15)	150	2	~90	~88	–	51
26.	Cellobiose	PVC-AC-673	100	7	~50	~50	–	57
27.	Cellobiose	SO ₃ H, CO ₂ H and OH functionalized carbon	90	15	~85	81	–	25.
28.	Inulin	HY (Si/Al = 15)	90	2	100	–	92	51
29.	Starch	Amberlyst-15	130	6	–	25	–	21
30.	Starch	Cs _{2.5} H _{0.5} PW ₁₂ O ₄₀	120	5	–	43	–	42
31.	Starch	[C ₁₆ H ₃₃ N(CH ₃) ₃]H ₂ PW ₁₂ O ₄₀	120	5	–	82	–	42
32.	Starch	Et-HMM-one pot	130	24	–	~67	–	21
33.	Starch	Ph-HMM-graft	130	24	–	~67	–	21
34.	Starch	HNbMoO ₆	100	72	–	45	–	22
35.	Starch	HY (Si/Al = 15)	150	2	–	~95	–	51
36.	Starch	AC-SO ₃ H	120	~70	–	~90	–	52
37.	Ball milled cellulose	Sn _{0.75} PW ₁₂ O ₄₀	150	15	~52	–	~40	35
38.	Ball milled cellulose	H β (Si/Al = 75)	150	24	–	13	–	52
39.	Ball milled cellulose	AC-SO ₃ H	150	24	–	41	–	52
40.	Ball milled cellulose	AC-N-SO ₃ H-250	150	24	74	63	–	59
41.	Ball milled cellulose	CMK-3-SO ₃ H	150	24	94	75	–	59
42.	Ball milled cellulose	Si ₃₃ C ₆₆ -823-SO ₃ H	150	24	61	50	–	60
43.	Cellohexaose	SO ₃ H, CO ₂ H and OH functionalized carbon	90	15	100	85	–	25
44.	Microcrystalline cellulose in IL	NKC-9	MW	3m	–	27	–	32
45.	Microcrystalline cellulose in IL	Nafion NR-50	160	4	–	35	–	33
46.	Microcrystalline cellulose in IL	Dowex 50wx8-100	100	4	–	83	–	34
47.	Microcrystalline cellulose in IL	HY (Si/Al = 4)	130	2	–	50	–	53
48.	Microcrystalline cellulose	Cs _{2.5} H _{0.5} PW ₁₂ O ₄₀	170	6	–	21	–	41
49.	Microcrystalline cellulose	[C ₁₆ H ₃₃ N(CH ₃) ₃]H ₂ PW ₁₂ O ₄₀	170	8	–	39	–	41
50.	Microcrystalline cellulose	[C ₁₆ H ₃₃ N(CH ₃) ₃]H ₅ P ₂ W ₁₈ O ₆₂	160	9	87	69	–	42
51.	Microcrystalline cellulose	ChH ₄ AlW ₁₂ O ₄₀	140	3	95	76	–	43
52.	Microcrystalline cellulose	HNbMoO ₆	130	12	–	~4	–	22
53.	Cellulose	SO ₄ ²⁻ /TiO ₂	190	4	~35	~26	~1	48

Table-1 (contd.)

54.	Cellulose	MoO ₃ /TiO ₂	190	4	~35	~10	<1	48
55.	Microcrystalline cellulose	SO ₃ H, CO ₂ H and OH functionalized carbon	100	3	~70	4	–	28
56.	Microcrystalline cellulose	BC-SO ₃ H	90 (MW)	1	–	20	–	59
57.	Cellulose isolated from rice straw	HTSACF	150	24	33	30	–	62

4.1.1. Performance of ion-exchanged resins as catalyst:

It is well recognized that ion-exchanged resins having sulfonic acid functionality (strong acids) can show good performance for hydrolysis reaction. It was shown that the hydrolysis reaction activity is dependent on the acid amount of catalyst and therefore, Amberlyst-15 resin (acid amount = 4.65 mmol/g) is better active compared to Nafion NR-50 resin (acid amount = 0.8 mmol/g) and Nafion-silica resin (acid amount = 0.17 mmol/g) in sucrose hydrolysis reaction^{21, 22}. In another report, it was verified that due to similar acid amount present in Amberlite A120 resin (acid amount = 5.09 mmol/g) and Amberlite 200 resin (acid amount = 4.38 mmol/g), almost same amount (82–98%) of sugar formation is possible from sucrose²³. It was also mentioned that the stability of 1,4-glycosidic linkages is higher compared to 1,2-glycosidic linkages, which has been clearly reflected in poorer hydrolysis activity of cellobiose (conversion = 19%) than sucrose (conversion = 99%) using Amberlite 200 resin. However, it should be kept in mind that increases in degree of resin cross-linkages can disturb the access of resin acid sites by substrate molecules. For an example, in complete hydrolysis of maltose, 8% cross-linked resin (Dowex 50×8-100) requires higher processing temperature (130°C) than the processing temperature (120°C) with 2% cross-linked resin (Dowex 50×2-100)²⁴. Another report presented 61% glucose formation from ~62% cellobiose hydrolysis in presence of Amberlyst-15 catalyst²⁵. Use of starch (α -1,4-D-glucose polymer) in presence of Amberlyst-15 resin provided only 25% glucose formation along with 12% maltose (α -1,4-D-glucose polymer) formation at 130°C²¹. This result undeniably points toward the insufficient catalytic activity of Amberlyst-15 resin in complete hydrolysis of starch under the reaction condition employed. Nevertheless, from the understanding of all the above mentioned work it is clear that the fundamental phe-

nomenon of labile proton transfer from catalyst to reaction center through water medium (via formation of hydronium ions, H₃O⁺)^{26,27} is mainly influencing the hydrolysis mechanism to produce sugar monomers. At the same time, strongly acidic resins with labile protons were not very active for hydrolysis of microcrystalline cellulose (β -1,4-D-glucose polymer) because of presence of strong intra-molecular, inter-molecular and inter-sheet H-bonding in cellulose (Fig. 3)^{6,28}. To reduce crystallinity in microcrystalline cellulose, a handful of physical, physico-chemical and chemical methods were proposed and those are well-summarized in many reports^{6,29-31}. Pre-treatment of microcrystalline cellulose eventually ends up with formation of lower crystalline or amorphous cellulose and hence, those can easily access the acid sites in catalyst to give hydrolysis reaction. Few works have demonstrated that combined use of resin catalyst and ionic liquids (ILs) are helpful in hydrolysis of microcrystalline cellulose where, ILs act as both pre-treatment agent and reaction solvent. A good improvement in glucose yields (27–83%) has been offered in presence of NKC-9 resin, Nafion NR-50 resin and Dowex 50wx8-100 resin using various ILs viz. [C₄min]Cl, [BMIM]Cl and [EMIM]Cl³²⁻³⁴. Although, some of the processes for hydrolysis reaction were demonstrated with resin catalysts but, from the view point of their hydrothermal instability at moderate temperature (<150°C), those cannot provide sustainable future technology.

4.1.2. Performance of heteropoly acids as catalyst:

Super acidic nature of various polyoxometalates or heteropoly acids (HPA) having Keggin and Dawson framework, eventually finds their applications in sugar synthesis reaction. Moreover, the commonly known homogeneous HPA's are made heterogeneous after partial replacement of small protons by larger ions such as Cs⁺, Ag⁺, Sn⁴⁺, Ru³⁺ etc. Partial replacement of protons by various metal ions not

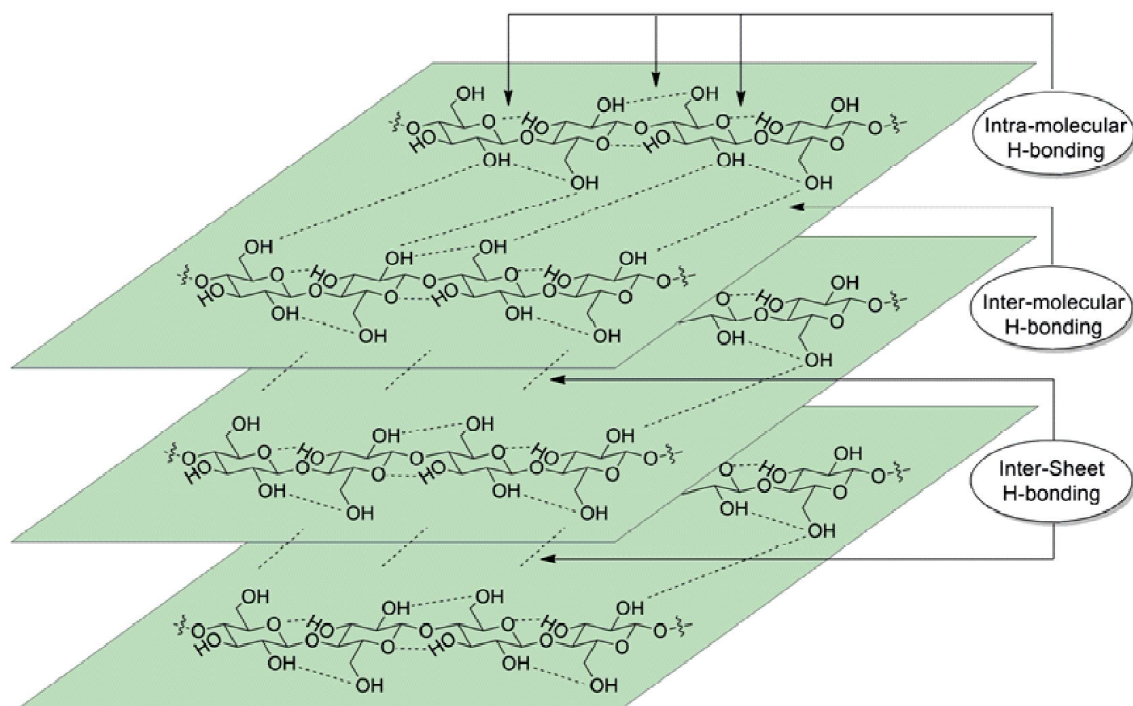


Fig. 3. Illustration for H-bonding in cellulose⁶.

only make HPA's heterogeneous but also introduce Lewis acidity to HPA's along with Brønsted acidity³⁵. Cellobiose hydrolysis has been carried out with these Lewis acid incorporated heterogeneous HPA's and it was reported that stronger Brønsted acidity in catalyst helps to achieve highest hydrolysis rate of β -1,4-glycosidic linkages. Ball milled cellulose (pre-treated) was also examined as substrate using the same metal ions incorporated HPA. When the catalysts have almost similar Brønsted acidity, the cellulose hydrolysis reaction activity has increased with the Lewis acid strength of catalysts. Although, with increasing Lewis acid strength hydrolysis rate can be improved but concurrently rate of degradation reaction was found to be enhanced. Therefore, $\text{Sn}_{0.75}\text{PW}_{12}\text{O}_{40}$ catalyst with moderate Lewis acidity offered ~40% total reducing sugars formation from ball milled cellulose. The influence of catalyst hydrophilicity-hydrophobicity property on reaction activity has been demonstrated in many organic transformations³⁶⁻⁴⁰. Similarly, micellar HPA, $[\text{C}_{16}\text{H}_{33}\text{N}(\text{CH}_3)_3]\text{H}_2\text{PW}_{12}\text{O}_{40}$ was prepared to correlate the effect of catalyst hydrophilicity-hydrophobicity on hydrolysis reaction of starch and microcrystalline cellulose⁴¹. Due to hydrophilic interaction between substrate having -OH groups

and micellar core, $[\text{C}_{16}\text{H}_{33}\text{N}(\text{CH}_3)_3]\text{H}_2\text{PW}_{12}\text{O}_{40}$ catalyst offered better glucose formation (from starch: 82%, from cellulose: 39%) than $\text{Cs}_{2.5}\text{H}_{0.5}\text{PW}_{12}\text{O}_{40}$ (from starch: 43%, from cellulose: 21%) at 170°C. In a recent report, $[\text{C}_{16}\text{H}_{33}\text{N}(\text{CH}_3)_3]\text{H}_5\text{P}_2\text{W}_{18}\text{O}_{62}$ catalyst was demonstrated for cellulose hydrolysis (87%) to produce 69% glucose at 160°C⁴². The improved catalytic activity was explained in terms of strong Brønsted acidity in catalyst and significant cellulose adsorption over catalyst micellar assembly. Choline cation incorporated HPA, $[(\text{CH}_3)_3\text{NCH}_2\text{CH}_2\text{OH}]\text{H}_4\text{AlW}_{12}\text{O}_{40}$ was also used for cellulose hydrolysis⁴³. Temperature switchable properties of the catalyst allowed solubilizing choline cation at reaction temperature and thus, the soluble heteropoly acid part can catalyze cellulose hydrolysis homogeneously. Later, upon cooling of reaction solution at room temperature precipitated back the catalyst. The combined influence of temperature switchable property, Brønsted acidity and Lewis acidity in catalyst assisted to achieve 76% glucose formation from 95% cellulose hydrolysis in water at 140°C. However, to use HPA's as suitable catalyst, researchers have to design the catalyst in such a way that it should eliminate the issue of leaching of its anionic part under hydrothermal reaction conditions.

4.1.3. Performance of mesoporous silica resin as catalyst:

Researchers have also validated the applicability of many mesoporous (pore dimension of 2–50 nm) silica materials either in original form or in surface modified form for sugar synthesis. However, it can be predicted that the original form of silica materials is not very active because of the absence of sufficient acidity in material. Hence, sulfonic acid functionalization to mesoporous silica materials is recommended to obtain noticeable catalytic activity. Highly ordered, FSM-16 (Folded Sheet Mesoporous/Material) having pore diameter of 2.0 nm (mesoporous) was surface functionalized with sulfonic acid groups via post-synthesis grafting method to provide acid amount of 1.11 mmol/g and upon its use for sucrose hydrolysis, 90% glucose and 89% fructose were produced²¹. Co-condensation and post-synthesis grafting methods were also adopted for sulfonic acid functionalization to two different silica materials namely, phenylene-bridged mesoporous silica (Ph-HMM) and ethylene-bridged mesoporous silica (Et-HMM) to introduce acid amount of 0.31–0.90 mmol/g in materials²¹. These materials were capable of producing very good amount of glucose (81–90%) and fructose (80–90%) from sucrose hydrolysis. At the same time, different acid groups (butylcarboxylic acid, propylsulfonic acid and arenesulfonic acid) were functionalized to an organic-inorganic hybrid mesoporous silica material to understand the influence of acid functionality on cellobiose hydrolysis reaction⁴⁴. Although, all the acid functionalized silica materials offered similar activation energy (110–138 kJ/mol) for cellobiose hydrolysis reaction but, butylcarboxylic acid functionalized silica was less active (cellobiose conversion \approx 15%) compared to both propylsulfonic acid and arenesulfonic acid functionalized silica materials (cellobiose conversion \approx 99%) under similar reaction conditions. Authors have been clarified this issue by the help of acid sites generation ability of catalyst in water, which illustrated that butylcarboxylic acid functionalized silica generates less protons in water (pH = 4.90) than the other two silica materials (pH = 2.67–2.89) and thus offered poor hydrolysis of cellobiose. From the results, it is clear that the reaction is mainly guided by hydrated protons not by the mass transfer limitation. Hydrolysis of starch was examined using sulfonic acid functionalized Et-HMM-one pot (acid amount = 0.4 mmol/g) and Ph-HMM-graft (acid amount = 0.9 mmol/g) catalysts²¹. In spite of the acidity difference in these catalysts, both yielded similar amount of glucose (\sim 67%) when acid concentration was kept

constant in reaction. Even though, some of the investigators tried to prepare stable materials but, leaching of acid functionality under hydrothermal conditions is a key problem with acid functionalized silica.

4.1.4. Performance of transition metals oxide as catalyst:

Few transition metal oxides were also checked for their activity in C6 sugar synthesis reaction. Sucrose hydrolysis reaction was reported with $\text{SiO}_2\text{-Al}_2\text{O}_3$, $\text{SiO}_2\text{-ZrO}_2$, Nb_2O_5 and $\text{Nb}_2\text{O}_5\text{-PO}_4$ catalysts; wherein $\text{Nb}_2\text{O}_5\text{-PO}_4$ produced the maximum amount (62%) of glucose²³. Very poor activity (\sim 5% glucose formation) of niobic acid ($\text{Nb}_2\text{O}_5\cdot n\text{H}_2\text{O}$) was presented for sucrose hydrolysis²². But, HTiNbO_5 material with exfoliated nanosheet structure has improved the sucrose hydrolysis reaction activity to achieve \sim 42% glucose and fructose yields. Further enhancement in sucrose hydrolysis reaction activity was demonstrated using layered HNbMoO_6 catalyst, which offered complete sucrose hydrolysis with \sim 100% formation of glucose and fructose. It was explained that due to favorable interaction between sucrose and interlayer of HNbMoO_6 , sucrose access acid sites of catalyst very easily and allowed the reaction to proceed in faster rate (rate: 24.1 mmol/g/h, TOF: 12.7/h) compared to HTiNbO_5 catalyst (rate: 2.2 mmol/g/h, TOF: 5.7/h). Moreover, the higher acid concentration (1.9 mmol/g) in HNbMoO_6 helps to attain better catalytic activity than HTiNbO_5 having lower acid concentration (0.4 mmol/g). Eventually, the intercalation ability of sucrose (1.12 mol%/mol catalyst) is higher than that of cellobiose (0.21 mol%/mol catalyst), which clearly reflected in the lower reaction rate of 1.18 mmol/g/h for cellobiose hydrolysis reaction using HNbMoO_6 catalyst. Due to poor intercalation of cellobiose, it is very difficult to hydrolyze β -1,4-glycosidic linkages and thus, hydrolysis of cellulose (polymer) showed only \sim 4% glucose formation. But, use of starch in presence of layered HNbMoO_6 catalyst produces 45% glucose. Another report verified the formation of strongly acidic Nb_3W_7 oxide species in Nb-W mixed oxide catalyst which was suitable for 65% glucose formation from sucrose; but the acid concentration in catalyst was not enough to initiate cellobiose hydrolysis reaction⁴⁵. Silica-protected cobalt spinel ferrite nanoparticle ($\text{CoFe}_2\text{O}_4\text{-SiO}_2$) was used as catalyst for enabling easy separation of magnetic catalyst from reaction solution by the help of magnet⁴⁶. After sulfonic acid functionalization, the catalyst produced 50% of glucose from cellobiose. Although, the catalyst was easily separated after

reaction but couldn't offer similar activity in next run due to leaching of approx. 40% of sulfonic acid groups. The similar magnetic property of Zn-Ca-Fe oxide nano-catalyst was also applied for crystalline cellulose hydrolysis into glucose⁴⁷. In a recent report, $\text{SO}_4^{2-}/\text{TiO}_2$ and $\text{MoO}_3/\text{TiO}_2$ catalysts with both Brønsted and Lewis acid properties were used for cellulose hydrolysis reaction at 90°C⁴⁸. The added acidity in these materials improved the cellulose conversion (25–35%) and glucose yields (10–26%) in comparison to pristine TiO_2 reaction (cellulose conversion: ~21%, glucose yield: ~16%) and non-catalytic reaction (cellulose conversion: ~15%, glucose yield: ~20%). Formation of many other products such as oligomers, 1,6-anhydroglucose, fructose, HMF, formic acid, levulinic acid and lactic acid in addition to glucose were also reported.

4.1.5. Performance of zeolites as catalyst:

For C6 sugar synthesis, zeolite (microporous aluminosilicate) such as HMOR, HUSY, HZSM-5, HY etc. were widely applied because of their high surface area, tunable acidity, hydrophilicity etc. In general, increase in Si/Al ratio in zeolite material improves acidity up to a certain limit as well increase hydrophobicity in zeolite^{49,50}. The enhancement of hydrophobicity in H β zeolite by increasing Si/Al ratio was proven helpful for raise in maltose hydrolysis reaction rate because, hydrophobic zeolite attracts more maltose molecules²⁴. Consequently, higher glucose formation (80%) was detected with H β (Si/Al = 50) zeolite than H β (Si/Al = 12.5) zeolite (43%) under similar reaction conditions. Similarly, HMOR with Si/Al = 12 yielded higher amount of glucose (66%) than Si/Al = 7 (56%). Another report demonstrated hydrolysis of some disaccharides (sucrose, maltose and cellobiose) and poly-saccharides (inulin and starch) into sugars using HY (Si/Al = 15) zeolite⁵¹. Facile adsorption of substrate molecules on catalyst surface improves reaction rate and hence, excess amount of catalyst was used in hydrolysis reaction wherein, some amount of catalyst used for adsorption of saccharides and some amount of catalyst used for catalysis. By virtue of this technique, formation of ~100% glucose and fructose was attained from ~100% sucrose conversion. When inulin was used as substrate, a maximum of 92% fructose formation was evident. Later, use of maltose, cellobiose and starch as substrate in presence of HY zeolite yielded 83–95% of glucose. Zeolite hydrophobicity also has influence in ball milled cellulose hydrolysis reaction in water and thus H β (Si/Al =

75) yielded maximum glucose (13%) than H β (Si/Al = 12), HMOR (Si/Al = 10), and HZSM-5 (Si/Al = 45) zeolites⁵². It should be noted that those zeolites were not very effective in hydrolysis reaction, even after ball milling treatment given to microcrystalline cellulose. However, upon the use of [BMIM]Cl + H₂O solvent system improved glucose formation to ca. 50% from ball milled cellulose in presence of HY catalyst⁵³. The addition of ionic liquid in water effectively solubilizes cellulose, which ultimately increase the rate of reaction. Nevertheless, instability of zeolite under hydrothermal reaction conditions due to leaching of its active components is a big issue to be sorted out before their implementation in sustainable method development^{24,54,55}.

4.1.6. Performance of carbons as catalyst:

Recently, carbon materials have gained its focus as a catalyst or as a support in many biomass transformation reaction due to their large specific surface area, high porosity, excellent electron conductivity and relative chemical inertness⁵⁶. In many reports, carbon materials were surface functionalized with acid sites for application in C6 sugar synthesis reaction. Starch hydrolysis reaction was carried out in presence of sulfonated activated carbon (AC-SO₃H) catalyst having 1.63 mmol/g acid concentration to produce ~90% glucose but the reaction took very long time (~70 h) at 120°C⁵². On the other hand, presence of hydrophobic graphene planes in AC-SO₃H catalyst helps ball milled cellulose to adsorb on catalyst surface and thus 41% glucose was evident at 150°C within 24 h. In order to improve the hydrolysis reaction rate, a carbon material (PVC-AC-673) was prepared by partial carbonization of polyvinyl chloride (PVC) followed by sulfonation using fuming H₂SO₄, where some of the flexible aliphatic hydrocarbons are linked via sp³ bonds to the rigid sp² bonded carbon sheet⁵⁷. This additional flexible carbon network speed-up the diffusion rate of cellobiose molecules through catalyst pores and thus, can easily access sulfonic acid sites (2.4 mmol/g) of catalyst. A maximum of 50% glucose formation from cellobiose hydrolysis was evident at 100°C within 7 h using PVC-AC-673 catalyst. Yet in another work, a carbon material was prepared via partial carbonization of cellulose followed by surface functionalization with fuming sulfuric acid, which end-up with an amorphous carbon material having -SO₃H, -CO₂H and -OH groups²⁵. The presence of surface -OH groups on carbon facilitates strong H-bonding with the saccharides glycosidic

oxygen and thereby helps to adsorb saccharides on catalyst surface. This eventually enhances the access of carbon acid sites (1.5 mmol/g) for hydrolysis of adsorbed saccharides. Because of this phenomenon, cellobiose hydrolysis carried out in presence of carbon catalyst having $-\text{SO}_3\text{H}$, $-\text{CO}_2\text{H}$ and $-\text{OH}$ groups yielded very high amount of glucose (81%) at 90°C within 15 h. The similar influence of catalyst surface adsorption was also valid for hydrolysis reaction of cellohexaose where the substrate undergoes step-wise conversion via cellohexaose \rightarrow cellopentaose \rightarrow cellotetraose \rightarrow cellotriose \rightarrow cellobiose \rightarrow glucose (85%). In another report, the phenomenon of adsorption of substrate on catalyst (carbon material with $-\text{OH}$, $-\text{CO}_2\text{H}$ and $-\text{SO}_3\text{H}$ surface groups) was adopted for hydrolysis of microcrystalline cellulose directly into 4% glucose and 64% oligomers (DP = 2–4)²⁸. It has been claimed that due to cellulose adsorption on carbon catalyst surface the activation energy for hydrolysis reaction was minimized (26.3 kcal/mol with carbon catalyst in contrary to 40.6 kcal/mol with sulfuric acid), which eventually favors better catalytic activity. Microwave heating has influence in cellulose crystallinity reduction and thus was used in cellulose hydrolysis reaction instead of conventional heating⁵⁸. Under microwave heating, a maximum of 20% glucose formation from microcrystalline cellulose hydrolysis was observed in presence of carbon catalysts having $-\text{SO}_3\text{H}$, $-\text{CO}_2\text{H}$ and $-\text{OH}$ groups (BC- SO_3H). Nevertheless, the problem of sulfonic acid group leaching under reaction conditions was reported with this catalyst. Sulfonation to activated carbon (AC) catalyst at various temperature has a big influence on the surface properties of catalyst⁵⁹. It was found that sulfonation carried out at 250°C , prepared a catalyst with higher surface area ($762\text{ m}^2/\text{g}$) and higher $-\text{SO}_3\text{H}$ group concentration (0.44 mmol/g) than the sulfonation carried out at 150°C , 200°C , 280°C and 300°C (surface area = 30–741 m^2/g , $-\text{SO}_3\text{H}$ group concentration = 0.12–0.34 mmol/g). Eventually, better amount of glucose formation (63%) from ball milled cellulose was reported with AC-N- SO_3H -250 catalyst than others (19–58%). In the same report, sulfonated mesoporous carbon (CMK-3- SO_3H) was used to improve glucose formation (75%) from ball milled cellulose hydrolysis. With an aim to improve catalyst stability a sulfonated Si/C nanocomposite was prepared, where incorporation of silica was expected to provide better mechanical and thermal stability to catalyst⁶⁰. Due to favorable cellulose adsorption on catalyst ($\text{Si}_{33}\text{C}_{66}$ -823- SO_3H) surface and by the action of Brønsted acidity

($-\text{SO}_3\text{H}$ groups), 50% of glucose formation was achieved from ball milled cellulose hydrolysis. But, the problem of $-\text{SO}_3\text{H}$ groups leaching from catalyst couldn't be resolved. Mesoporous carbon nanoparticles (MCN) has the ordered aromatic rings, which favors strong CH- π interactions with glucan (glucose polymer) hydrogen leading to glucan adsorption of MCN surface⁶¹. Particularly, long chain glucans preferred to adsorb on MCN surface up to a glucan mass uptake of 30% due to more number of interaction (Fig. 4), which lowers the free energy of adsorption (~ 0.4 kcal/mol with each glucose unit in glucan). This information could be useful for future design of catalyst for cellulose hydrolysis reaction. Lignin derived one dimensional mesoporous carbon fibrous catalyst (HTSACF) was prepared and sulfonated to attain 0.56 mmol/g sulfonic and 0.88 mmol/g total acid sites⁶². The usability of this catalyst was tested for cellulose (isolated from rice straw; crystallinity: 72%) hydrolysis in water at 150°C to obtain 30% glucose from 33% conversion. However, a rapid decrease in catalytic activity was reported when reused might be due to leaching of acid sites.

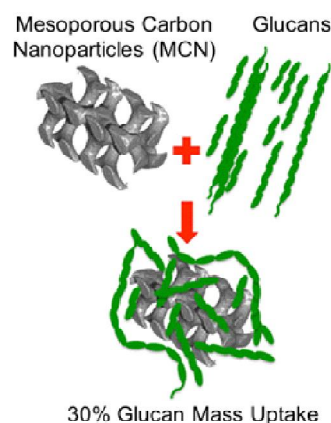


Fig. 4. Long chain glucan adsorption over mesoporous MCN surface due to CH- π interactions⁶¹.

4.1.7. Performance of supported metals as catalyst:

Sugar synthesis as an intermediate chemical from cellulose transformation has been demonstrated in presence of supported metal catalysts by some of the research groups. The basic concept was to generate protons (Brønsted acid sites) in water in presence of supported Pt, Ru, Ni catalysts by hetero cleavage of molecular hydrogen^{63–68}. These *in situ* generated protons acts like mineral acid sites and efficiently hydrolyze glycoside linkages present in cellulose lead-

ing to formation of glucose. However, after formation of glucose (intermediate chemical), those immediately hydrogenated into sorbitol and mannitol under the reaction conditions due to presence of molecular hydrogen and supported metal catalyst. One of the report has proven that the hydrogen adsorption ability of carbon nanotube (CNT) favors its use as support material because the adsorbed hydrogen can now be easily split into protons by metal (Ru) center, which enhanced the catalytic activity⁶⁷. Nevertheless, we have not emphasized more on these processes since; sugars are formed in these reactions as an intermediate chemical.

4.2. Sugars from real biomass feedstock

The methodologies developed for sugar synthesis from various di- and poly-saccharides in presence of solid acid catalysts have discussed above. Hydrolysis of microcrystalline cellulose encounters difficulty because of the presence of strong H-bonding in microcrystalline cellulose^{6,69,70}. To make suitable access of catalyst acid sites by the substrate reaction sites, microcrystalline cellulose was subjected for pre-treatment before using them as substrate. On extrapolation, we may say that direct processing of cellulose from real biomass is very complicated because of biomass complex composition (cellulose + hemicellulose + lignin + others), cellulose crystalline structure and metal impurity in biomass (can reduce catalyst acidity by replacement of protons with metal ions⁵⁴). Very recently, few of the research groups have succeeded to transform hemicellulose part directly from real biomass in presence of solid acid catalyst, where it was presented that the suitable process design can suppress challenges in real biomass conversion^{40,71–73}. For hydrolysis of cellulose and hemicellulose parts of *Eucalyptus* flake and corn cob into water soluble oligosaccharides and sugars (C6 and C5) carbon catalyst having $-\text{SO}_3\text{H}$, $-\text{CO}_2\text{H}$ and $-\text{OH}$ groups were used^{28,74}. As discussed earlier, due to strong adsorption (H-bonding) of substrate on carbon surface and by the catalytic action of Brønsted acid sites, the hydrolysis of saccharide part of real biomass was possible. However, more work is needed on suitable process development for sugar synthesis from real biomass feedstock, prior to commercialization.

4.3. Sugar synthesis via isomerization process

In 1885, Cornelis Adriaan Lobry van Troostenburg de Bruyn and Willem Alberda van Ekenstein has been demonstrated the possibility of isomerization of aldose sugar into

ketose sugar in presence of a base; and the process was termed as Lobry de Bruyn-van Ekenstein transformation⁷⁵. According to the transformation process, Brønsted base catalyst can isomerize glucose (sugar monosaccharide) into fructose (glucose ketonic sugar) via enediol intermediate formation (Fig. 5). As can be seen from Fig. 5, glucose to fructose transformation is a reversible reaction and preferred to remain in equilibrium; hence, an extra driving force in terms of reaction conditions optimization is required to achieve higher fructose yields. In addition to fructose, formation of inverted sugar (mannose) is also possible from glucose reaction with base catalyst (Fig. 5).

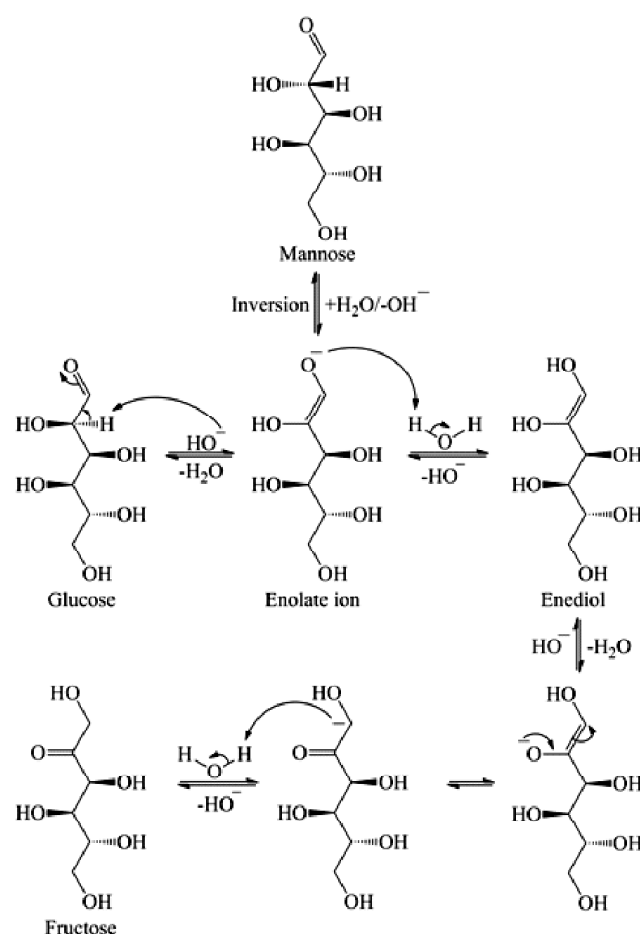


Fig. 5. Reaction pathway for Brønsted base catalyzed transformation of glucose.

In general, use of homogeneous bases (mineral: KOH and NaOH, organic: trimethylamine, morpholine, pyrrolidine, piperidine etc., others: sodium aluminate etc.) leads to the formation of equilibrium amount (17–50%) of fructose due to

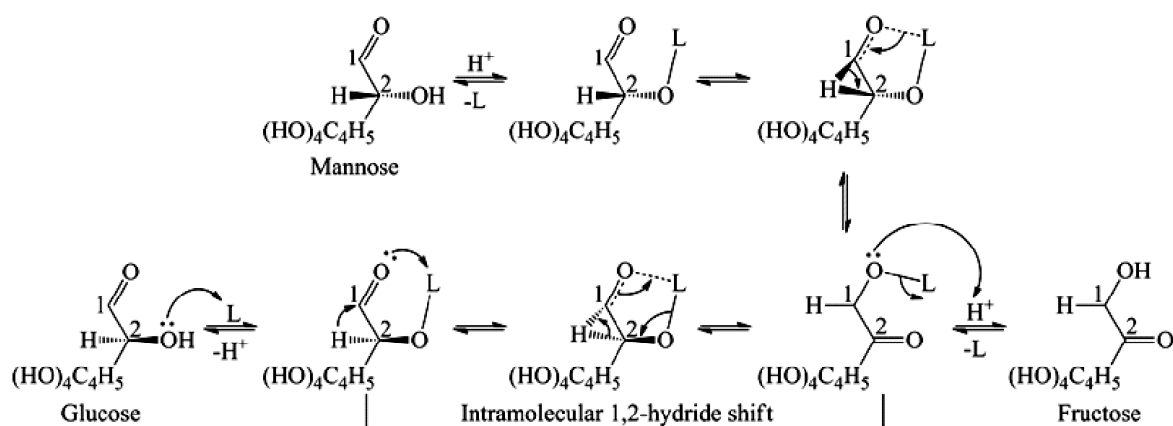
Table 2. Solid Brønsted base catalyzed glucose isomerization into fructose

Sr. no.	Catalyst	T (°C)	t (min)	Conv. (%)	Yield (%)	Ref.
1.	Li, Na, K, Cs incorporated A, X and Y-zeolite	95	–	<34	<22	80
2.	Metallosilicates	100	120	30–56	20–39	81
3.	Aluminate resin	27	–	90	72	82
4.	HT (Mg/Al = 3)	95	–	42	25	80
5.	HT (Mg/Al = 9)	90	20	15	14	83
6.	HT (Mg/Al)	100	180	62	38	84
7.	HT (Mg/Al = 3)	50	–	–	20	85

reversible reaction^{76–79}. Very small amount of mannose (inverted sugar) formation (2–7%) was also observed in these reactions. The solid Brønsted base catalyzed methods for glucose isomerization into fructose are shown in Table 2. Many solid Brønsted bases were also applied to improve fructose production from glucose. A-type, X-type and Y-type zeolites exchanged with various alkali and alkaline earth metals (Li, Na, K, Cs, Ca and Ba) were capable of glucose isomerization (7–34%) into fructose (4–22%)⁸⁰. Slight improvement in fructose formation (20–39%) was presented in presence of titanium silicates, sodium yttrium silicate, alkali calcium silicate and calcium silicate catalysts⁸¹. Use of aluminate resin as catalyst facilitated glucose isomerization reaction into fructose by the action of free hydroxyl ions (OH⁻) liberated in reaction water from catalyst as well aluminate resin can form stable complex with fructose, which can minimize the reverse isomerization of fructose⁸². The influence of catalyst eventually enhanced the fructose formation (72%)

from glucose transformation (90%). Some other research groups have also been used basic Mg/Al hydrotalcite (HT) catalyst for glucose isomerization (15–62%) into fructose (14–38%)^{80,83–85}. It was commented that during preparation HT, formation of magnesium aluminate (MgAl₂O₄) or (M⁺AlO₂⁻) is possible, which cut off the reverse reaction of fructose by formation of stable complex with catalyst and therefore, fructose with better selectivity was achieved. However, it should be noted that using the reported base catalyst very less amount of fructose formation is possible and an attempt to improve fructose yield by increasing reaction temperature was unsuccessful because of favorable degradation reactions⁷⁹.

On the other hand, glucose isomerization reaction can be catalyzed by Lewis acids via intramolecular 1,2-hydride shift mechanism (Fig. 6). This process also allows the C2 epimerization (inversion) of glucose to form mannose. It was proven by the help of NMR study of isotope labelled glucose

**Fig. 6.** Reaction pathway for Lewis acid catalyzed transformation of glucose (Lewis acid is represented by 'L').

that an intramolecular 1,2-hydride shift mechanism is only possible using a Lewis acid catalyst but not the base catalyst⁸⁶. Sn β zeolite generates a partially hydrolyzed Sn framework [(SiO)₃Sn(OH)] in water under the reaction conditions, which favors 1,2-hydride transfer in glucose (conversion = 45%) to form fructose (32%) and epimerization to form mannose (9%) (Table 3)^{86,87}. To further confirm the influence of Sn, another research work has demonstrated the use of Sn incorporated MFI and BEA zeolite in glucose isomerization⁸⁸. Due to larger pore opening in BEA zeolite (7.7 Å), glucose molecule (size = 7.3 Å) can easily access the metal sites located inside zeolite pores and thus offered good activity (glucose conversion = 65%, fructose yield = 34%, mannose yield = 17%) (Table 3). In comparison, diffusion limitation to access Sn-sites in small pore MFI zeolite (5.6 Å) lowers its catalytic activity (glucose conversion = 9%, fructose yield = 4%) (Table 3). In yet another report, simultaneous conversion of glucose into fructose and fructose into 5-hydroxymethylfurfural (HMF) was demonstrated, which was catalyzed by the action of Lewis acid sites and Brønsted acid sites present in SAPO-44 catalyst, respectively³⁸.

Table 3. Solid Lewis acid catalyzed glucose isomerization into fructose

Sr. no.	Catalyst	T (°C)	t (min)	Conv. (%)	Yield (%)	Ref.
1.	Sn-Beta	110	30	45	32	87
2.	Sn-Beta	90	210	65	34	88
3.	Sn-MFI	90	210	9	4	88

5. Conclusions and future scope

The availability of free C6 sugars in natural resources is limited but the demand is high in pharmaceuticals, agricultural, cosmetics and fine chemicals industries. Considering the importance, developed methodologies for C6 sugar synthesis are extensively reviewed here. Plant-derived carbohydrates resources such as disaccharide (maltose, sucrose, and cellobiose) and polysaccharide (starch, inulin, cellulose, and hemicellulose) are profusely available and being carbon neutral resources are utilized for C6 sugar production both in commercial and lab scale processes. Hydrolysis and isomerization are the processes to guide stepwise transformation of these resources into C6 sugars via catalysis. It can be seen that solid catalysts are designed preferably in lab scale to enable safe, economic and environment friendly

processes. Influence of catalyst acid strength, acid amount, acid type (Brønsted/Lewis), surface type (hydrophilic/hydrophobic), extent of absorption over surface, amount of accessible acid sites etc. on C6 production are discussed, based on published works. It is also found that degree of substrate polymerization, energy of substrate absorption over catalyst, crystallinity of substrate, suitable diffusion of substrate through pores of catalyst are vital factors in deciding ease production of C6 sugars. Although, many effective catalytic methodologies for C6 sugar production have been developed mainly from disaccharides and isolated polysaccharides, but those need to be again isolated from real biomass wastes (such as bagasse, grass, wheat straw, rice husks etc.). So, future work should be emphasized for exploitation of real biomass wastes directly and subsequent stable catalyst designing to facilitate commercial implication.

References

1. D. R. Dodds and R. A. Gross, *Science*, 2007, **318**, 1250.
2. D. C. Elliott, in: 'Encyclopedia of Energy', ed. C. J. Cleveland, Elsevier, New York, 2004, Vol. 1, pp. 163-174.
3. P. Gallezot, *Chem. Soc. Rev.*, 2012, **41**, 1538.
4. P. D. Cara, M. Pagliaro, A. Elmekawy, D. R. Brown, P. Verschuren, N. R. Shiju and G. Rothenberg, *Catal. Sci. Technol.*, 2013, **3**, 2057.
5. P. Bhaumik, T. Kane and P. L. Dhepe, *Catal. Sci. Technol.*, 2014, **4**, 2904.
6. P. Bhaumik and P. L. Dhepe, in: 'Biomass Sugars for Non-Fuel Applications', eds. D. Murzin and O. Simakova, The Royal Society of Chemistry, 2015, Vol. 44, Chap. 1, pp. 1-53.
7. H. Braconnot, *Ann. Chim. Phys.*, 1819, **12**, 172.
8. W. L. Faith, *Ind. Eng. Chem.*, 1945, **37**, 9.
9. M. L. Rabinovich, *Cellulose Chem. Technol.*, 2010, **44**, 173.
10. M. Oshima, "Wood chemistry process engineering aspects", Noyes Development Corp., Pearl River, New York, 1965.
11. J.-L. Wertz, O. Bedue and J. P. Mercier, eds., "Cellulose Science and Technology", CRC Press, Taylor & Francis Group, London, 2010.
12. P. Binod, K. U. Janu, R. Sindhu and A. Pandey, in: 'Biofuels', eds. A. Pandey, C. Larroche, S. C. Ricke, C.-G. Dussap and E. Gnansounou, Academic Press, Amsterdam, 2011, Chap. 10, pp. 229-250.
13. T. E. Timell, *Can. J. Chem.*, 1964, **42**, 1456.
14. O. Bobleter, W. Schwald, R. Concin and H. Binder, *J. Carbohydr. Chem.*, 1986, **5**, 387.
15. N. S. Mosier, C. M. Ladisch and M. R. Ladisch, *Biotechnol. Bioeng.*, 2002, **79**, 610.

16. H. Arthur E, in: 'Hydrolysis of Cellulose: Mechanisms of Enzymatic and Acid Catalysis', eds. J. Ross D. Brown and L. Jurasek, ACS, 1979, Vol. 181, Chap. 2, pp. 25-53.
17. J.-P. Franzidis, A. Porteous and J. Anderson, *Conserv. Recy.*, 1982, **5**, 215.
18. I. A. Malester, M. Green and G. Shelef, *Ind. Eng. Chem. Res.*, 1992, **31**, 1998.
19. H. Kraessig, *J. Polym. Sci., Part C: Polym. Lett.*, 1987, **25**, 87.
20. D. Klemm, B. Philipp, T. Heinze, U. Heinze and W. Wagenknecht, in: 'Comprehensive Cellulose Chemistry', Wiley-VCH Verlag GmbH & Co. KGaA, 2004, Vol. 1, Chap. 2.3-2.3.7, pp. 83-129.
21. P. Dhepe, M. Ohashi, S. Inagaki, M. Ichikawa and A. Fukuoka, *Catal. Lett.*, 2005, **102**, 163.
22. A. Takagaki, C. Tagusagawa and K. Domen, *Chem. Commun.*, 2008, 5363.
23. M. Marzo, A. Gervasini and P. Carniti, *Carbohydr. Res.*, 2012, **347**, 23.
24. A. Abbadi, K. F. Gotlieb and H. van Bekkum, *Starch - Stärke*, 1998, **50**, 23.
25. M. Kitano, D. Yamaguchi, S. Suganuma, K. Nakajima, H. Kato, S. Hayashi and M. Hara, *Langmuir*, 2009, **25**, 5068.
26. J. Sauer, H. Horn, M. Haser and R. Ahlrichs, *Chem. Phys. Lett.*, 1990, **173**, 26.
27. P. Bhaumik and P. L. Dhepe, *Catal. Today*, 2015, **251**, 66.
28. S. Suganuma, K. Nakajima, M. Kitano, D. Yamaguchi, H. Kato, S. Hayashi and M. Hara, *J. Am. Chem. Soc.*, 2008, **130**, 12787.
29. N. Mosier, C. Wyman, B. Dale, R. Elander, Y. Y. Lee, M. Holtzapple and M. Ladisch, *Bioresour. Technol.*, 2005, **96**, 673.
30. L. Olsson, M. Galbe and G. Zacchi, in: 'Biofuels', Springer Berlin Heidelberg, 2007, Vol. 108, pp. 41-65.
31. V. B. Agbor, N. Cicek, R. Sparling, A. Berlin and D. B. Levin, *Biotechnol. Adv.*, 2011, **29**, 675.
32. Z. Zhang and Z. K. Zhao, *Carbohydr. Res.*, 2009, **344**, 2069.
33. S.-J. Kim, A. A. Dwiatmoko, J. W. Choi, Y.-W. Suh, D. J. Suh and M. Oh, *Bioresour. Technol.*, 2010, **101**, 8273.
34. X. Qi, M. Watanabe, T. Aida and R. Smith (Jr.), *Cellulose*, 2011, **18**, 1327.
35. K.-i. Shimizu, H. Furukawa, N. Kobayashi, Y. Itaya and A. Satsuma, *Green Chem.*, 2009, **11**, 1627.
36. S. V. d. Vyver, J. Geboers, L. Peng, F. d. Clippel, M. Dusselier, T. Vosch, L. Zhang, G. V. Tendeloo, C. J. Gommès, B. Goderis, P. A. Jacobs and B. F. Sels, *Sustainable Chem.*, 2011, **154**, 129.
37. P. Bhaumik and P. L. Dhepe, *ACS Catal.*, 2013, **3**, 2299.
38. P. Bhaumik and P. L. Dhepe, *RSC Adv.*, 2013, **3**, 17156.
39. M. Yabushita, H. Kobayashi, J. Y. Hasegawa, K. Hara and A. Fukuoka, *ChemSusChem.*, 2014, **7**, 1443.
40. P. Bhaumik and P. L. Dhepe, *RSC Adv.*, 2014, **4**, 26215.
41. M. Cheng, T. Shi, H. Guan, S. Wang, X. Wang and Z. Jiang, *Appl. Catal. B: Environ.*, 2011, **107**, 104.
42. Z. Sun, X. Zhang, S. Wang, X. Li, X. Wang and J. Shi, *RSC Adv.*, 2015, **5**, 94155.
43. Z. Sun, L. Xue, S. Wang, X. Wang and J. Shi, *Green Chem.*, 2016, **18**, 742.
44. J. A. Bootsma and B. H. Shanks, *Appl. Catal. A: Gen.*, 2007, **327**, 44.
45. C. Tagusagawa, A. Takagaki, A. Iguchi, K. Takanabe, J. N. Kondo, K. Ebitani, S. Hayashi, T. Tatsumi and K. Domen, *Angew. Chem. Int. Ed.*, 2010, **49**, 1128.
46. L. Pena, M. Ikenberry, B. Ware, K. L. Hohn, D. Boyle, X. S. Sun and D. Wang, *Biotechnol. Bioprocess Eng.*, 2011, **16**, 1214.
47. Z. Fan, D. Xin, F. Zhen, Z. Hongyan, T. Xiaofei and J. A. Kozinski, *Petrochem. Technol.*, 2011, 4348.
48. R. M. de Almeida, N. J. A. de Albuquerque, F. T. C. Souza and S. M. P. Meneghetti, *Catal. Sci. Technol.*, 2016, **6**, 3137.
49. I. Petrovic, A. Navrotsky, M. E. Davis and S. I. Zones, *Chem. Mater.*, 1993, **5**, 1805.
50. R. M. Ravenelle, F. Schubler, A. D'Amico, N. Danilina, J. A. van Bokhoven, J. A. Lercher, C. W. Jones and C. Sievers, *J. Phys. Chem. C*, 2010, **114**, 19582.
51. C. Moreau, R. Durand, J. Duhamet and P. Rivalier, *J. Carbohydr. Chem.*, 1997, **16**, 709.
52. A. Onda, T. Ochi and K. Yanagisawa, *Green Chem.*, 2008, **10**, 1033.
53. H. Cai, C. Li, A. Wang, G. Xu and T. Zhang, *Appl. Catal. B: Environ.*, 2012, **123-124**, 333.
54. P. Bhaumik, A. K. Deepa, T. Kane and P. L. Dhepe, *J. Chem. Sci.*, 2014, **126**, 373.
55. P. Bhaumik and P. L. Dhepe, *Catal. Rev.*, 2016, **58**, 36.
56. E. Lam and J. H. T. Luong, *ACS Catal.*, 2014, **4**, 3393.
57. S. Suganuma, K. Nakajima, M. Kitano, S. Hayashi and M. Hara, *ChemSusChem*, 2012, **5**, 1841.
58. Y. Wu, Z. Fu, D. Yin, Q. Xu, F. Liu, C. Lu and L. Mao, *Green Chem.*, 2010, **12**, 696.
59. J. Pang, A. Wang, M. Zheng and T. Zhang, *Chem. Commun.*, 2010, **46**, 6935.
60. S. Van de Vyver, L. Peng, J. Geboers, H. Schepers, F. de Clippel, C. J. Gommès, B. Goderis, P. A. Jacobs and B. F. Sels, *Green Chem.*, 2010, **12**, 1560.
61. P.-W. Chung, A. Charmot, O. M. Gazit and A. Katz, *Langmuir*, 2012, **28**, 15222.
62. S. Hu, F. Jiang and Y.-L. Hsieh, *ACS Sustainable Chem. Eng.*, 2015, **3**, 2566.
63. A. Fukuoka and P. L. Dhepe, *Angew. Chem. Int. Ed.*, 2006, **45**, 5161.

64. N. Yan, C. Zhao, C. Luo, P. J. Dyson, H. Liu and Y. Kou, *J. Am. Chem. Soc.*, 2006, **128**, 8714.
65. C. Luo, S. Wang and H. Liu, *Angew. Chem. Int. Ed.*, 2007, **46**, 7636.
66. N. Ji, T. Zhang, M. Zheng, A. Wang, H. Wang, X. Wang and J. G. Chen, *Angew. Chem. Int. Ed.*, 2008, **47**, 8510.
67. W. Deng, X. Tan, W. Fang, Q. Zhang and Y. Wang, *Catal. Lett.*, 2009, **133**, 167.
68. D. S. Park, D. Yun, T. Y. Kim, J. Baek, Y. S. Yun and J. Yi, *ChemSusChem*, 2013, **6**, 2281.
69. A. Brandt, J. Grasvik, J. P. Hallett and T. Welton, *Green Chem.*, 2013, **15**, 550.
70. H. Kobayashi and A. Fukuoka, *Green Chem.*, 2013, **15**, 1740.
71. R. Sahu and P. L. Dhepe, *ChemSusChem*, 2012, **5**, 751.
72. Z. Xu, W. Li, Z. Du, H. Wu, H. Jameel, H.-m. Chang and L. Ma, *Bioresour. Technol.*, 2015, **198**, 764.
73. P. Bhaumik and P. L. Dhepe, *ChemCatChem*, 2017, **9**, 2709.
74. Y. Jiang, X. Li, X. Wang, L. Meng, H. Wang, G. Peng, X. Wang and X. Mu, *Green Chem.*, 2012, **14**, 2162.
75. J. C. Speck (Jr.), *Adv. Carbohydr. Chem.*, 1958, **13**, 63.
76. Y. Z. Lai, *Carbohydr. Res.*, 1973, **28**, 154.
77. A. J. Shaw lii and G. T. Tsao, *Carbohydr. Res.*, 1978, **60**, 327.
78. J. M. De Bruijn, A. P. G. Kieboom and H. van Bekkum, *Starch - Stärke*, 1987, **39**, 23.
79. C. Liu, J. M. Carraher, J. L. Swedberg, C. R. Herndon, C. N. Fleitman and J.-P. Tessonnier, *ACS Catal.*, 2014, **4**, 4295.
80. C. Moreau, R. Durand, A. Roux and D. Tichit, *Appl. Catal. A: Gen.*, 2000, **193**, 257.
81. S. Lima, A. S. Dias, Z. Lin, P. Brandao, P. Ferreira, M. Pillinger, J. Rocha, V. Calvino Casilda and A. A. Valente, *Appl. Catal. A: Gen.*, 2008, **339**, 21.
82. J. A. Rendleman (Jr.) and J. E. Hodge, *Carbohydr. Res.*, 1979, **75**, 83.
83. J. Lecomte, A. Finiels and C. Moreau, *Starch - Stärke*, 2002, **54**, 75.
84. A. Takagaki, M. Ohara, S. Nishimura and K. Ebitani, *Chem. Commun.*, 2009, 6276.
85. A. Tathod, T. Kane, E. S. Sanil and P. L. Dhepe, *J. Mol. Catal. A: Chem.*, 2014, **388-389**, 90.
86. Y. Roman-Leshkov, M. Moliner, J. A. Labinger and M. E. Davis, *Angew. Chem. Int. Ed.*, 2010, **49**, 8954.
87. M. Moliner, Y. Roman-Leshkov and M. E. Davis, *Proc. Nat. Acad. Sci.*, 2010, **107**, 6164.
88. C. M. Lew, N. Rajabbeigi and M. Tsapatsis, *Microporous Mesoporous Mater.*, 2012, **153**, 55.