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Heteropoly acid catalyzed hydrolysis of glycogen to glucose

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ABSTRACT

Complete conversion of glycogen to glucose is achieved by using $H_3PW_{12}O_{40}\cdot nH_2O$ (HPW) and $H_4SiW_{12}O_{40}\cdot nH_2O$ (HSiW) as catalysts for the hydrolysis under optimized hydrothermal conditions (mass fraction of catalyst 2.4%, 373 K and 2 h reaction time). The reusability of the catalyst (HPW) was demonstrated. In addition to carrying out the glycogen hydrolysis in an autoclave, other novel methods such as microwave irradiation and sonication have also been investigated. At higher mass fraction of the heteropoly acids (10.5%), glycogen could be completely converted to glucose under microwave irradiation. Sonication of an aqueous solution of glycogen in the presence of HPW and HSiW also yielded glucose. Thus, heteropoly acids are efficient, environmentally friendly and reusable catalysts for the conversion of glycogen to glucose.

1. Introduction

Increasing demand for transportation fuel is one of the main challenges facing the society today. Alternate fuels, preferably, biofuels can be a substitute to the fast depleting fossil fuels. Moreover, such fuels are environmentally friendly [1,2]. Fuels generated from biological sources like glycogen, starch, biomass (lignocellulosic materials) are termed as biofuels [3–6].

Glycogen is relatively less examined feedstock for biofuels production. Animal remains are currently the major source of glycogen [7]. Glycogen, a biopolymer of glucose, is a better feedstock for glucose production relative to lignocellulosic biomass as it needs no additional pre-treatment. Glycogen has the potential to become a promising alternative to fossil resources for the sustainable production of fuels. The synthesis of glycogen from CO_2 by photosynthesis and its subsequent hydrolysis to glucose with high selectivity makes glycogen an abundant and renewable feedstock for the production of glucose [8].

Methods for producing glycogen in large amounts using CO_2 from the environment are being developed [8–11]. This prompts the need for developing viable methods for the production of fermentable sugars (glucose) from glycogen. The glucose thus generated from glycogen could be converted to bioethanol in a subsequent fermentation reaction using yeast

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[12,13]. As bioethanol is produced from biological sources, it is both environmentally friendly (carbon neutral) and renewable fuel. This makes bioethanol a promising transportation fuel.

Carbohydrate hydrolysis is one of the most widely studied processes: some reactions are being conducted enzymatically, whereas others are carried out chemically. Enzymatic methods are expensive and time consuming. Problems are also associated with the separation and reuse of the enzymes. Chemical methods involve the use of either homogeneous mineral acids or solid acid catalysts [14–16]. The main drawbacks with the chemical hydrolysis processes include: the degradation of glucose to by-products, namely, hydroxyl methyl furfural (HMF), levulinic acid and formic acid, corrosion risk, generation of large amounts of acidic waste water, and also the separation of acids [17–19]. Vigorous research is being carried out to overcome the problems and also to develop a cost effective hydrolysis process for the production of glucose from renewable feedstock and the subsequent fermentation of the sugars to ethanol [20,21].

Recently, Aikawa et al., converted glycogen rich cyanobacterium directly to ethanol (ethanol concentration, 6.5 kg m^{-3}) using amylase expressing *Saccharomyces cerevisiae* yeast in combination with chicken egg white lysozyme [22]. Eventhough, cellulose and starch hydrolysis were extensively investigated [14–19,23], there has been only limited studies on glycogen hydrolysis. With the aid of microwave (MW) irradiation and in the presence of mineral acid (HCl) catalyst glycogen was converted to glucose (62 wt. % yield) [17]. However, HCl is corrosive, and its separation needs further steps.

Heteropoly acids (HPA's) are known as effective homogeneous and heterogeneous solid acid catalysts with industrial applications [24,25]. Unique features of heteropoly acids include: stronger acidity compared to many mineral acids i.e. phosphoric acid, non-corrosive, easy to separate, reusability, fewer side products and less waste generated, if any, it is non-toxic, easy to handle, and greener than conventional acid catalysts [24,26]. HPA's are being employed for the hydrolysis of cellulose [24].

The aim of the current study is to develop an environmentally friendly and fast process for glycogen hydrolysis to produce glucose using solid acid catalysts.

2. Experimental

2.1. Materials

Glycogen from bovine liver was purchased from Sigma-Aldrich Co., (St. Louis, MO, USA). In addition, glycogen synthesized from cyanobacteria was also used for comparative studies. α–D anhydrous glucose 96% and tungstosilicic acid hydrate ($H_4SiW_{12}O_{40}$ nH_2O, HSiW, 99%) were purchased from Sigma-Aldrich Co., (St. Louis, MO, USA). Phosphotungstic acid ($H_3PW_{12}O_{40}$ nH_2O, HPW) was purchased from STREM Chemicals (Newburyport, MA USA). The water used was doubly distilled.

2.2. Glycogen hydrolysis reaction

For glycogen hydrolysis process a stainless steel home-made autoclave of 3 cm^3 volume was used. Typically, 50 mg glycogen and different amounts of HPW were dissolved in 2 cm^3 water and put into the autoclave under ambient conditions. The mass fraction of the catalyst (%) is interpreted as the mass of catalyst (in g) per 100 g of system (reactant, catalyst and water). The autoclave was then placed in a regular air oven for the hydrothermal treatment of glycogen. Reaction parameters such as time of the hydrothermal treatment, temperature of heating, weight ratio of HPW and glycogen were varied to optimize the hydrolysis process.

The glycogen hydrolysis reaction was also carried out under microwave (MW) irradiation. For this purpose a domestic MW oven was modified to have provision for a distillation column passing through the MW oven (for enhanced operation safety). The MW system (Sharp model R390L(S)) also contained a stirring facility that operated during the reaction [27]. The MW oven was operated at 2.45 GHz in a batch mode under air at atmospheric pressure. The output of the applied MW reactor was 1200 W. Reaction parameters such as the weight ratio of HPW and glycogen, MW irradiation time were varied to optimize the hydrolysis process. In addition, the glycogen hydrolysis reaction was also carried out under sonication (Sonics and Materials, VC-600, 20 kHz, 1.27 cm Ti horn at 30% efficiency). In a typical reaction, 200 mg glycogen and different amounts of HPW dissolved in 10 cm^3 water were taken in a sonication flask and sonicated for 1 h–6 h using 180 W power. To prevent the overheating of the reaction, the sonication flask was immersed in a water bath (at 298 K) for cooling. The reaction temperature during the sonication was controlled using a thermocouple at 353 K. For comparison, the glycogen hydrolysis reaction was also carried out under conventional heating employing an oil bath at 353 K for 3 h.

The best reaction conditions identified for glycogen hydrolysis using HPW catalyst were further used for the reactions with HSiW.

The reusability of HPW was investigated. After the reaction run under optimal reaction conditions, the HPW was recovered from the solution by extraction using diethyl ether, followed by its evaporation. The HPW thus regenerated was used for a second run under identical hydrothermal reaction conditions. The reusability of the catalyst was tested twice. The concentration of phosphorous before and after the hydrolysis reaction was determined by inductive coupled plasma (ICP) analysis using ULTIMA JY 2501 instrument.

The progress of the glycogen hydrolysis reaction was monitored using ^{13}C NMR spectroscopic analysis on a Bruker Avance DPX 300 instrument. The conversion of glycogen as well as glucose formation was deduced from ^{13}C NMR spectra. D_2O is used as a solvent. ^{31}P NMR spectra of the fresh and regenerated catalysts in solution state were recorded on a Bruker Avance DPX 400 instrument using D_2O as a solvent.

3. Results and discussion

3.1. Glycogen hydrolysis under hydrothermal reaction conditions

The hydrothermal reaction of glycogen hydrolysis was carried out under various reaction conditions for the production of

glucose. The details of the optimization studies are provided below.

3.1.1. *Effect of reaction time and temperature on the product distribution in the hydrothermal hydrolysis of glycogen*

To evaluate the effect of time of hydrothermal treatment, the glycogen hydrolysis reaction was carried out for 1.5 h, 2 h and 3 h and at a constant temperature of 373 K with 50 mg each of the reactant (glycogen) and the catalyst (HPW) resulting in a mass ratio of 1:1. The autoclave being a closed vessel, the pressure in the autoclave is higher than the atmospheric pressure and the reactions will be, in general, faster. A duration of 2 h was found to be the optimal time where a complete conversion of glycogen exclusively to glucose was observed. The ^{13}C NMR spectrum of the reaction product (hydrolyzate of glycogen) obtained under optimal reaction conditions was depicted in Fig. 1.

Peaks typical of glucose were observed (60.3 (C6), 69.2 (C4), 72.4 (C2), 73.7 (C3), 75.3 (C5), 92 (C1α) and 95.3 (C1β)) in the ^{13}C NMR spectrum (Fig. 1). Moreover, peaks characteristic of glycogen (60.6 (C6), 69.4 (C4), 71.8 (C2), 73.4 (C3), 76.8 (C5), 99.6 (C1) ppm) were absent [17]. Thus the complete conversion of glycogen to exclusively glucose is revealed (Fig. 1). In addition, under the optimum reaction conditions, no by-products like HMF (177 (C1), 161 (C2), 152 (C3), 123 (C4), 110 (C5) and 57 (C6) ppm), levulinic acid (27.9 (C1), 29.1 (C2), 37.7 (C3), 177.4 (C4) and 213.7 (C5) ppm) and formic acid (166.3 ppm) were observed [17,19]. The details of the experimental studies that have led to the deduction of optimum reaction conditions for the hydrolysis of glycogen have been summarized in Table S1A.

Once the time of hydrothermal treatment of 2 h at 373 K was found to be the optimum value, the reaction temperature has been varied (353 K–393 K). The optimum temperature was found to be 373 K at which the complete conversion of glycogen to exclusively glucose was obtained (Table S1B). Thus the optimum reaction conditions were 373 K and 2 h for the hydrothermal treatment.

3.1.2. *Effect of catalyst amount*

The mass ratio of the reactant (glycogen) and the catalyst (HPW) was varied from 4:1, 2:1 to 1:1. ^{13}C NMR spectra of the hydrolyzate of glycogen hydrolysis generated with glycogen and varying amounts of HPW were depicted in Fig. 2.

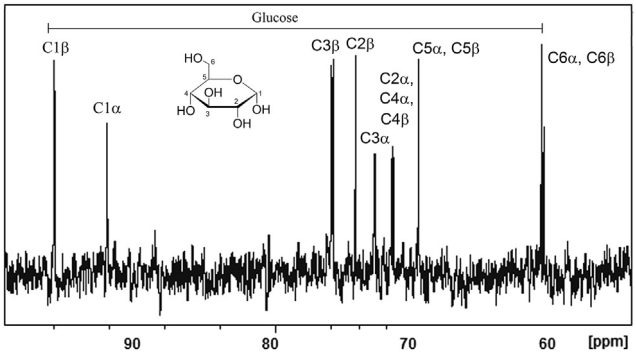

Fig. 1 – ^{13}C NMR spectrum of the hydrolyzate from glycogen hydrolysis generated under optimum hydrothermal reaction conditions (50 mg glycogen, 50 mg HPW, 2 cm^3 water in an autoclave, 2 h, 373 K).

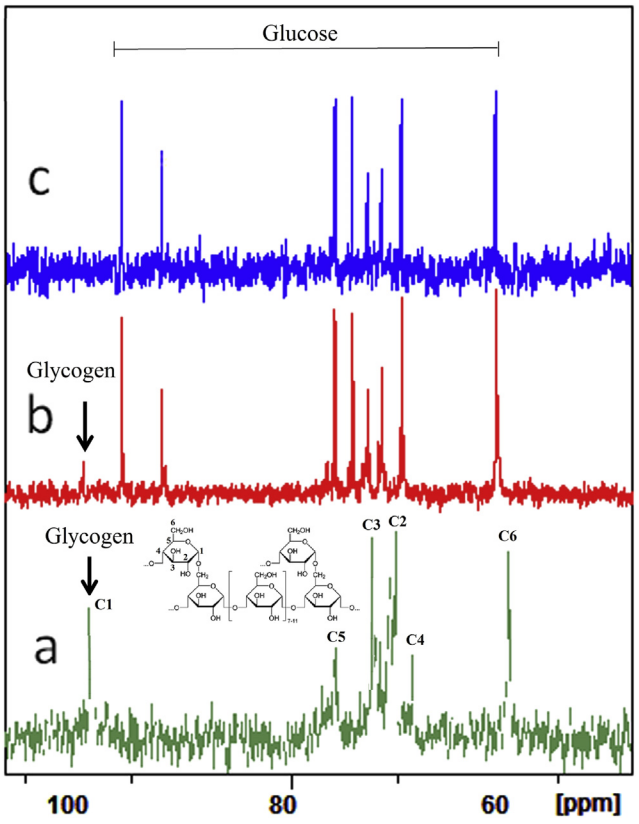

Fig. 2 – ^{13}C NMR spectra of the hydrolyzate from glycogen hydrolysis at different mass ratios of glycogen and HPW: (a) 4:1, (b) 2:1, (c) 1:1. (Reaction time, 2 h and temperature, 373 K).

At a mass ratio of 4:1 (glycogen:HPW) no glucose was formed and peaks typical of glycogen alone were observed (Fig. 2a). When the mass ratio of glycogen to HPW was 2:1, both glycogen and glucose were observed in the hydrolyzate (Fig. 2b). This indicates that the amount of HPW is crucial for the complete conversion of glycogen to glucose. So as to achieve a complete conversion of glycogen, the ratio of glycogen to catalyst was further varied to 1:1. A complete conversion of glycogen to glucose was observed in this case (Fig. 2c). Thus the mass ratio of 1:1 (reactant: catalyst) is the optimum value for the complete conversion of glycogen to glucose. Interestingly, apart from glucose, no other sugars, such as xylose, were found in the hydrolyzate which were inevitably formed in the hydrolysis of lignocellulosic biomass [28]. As glucose could be fermented much faster than xylose, exclusive production of glucose in the hydrolysis of a polymer is an additional advantage of the current process.

3.1.3. *Up-scaling studies*

The viability of the acid hydrolysis process reported herein was tested with higher amounts of glycogen as well. For example, a ten-fold higher batch (amount of glycogen – 500 mg, HPW – 500 mg, water – 20 cm^3) was subjected to hydrothermal treatment for 2 h (373 K) in an autoclave of 50 cm^3 volume. The ^{13}C NMR spectra indicated that the conversion of glycogen is not complete. In the up-scaling reaction the ratio between

volume of autoclave and working solution was 2.4, however in the small batch experiments this ratio was 1.5. Probably, the higher volume ratio caused lower pressure in the vessel compared to the one used for the small batch resulting in an incomplete conversion of glycogen. So as to attain full conversion in the larger batch as well, the reaction time was increased to 3 h and then to 4 h. In spite of the increase in time no complete conversion could be observed. Subsequently, the temperature of the reaction has been increased to 393 K. At 393 K, a complete conversion of the glycogen to glucose was achieved in 4 h. The higher temperatures provided the needed energy for the completion of the hydrolysis of glycogen, which is an endothermic process. The higher temperature is needed because the larger volume led to a decrease in the collision frequency of glycogen and HPW. The up-scaling study was further extended to 1 g of glycogen with 1 g of HPW in 40 cm^3 water. The hydrolysis process was carried out under similar conditions (including the same reaction vessel) as those employed for 500 mg glycogen (4 h of heating, 393 K). Complete conversion of glycogen to glucose was observed (Fig. S1).

3.1.4. *Reusability of the solid acid catalyst*

The reusability of HPW was investigated. After the first run under optimal hydrothermal conditions (1 g glycogen, 1 g HPW, 393 K, 4 h heating), the HPW was recovered from the hydrolyzate. The regenerated catalyst (HPW, 250 mg) was subsequently used for a second run under identical reaction conditions (250 mg glycogen, 393 K, 4 h heating) leading to the formation of glucose. However, the conversion of glycogen is incomplete (Fig. 3). In contrast, the use of fresh HPW under identical conditions lead to the complete conversion of glycogen to glucose. The incomplete conversion of glycogen in the second run is not due to chemical change of HPW but perhaps because of the smaller quantity of catalyst used. By smaller quantity we mean that even though 250 mg of catalyst is regenerated, the catalyst has traces of glucose and the 250 mg material is not exclusively the catalyst. This is evidenced from the fact that a gel-like material and not a fine powder is obtained after the ether extraction of the catalyst at the end of the reaction.

^{31}P NMR spectra of the catalyst before and after the hydrolysis showed identical peak positions for the ^{31}P peak. No shift in the phosphorus peak position is noticed. This indicates that the structural integrity of the catalyst (Keggin type poly anion) is unaltered after the hydrolysis process (Fig. 4).

To prove that HPW is indeed a catalyst and was not consumed in the reaction, a solution containing 20 cm^3 water, 500 mg HPW and 500 mg glycogen was titrated with NaOH before and after the hydrolysis reaction (4 h of heating under hydrothermal reaction conditions). The amount of NaOH needed for the neutralization of acid was found to be 2 mmol in both the cases. Moreover, no change in the amount of phosphorous before and after the hydrolysis reaction was noticed from the ICP analysis. This indicates that the amount of HPW is not altered after the hydrolysis reaction and HPW is indeed a catalyst in the hydrolysis reaction.

The recovery of HPW from the hydrolyzate is poor, probably owing to the ineffectiveness of the ether extraction process. Thus, the HPW used in the reaction is a catalyst and not a reactant owing to the fact that the acidity is maintained at the same level at the end of reaction and the phosphorous amount also remained unchanged.

3.2. *Glycogen hydrolysis under microwave irradiation*

3.2.1. *Effect of time of irradiation on the hydrolysis*

The influence of time of irradiation on the MW assisted hydrolysis of glycogen was tested. Initially, the solution containing 200 mg HPW and 200 mg of glycogen in 10 cm^3 of water was subjected to MW irradiation for 300 s and 600 s. Peaks typical of glycogen alone were detected and no trace of glucose was observed. Thus under the reaction conditions (which are very moderate) there is no conversion of glycogen to glucose. Subsequently, the reaction time was increased to 900 s. The hydrolyzate contained peaks typical of glucose (Fig. S2a). Glucose formation is a result of the higher reaction temperatures obtained during MW irradiation [17].

As a further increase in the time of irradiation for achieving a complete conversion of glycogen is energy intensive, the option of increasing the catalyst amount was preferred.

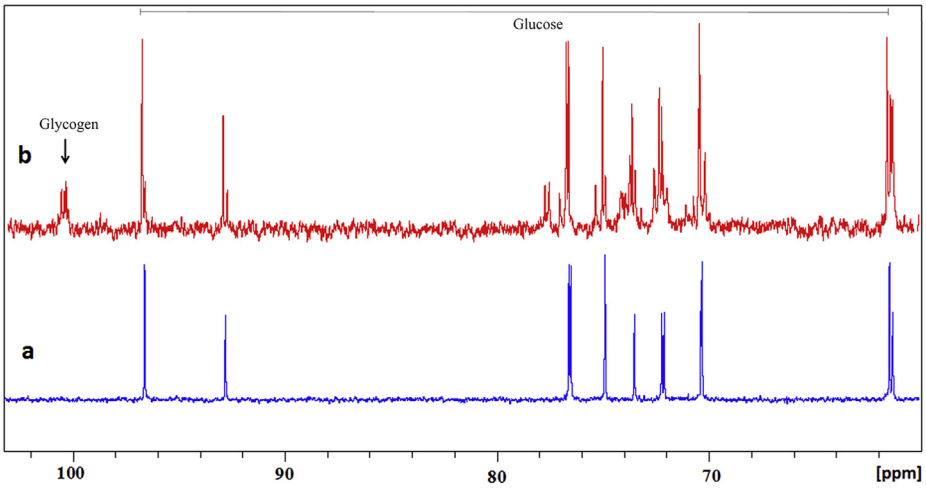

Fig. 3 – ^{13}C NMR spectra of the hydrolyzate from glycogen in two reaction runs: (a) first run: 1 g glycogen, 1 g HPW, 40 cm^3 water, 393 K, 4 h heating, and (b) second run: 250 mg glycogen, 250 mg HPW recovered, 10 cm^3 water, 393 K, 4 h heating.

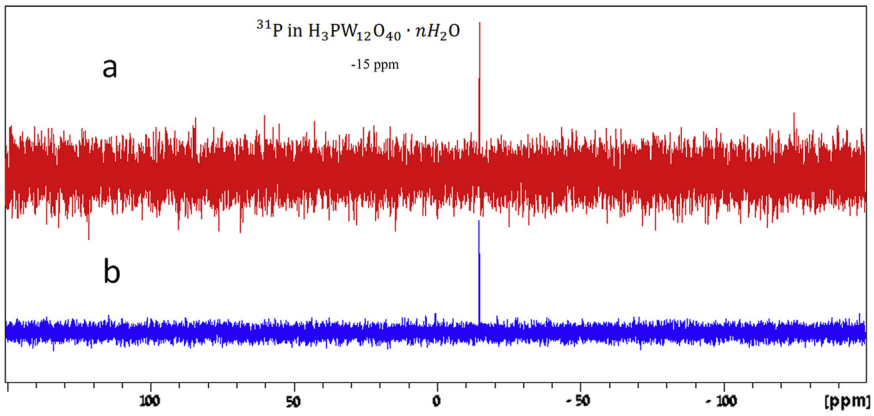

Fig. 4 – ^{31}P NMR spectra of the HPW catalyst before (a) and after (b) hydrolysis reaction.

3.2.2. *Effect of catalyst amount*

The mass fraction of the catalyst was optimized so as to obtain the highest yield of glucose from glycogen. The composition of the products was tested. Different mass fractions of HPW (1.9 %–10.5 %) were examined and 10.5% of catalyst was found to be the optimum with a complete conversion of glycogen to glucose upon MW irradiation of 900 s (Table 1, Fig. S2). The amount of HPW was indeed crucial for the complete conversion of glycogen.

Under aforementioned experimental conditions, in addition to glucose, by-products such as levulinic (major peaks, 27.9 (C1), 29.1 (C2), 37.7 (C3), are marked in Fig. S2c) and formic acids (166.3 ppm was not included in the presented region of the spectrum in Fig. S2c) were formed through the formation and decomposition of HMF [29]. To check this hypothesis, the MW reaction starting with HMF was carried out (120 s, 200 mg HMF, 1.2 g HPW, 20 cm^3 H_2O). The ^{13}C NMR spectra of the reaction product showed the presence of levulinic acid and formic acid. HMF itself was obtained from the hydration of glucose under MW radiation [17]. It is therefore possible that the high temperature generated in the MW oven (hot spots) enable the decomposition of the glucose to the by-products (Table 1).

Unlike, the reaction under the MW irradiation, the hydrolysis reaction under hydrothermal conditions yielded exclusively glucose. But each one of the methods has its own advantages. With the MW process, the time of completion of reaction is much shorter (900 s versus 2 h), whereas with the hydrothermal process the reaction is selective towards glucose. The selective nature of the glycogen hydrolysis under hydrothermal process may be due to the relatively lower mass fraction of catalyst being used (2.4%) for the complete conversion unlike the 10.5% catalyst required under MW conditions.

3.3. *Glycogen hydrolysis under sonochemical reaction*

The hydrolysis of glycogen and the production of glucose were also carried out under ultrasonic irradiation. To the best of our knowledge, the conversion of biomass like glycogen to glucose under sonochemical irradiation was not investigated until now. Initially, solutions containing different amounts of HPW (250 mg–1.5 g) and glycogen (250 mg) in water (10 cm^3) were subjected to sonochemical irradiation for 3 h. The product was analyzed by ^{13}C NMR (Fig. S3) and the results were summarized in Table 2.

It was observed that the intensity of the peak related to glycogen decreased as the amount of HPW increased. The ratio of intensity of glycogen to glucose is an indication of the relative amounts of glycogen and glucose in the product. With

Table 1 – Effect of HPW mass fraction (%) on the hydrolysis of glycogen under microwave irradiation (glycogen – 200 mg, water – 10 cm^3, 900 s).

HPW (%)	Reactant	Reaction products			
	Glycogen	Glucose	LA[a]	FA[b]	HMF[c]
1.9	+[d]	+	–[e]	–	–
3.7	+	+	–	–	–
7.3	+	+	–	–	–
8.9	+	+	–	–	–
10.5	–	+	+	+	+

[a] LA – Levulinic acid.
[b] FA – Formic acid.
[c] HMF – Hydroxy methyl furfural.
[d] '+' present.
[e] '–' absent.

Table 2 – Effect of HPW mass fraction (%) on the hydrolysis of glycogen under sonochemical irradiation (glycogen – 250 mg, water – 10 cm^3, 3 h).

HPW (%)	Reactant	Reaction products			
	Glycogen	Glucose	LA[a]	FA[b]	HMF[c]
2.4	+[d]	+	–[e]	–	–
4.7	+	+	–	–	–
8.9	+	+	–	–	–
12.8	+	+	–	–	–

[a] LA – Levulinic acid.
[b] FA – Formic acid.
[c] HMF – Hydroxy methyl furfural.
[d] '+' present.
[e] '–' absent.

an increase in HPW amount, there is an increase in the glycogen conversion (Fig. S3).

To attain complete conversion of glycogen, the reaction time was increased to 4 h and then to 6 h. Even after 6 h, glycogen conversion is not complete and still a trace of glycogen is observed in the hydrolyzate. Intense peaks typical of glucose were observed (Fig. 5). Apart from glucose, no by-products were observed, indicating the specificity of the sonochemical hydrolysis process.

To be sure that the glycogen hydrolysis is due to the sonochemical effect and not due to the temperature, a control experiment was done. As the temperature of the reaction vessel under sonication is reaching 353 K, the control reaction was carried under identical conditions in a water bath kept at 353 K. Even after 3 h of heating at 353 K there was no trace of glucose in the hydrolyzate and only peaks typical to glycogen were observed. This result proves the significance of sonochemical irradiation for glycogen hydrolysis. During sonochemical irradiation, ultrasonic waves generate acoustic bubbles which collapse at a fast rate [30]. This collapse leads to a local high temperature formed upon the collapse. The importance of the high temperature was already demonstrated for the hydrolysis of glycogen [17].

3.4. *Glycogen hydrolysis catalyzed by tungstosilicic acid*

In order to investigate the performance of other heteropoly acids for glycogen hydrolysis, tungstosilicic (HSiW) acid was also employed as a catalyst. The reactions were carried out (in MW, under ultrasonic waves, and in an autoclave) under optimal conditions obtained with HPW catalyst. The sonochemical reaction was carried out for 3 h. The results were summarized in Table 3. It is evident that HSiW catalyzes the glycogen hydrolysis and leads to glucose formation as observed in the case of HPW catalyst. Moreover, after 3 h of sonication, the conversion of glycogen to glucose with HSiW is complete, whereas with HPW traces of glycogen were still observed even after 6 h. This result shows that the HSiW is a more effective catalyst compared to HPW in this process. Even though HPW is known to be a stronger acid relative to HSiW, the performance of HSiW is better for the glycogen hydrolysis. In addition to acidity, properties like stability of the catalyst may also play a role in the hydrolysis reaction. This result indicates that not only HPW but, heteropoly acids in general can be used as efficient catalysts for glucose production from glycogen. Unlike the previous report on glycogen hydrolysis using HCl as catalyst [17], the advantages of using solid acid catalysts reported herewith include (i) selective glucose production, (ii) reusability of the catalyst and (iii) non-corrosive.

Table 3 – Effect of HSiW on glycogen hydrolysis.

Method	Reactant	Reaction products		
	Glycogen	Glucose	LA[a]	FA[b]
Autoclave[c]	–[f]	+[g]	–	–
Microwave[d]	–	+	+	+
Sonication[e]	–	+	–	–

[a] LA- Levulinic acid.
[b] FA- Formic acid.
[c] glycogen – 50 mg, HSiW – 50 mg, water – 2 cm^3, 2 h, 373 K.
[d] glycogen – 200 mg, HSiW – 1.2 g, water – 10 cm^3, 900 s.
[e] glycogen – 250 mg, HSiW – 1.5 g, water – 10 cm^3, 3 h.
[f] '–' absent.
[g] '+' present.

3.5. *Estimation of energy efficiency of glucose production processes*

Estimation of energy return on energy invested (ERoEI) for glucose production based on hydrothermal vs. microwave and sonication methods were made. The parameter, ERoEI is a measure of the efficiency of a particular chemical process. The ERoEI values corresponding to the production of glucose from glycogen hydrolysis via various routes are calculated based on the following equation considering the highest possible batch in a particular process:

$$\text{ERoEI} = \text{Energy output (kJ/L)/Energy input (kJ/L)}$$ [31].

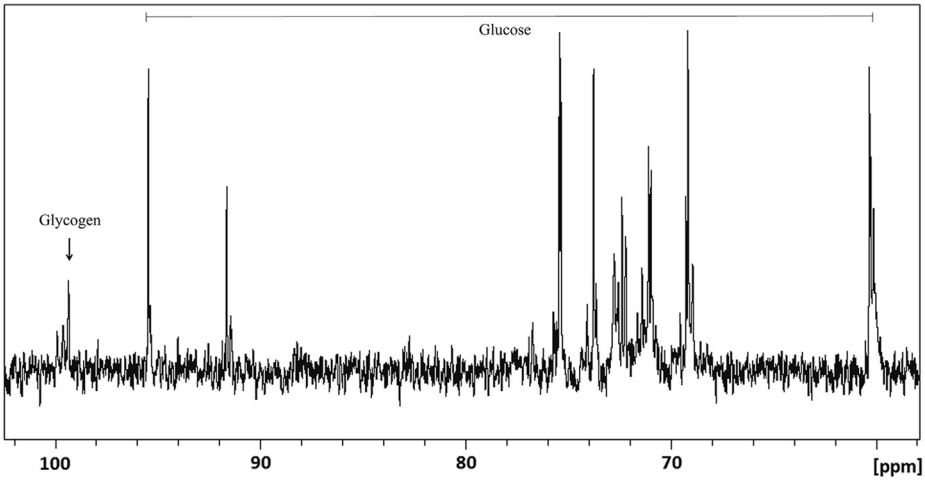

Fig. 5 – ^{13}C NMR spectra of the reaction product of glycogen hydrolysis (250 mg) carried out 6 h upon sonochemical irradiation (12.8% mass fraction of HPW, 10 cm^3 water).

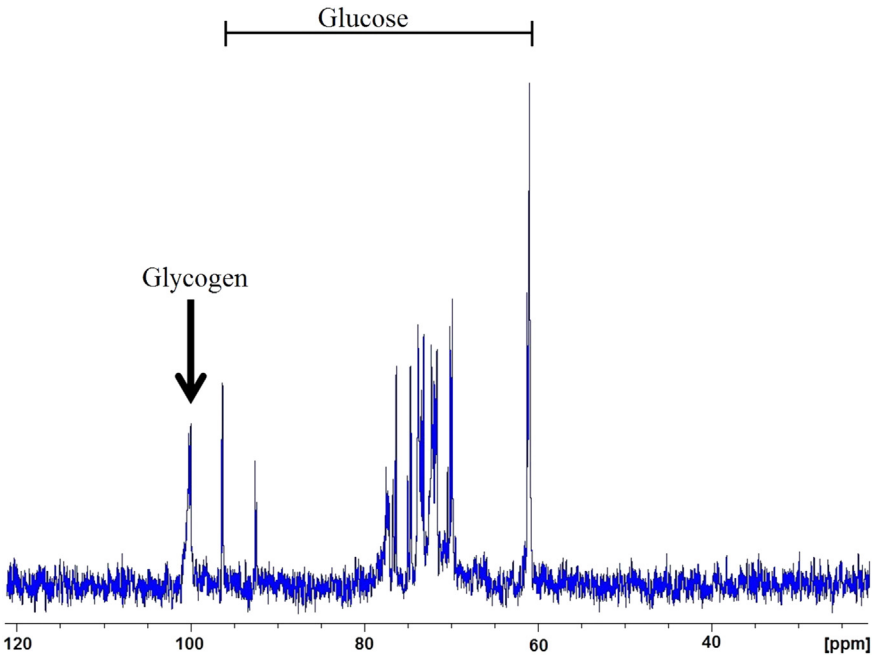

Fig. 6 – ^{13}C NMR spectra of the reaction product of biological glycogen hydrolysis (500 mg) carried out for 120 s upon microwave irradiation (500 mg of HSiW, 10 cm^3 water).

The details of ERoEI calculations were summarized in Table S2 (supporting material).

The ERoEI values corresponding to hydrothermal, sonication and microwave based glucose production processes were 1.3, 1.8 and 1.1 respectively implying that the three processes used were energetically efficient. The order of energetic feasibility of hydrolysis process via various routes is: sonication > hydrothermal > microwave. Even though the value of ERoEI is the least (close to unity) in a microwave irradiation based process, the process is appealing as it is faster.

3.6. *Hydrolysis of biological glycogen*

To evaluate the generality of the hydrolysis process, the methodology was extrapolated to the glycogen synthesized from cyanobacteria. Typical batch comprise of subjecting 500 mg glycogen, 500 mg HSiW and 10 cm^3 water to microwave irradiation (120 s). ^{13}C NMR spectrum of the hydrolyzate showed the formation of glucose (Fig. 6). In addition to glucose, peak typical of glycogen is also observed indicating that the glycogen conversion is not complete. An increase in the irradiation time to 600 s lead to the complete conversion of glycogen. Thus, glycogen from cyanobacteria is a renewable feedstock for the production of glucose.

4. Conclusion

Glycogen from bovine liver as well as from cyanobacteria has been converted to glucose in an acid catalyzed hydrolysis process. Microwave irradiation, sonication and hydrothermal pathways for glucose production were examined. Heteropoly acids were found to be green and reusable solid acid catalysts for glycogen hydrolysis. The glycogen hydrolysis process developed is selective, fast and green. Thus glycogen is a potential feedstock for the production of glucose.

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Appendix A. Supplementary data

Supplementary data related to this article can be found at http://dx.doi.org/10.1016/j.biombioe.2015.02.036

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