



Selective conversion of starch to glucose using carbon based solid acid catalyst



Vijay Bhooshan Kumar ^a, Indra Neel Pulidindi ^a, Aharon Gedanken ^{a, b, *}

^a Department of Chemistry and Bar-Ilan Institute for Nanotechnology & Advanced Materials, Bar Ilan University, Ramat-Gan 52900, Israel

^b National Cheng Kung University, Department of Materials Science & Engineering, Tainan 70101, Taiwan

ARTICLE INFO

Article history:

Received 24 August 2014

Accepted 30 December 2014

Available online

Keywords:

Carbon supported heteropoly acid

Glucose

Hydrolysis

Hydrothermal reaction

Starch

ABSTRACT

Activated carbon supported silicotungstic acid is used as catalyst for the hydrolysis of starch to glucose. The selectivity of the hydrothermal process for glucose production is demonstrated. Byproducts such as levulinic and formic acids are not formed. Separation of the catalyst is easy, and the catalyst reusability is demonstrated in five consecutive reaction runs. No appreciable loss in activity and selectivity of the catalyst is observed even after 5 consecutive reaction runs. Leaching of the heteropoly acid into the reaction medium is not observed. The yield of glucose (94 wt. %) is close to the theoretical yield (111 wt. %) possible from starch. Thus the glucose production process is atom efficient and green.

© 2015 Elsevier Ltd. All rights reserved.

1. Introduction

A trade-off between new energy sources and clean environment is the problem facing mankind. Energy independence and security are the prime priorities of many nations in the current world. Conventional energy sources are limited and non-renewable. Renewable and environmentally benign energy sources are inevitable [1]. The biomass rich in starch and cellulose is abundant in nature and forms a sustainable source of energy. The objective of this research is to selectively convert starch to glucose in an energy efficient and environmentally benign way.

Starch is the main component of several biomass, and is one of the most abundant renewable sources on earth. Starch is present in a wide variety of agricultural and staple food wastes such as potatoes, corn, rice, wheat and pasta. Chemically starch is made up of amylose (20–25 %, 1, 4- α -linked glucosyl units in linear form, water insoluble), and amylopectin (75–80 %, 1, 6- α -linked branched, water soluble).

Euis Hermiati et al. reported the conversion of starch (cassava pulp and tapioca flour) to glucose using microwave irradiation for 5 min at high temperature (200–220 °C). Use of activated carbon

was reported to suppress but not completely eliminate the formation of byproducts [2]. Kobasyashi et al. used simple activated carbon with trace amount of HCl to produce glucose from cellulose and the vicinal carboxylic and phenolic groups played a synergistic catalytic role for the hydrolysis reaction [3]. Divya Nair et al., produced glucose (yield, 70.5%) from cassava starch factory residue (CSFR) using a combination of hydrothermal pretreatment followed by enzymatic saccharification [4].

Orozco et al., hydrolyzed starch using hot compressed water in the presence of high pressure CO₂ to produce glucose (yield, 0.548 kg/kg starch) and the glucose was subsequently used for the production of biohydrogen. Hydroxy methyl furfural (HMF) was found to be a byproduct during the hydrolysis process which is a fermentation inhibitor. Activated carbon was used to effectively remove HMF from the hydrolyzate prior to the fermentation of glucose to biohydrogen [5]. Namchot et al., used sulphonated carbon catalyst derived from lignin for the hydrolysis of starch with a total reducing sugar yield of 96.5 wt. % [6]. Yamaguchi et al., used carbon based solid catalyst bearing acidic functional groups (–COOH, phenolic OH and SO₃H) [7].

Enzymatic [8–13] as well as acid [14–20] hydrolysis methods have been extensively investigated for the production of glucose from starch. Enzymatic hydrolysis of starch is currently the preferred method in the industrial sector, because of the high hydrolytic yields obtainable under mild conditions despite the cost of the enzyme production. The enzymatic process is also preferred because chemical hydrolysis leads to environmental and

* Corresponding author. Department of Chemistry and Bar-Ilan Institute for Nanotechnology & Advanced Materials, Bar Ilan University, Ramat-Gan 52900, Israel. Tel.: +972 3 5318315; fax: +972 3 7384053.

E-mail address: gedanken@mail.biu.ac.il (A. Gedanken).

equipment corrosion problems as well as the costs associated with concentrated acids and post-hydrolysis neutralization [21,22]. In contrast, hydrothermal hydrolysis based on solid acid catalysts is an environmentally benign method which has been the focus of current research [23,24].

Heteropoly acids are unique solid acid catalysts which are environmentally friendly and easy to handle [25]. Heteropoly acids catalyze a variety of chemical reactions, namely, hydrolysis, condensation, etherification, esterification, transesterification, hydration, dehydration, cyclization, isomerization, dealkylation and alkylation. In most of the cases, heteropoly acids were found to exhibit superior performance compared to conventional acids like *p*-toluene sulphonic acid, HCl, H₂SO₄ and AlCl₃. Owing to the potential of heteropoly compounds, Misono et al., reviewed the developments in their catalytic applications [26]. Anderson et al., demonstrated the potential of H₃PW₁₂O₄₀ (HPW)/MCM-41 catalyst for the acid catalyzed conversion of 1, 3, 5 triisopropyl benzene and found that 23 wt.% loading of the active component was the optimum value [27]. HPW exhibited exceptionally high activity for the synthesis of diphenyl methane compared to conventional mineral acids [28]. Izumi et al., demonstrated the highly active and selective nature of the heteropoly acids for the acetolysis of cyclic ethers (furan, THF, 2-methyl furan, 1, 4 dioxane) compared to either H₂SO₄ or *p*-toluene sulphonic acid [29].

To the best of our knowledge, the use of carbon-supported heteropoly acid as a catalyst for the selective conversion of starch to glucose has not been reported. Carbon supported heteropoly acids are environmentally friendly and reusable. Thus, the focus of the current investigation is to develop an economically viable and environmentally friendly chemical process for the production of glucose from starch using a HSiW/C catalyst under hydrothermal conditions. The aim of the current work is to design a selective, green, reusable and economically feasible solid acid catalyst for glucose production from starch. The novelty of the work involves the use of inexpensive activated carbon as support for silicotungstic acid in designing the solid acid catalyst for the exclusive production of glucose.

2. Experimental

2.1. Chemical reagents

Potato starch and Silicotungstic acid (H₄SiW₁₂O₄₀ nH₂O) ($\geq 99.9\%$), activated carbon (Norit CA1, from wood, chemically activated, powder) were purchased from Sigma Aldrich Ltd, Israel. All reagents were used without further purification. Double distilled water was used as a solvent.

2.2. Preparation of catalyst

Wet impregnation method is used for the preparation of activated carbon-supported heteropoly acid (20 wt. %) catalyst [30]. The method comprises of taking 1 g HSiW in 35 mL distilled water in a 250 mL beaker to which 4 g activated carbon (C) is added under stirring conditions at room temperature for 72 h. Subsequently, the supported catalyst is obtained by filtering the excess water. The residue is dried in an air oven at 100 °C overnight. The filtrate is analyzed for the presence of HSiW (if any) using UV–Vis spectrophotometry (Cary 100 Scan Varian). Based on the intensity of the peak at 265 nm which is typical of the heteropoly anion, in the filtrate, the amount that is not loaded on the carbon is found and subtracted from the initial HSiW used for catalyst preparation. The HSiW content in the activated carbon supported catalyst was found to be 19.5 ± 0.5 wt. %.

2.3. Hydrolysis of potato starch

Typical starch hydrolysis process comprised by taking a known amount of potato starch (0.2–1.0 g), of the catalyst, (HSiW/C, 0.2–2 g), 20 mL of water. The mixture was placed in a home made stainless steel autoclave with teflon lining inside. Hydrothermal treatment was carried out for 2–4 h at 373–423 K. The reaction conditions, like the reaction time, wt./wt. ratio of the reactant and the catalyst, were varied so as to improve the starch conversion and the yield of glucose. The catalyst is separated from the reaction products by filtration through a Whatman® (150 MM Φ) filter paper. The hydrolyzate obtained in each case was analyzed by ¹³C NMR (on a Bruker Avance DPX 300 instrument using D₂O as a solvent) to examine the reaction products [31]. The amount of glucose in the hydrolyzate was also analyzed using a non-enzymatic method based on the *insitu* generation of carbon nanoparticles from the glucose in the analyte [32].

2.4. Characterization of catalyst

The structural stability of heteropoly anion on the supported carbon was analyzed using FT-IR spectroscopy (Bruker Tensor 27). The catalyst (HSiW/activated carbon) was further analyzed after the hydrolysis reaction so as to ensure that the heteropoly acid is not decomposed. To evaluate the surface morphology of the catalyst, Scanning electron microscopy (SEM) analysis was performed on FEI Megallon 400L microscope. Elemental analysis was performed by the energy dispersive X-ray spectroscopy (EDS). UV–Vis experiments were conducted with Cary 100 Scan Varian. XPS analysis was conducted with an Omicron 95 Nanotechnology XPS system, (X-ray source: Al K α , 1486.6 eV).

3. Results and discussion

3.1. Characterization of HSiW/activated carbon catalyst

XPS provides an authentic evidence for the presence of a particular molecular species in a given analyte. The survey scans of the XPS of HSiW (pure) and HSiW/activated carbon (fresh catalyst and the catalyst at the end of the hydrolysis) were shown in (Supplementary content, Fig. S1). Peaks characteristic of the heteropoly anion (W (VI)) were seen for pure HSiW (532.8 eV for O1s and 35.9 eV for W 4f) as well as for the carbon supported catalyst (fresh and used) [30]. XP spectra of the W 4f region of pure and supported HSiW were depicted in Fig. 1. A well resolved spin-orbit doublet at the BE values of 35.9 and 38.1 eV in the case of pure HSiW attributable to the W 4f_{7/2} and W 4f_{5/2} corelevels respectively indicative of W(VI) species is observed. Even in the supported system, similar pattern was noticed with a spin-orbit doublet but at a slightly lower BE values. These slight shifts could be attributed to the metal (W) – support (activated carbon) interaction [33,34].

The surface morphology and the elemental composition of the HSiW/C catalyst were shown in Fig. 2. Loading of heteropoly acid (HSiW) on flakes of activated carbon, with irregular shapes, was confirmed by the presence of W and Si through EDS analysis. The EDS spectrum and the corresponding elemental composition (C, O, Si, W) were shown in the inset of Fig. 2. The symbols K and M in the EDS spectrum correspond to the respective atomic shells from which the X-ray emission takes place.

The structural integrity of the active component (HSiW) upon supporting on activated carbon was examined using FT-IR. FT-IR analysis yields a finger print of bands typical of the W–O and Si–O vibrations in the Keggin type poly anion, [SiW₁₂O₄₀]⁴⁻. The poly anion structure comprised of edge- and corner-sharing WO₆ octahedra linked to the central SiO₄ tetrahedra [35]. The FT-IR spectra of

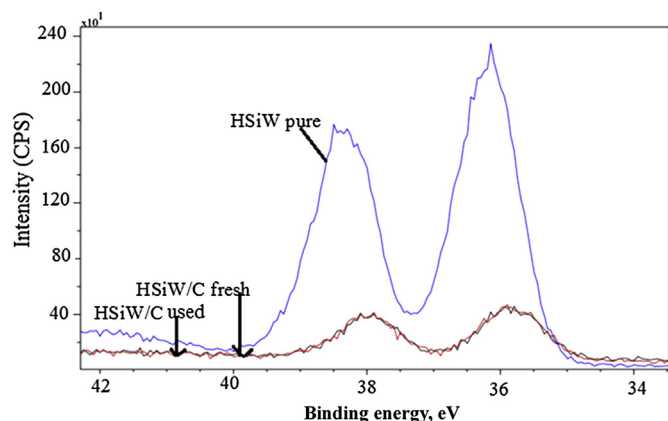


Fig. 1. XPS of the W 4f region of HSiW pure (blue), HSiW/C fresh (black), HSiW/C regenerated (red). (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

HSiW (pure) and HSiW/C (fresh and used) were shown in Fig. S2. The presence of four consecutive bands in the region of 800–1100 cm^{-1} confirmed the presence of undegraded heteropoly anion on the activated carbon surface [36].

3.2. Hydrolysis of starch

HSiW/C (19.7 wt.%) catalyst was exploited for the selective conversion of starch to glucose under hydrothermal reaction conditions. The reaction temperature, reaction time, optimal amount of catalyst and reusability of the catalyst were evaluated.

3.2.1. Optimization of reaction temperature

Starch hydrolysis was carried out at three different reaction temperatures (373, 393, and 423 K) for 4 h. The catalyst from the reaction product was separated by simple filtration as the catalyst was in solid form. The ¹³C NMR spectra of the hydrolyzate (filtrate) obtained in the reaction at 373, 393 and 423 K were shown in Fig. 3. Even though peaks typical of glucose (60.6 (C6), 69.5 (C4), 72.7 (C2), 75.7 (C3), 75.8 (C5) and 95.8 (C1)) were observed in the hydrolyzate obtained at 373 K, an additional peak at 100 ppm typical of starch was noticed. This indicates the presence of unreacted starch in the

hydrolyzate in addition to the reaction product, glucose. Interestingly, apart from glucose no other byproducts like HMF, levulinic acid and formic acid were observed indicating the selective nature of the HSiW/C catalyst. To achieve complete conversion of starch, the reaction temperature was raised from 373 to 393 K. But traces of starch (peak at 100 ppm) were still found. At 423 K, the hydrolyzate showed no indication of the presence of starch and the peaks characteristic of glucose alone are observed in the ¹³C NMR spectrum (Fig. 3). Thus 423 K is the optimum reaction temperature for the conversion of starch exclusively to glucose under hydrothermal reaction conditions with HSiW/C catalyst.

3.2.2. Optimization of reaction time

After finding the optimum reaction temperature for the complete conversion of starch to glucose to be 423 K, the effect of reaction time on the starch hydrolysis was studied. The hydrolysis of starch was carried out at 423 K for 2 and 4 h with HSiW/C catalyst. The signal typical of starch (100 ppm) is observed in the ¹³C NMR spectrum of the hydrolyzate after 2 h, but disappeared after 4 h (Fig. 4). The selective nature of the catalyst is reflected by the presence of only glucose peaks when the hydrolysis was carried out at 423 K for 4 h. Glucose formed from starch was not further degraded to the common degradation products, namely, HMF, levulinic acid and formic acid. Control experiment (hydrolysis of starch) was also carried out at 423 K for 4 h without any added catalyst. In this case, peaks characteristic of starch alone were observed and no trace of glucose was visible.

3.2.3. Optimization of catalyst amount

After finding the optimum conditions of reaction temperature and time for the selective conversion of starch to glucose, further studies were done on evaluating the minimum amount of catalyst required for the complete conversion of starch to glucose. Different ratios (1:5, 1:2.5 and 1:1 wt./wt.) of reactant (starch) and catalyst (HSiW/C) were used for the hydrolysis reaction (423 K, 4 h). The hydrolyzate obtained in each case was analyzed by ¹³C NMR as shown in Fig. S3. Interestingly even at a low catalyst (HSiW/C) amount complete conversion of starch to exclusively glucose is achieved. Thus the optimum ratio of substrate to catalyst was 1:1.

The reaction could be further scaled up to 1.0 g batch of the substrate and complete conversion of starch to glucose was achieved under optimum reaction conditions (423 K; 4 h; 1:1 (wt./wt. ratio of substrate to catalyst)) (Fig. S4).

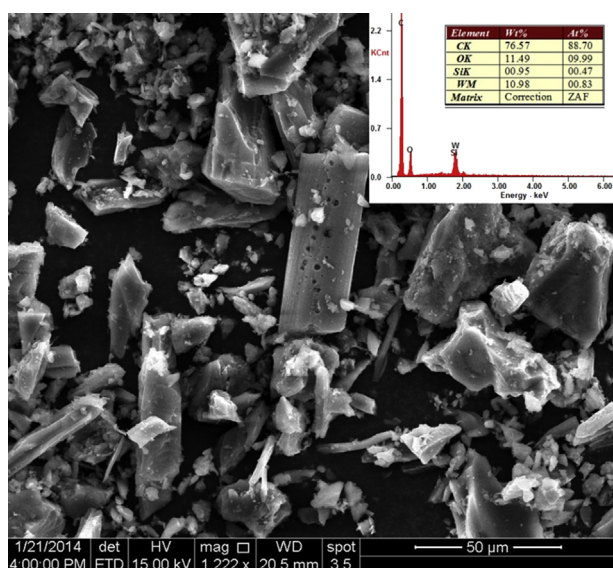


Fig. 2. SEM image of HSiW/activated carbon (Inset: EDX spectrum).

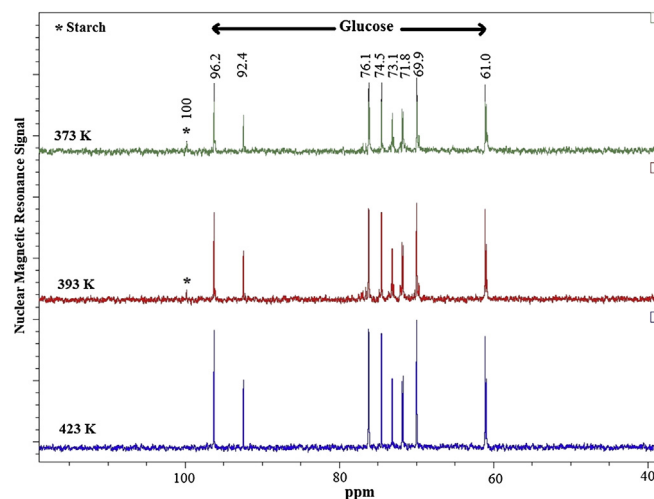


Fig. 3. ¹³C NMR spectra of the hydrolyzate obtained from starch hydrolysis at 373, 393, 423 K (Starch – 0.2 g; HSiW/C – 0.5 g; H₂O – 20 mL).

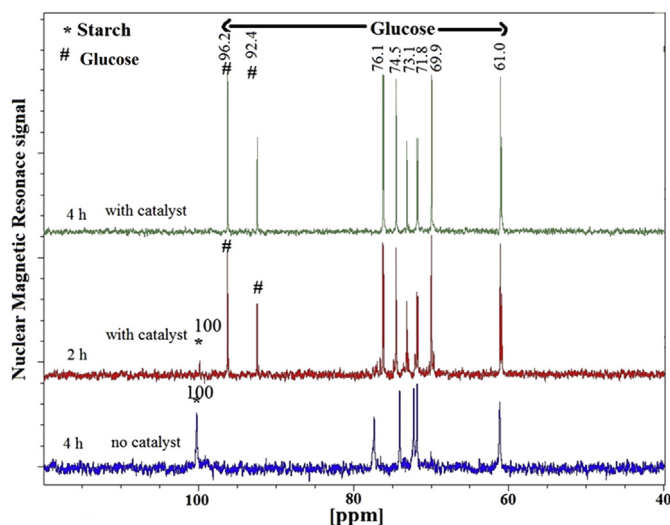


Fig. 4. ^{13}C NMR spectra of the hydrolyzate obtained from starch hydrolysis at different substrate to catalyst ratios (wt./wt.) (Starch – 0.2 g; HSiW/C – 0.2–1.0 g; H_2O – 20 mL; 423 K, 4 h).

3.2.4. Reusability of HSiW/C catalyst

The reusability of the HSiW/C was tested for five reaction runs under optimal reaction conditions. To reduce the loss of catalyst during separation and drying, the reaction product obtained in each case was separated from the catalyst by centrifugation. To the catalyst remaining as residual solid in the centrifugation tube fresh starch and water were added. The contents were transferred into the hydrothermal reactor and the reusability of the catalyst was evaluated. The glucose yield obtained in each cycle for five successive reactions was shown in Fig. 5. The glucose yield in each case was above 90 wt. %. The theoretical yield of D-glucose expected from starch is equal to 111 wt. % [37].

The effective reusability of the HSiW/C was attributed to strong binding of the heteropoly anions to the activated carbon support by strong metal-support interaction. This was further verified by evaluating if there was any leaching of the active component into the reaction medium during the hydrolysis reaction. The UV–vis spectrum of the reaction product from the fresh catalyst was shown in Fig. S5. No peak at 265 nm which was typical of the heteropoly anion was observed in the hydrolyzate indicating the

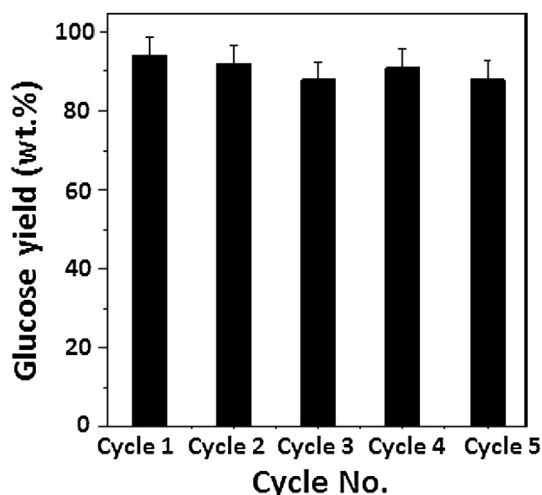


Fig. 5. Plot of glucose yield Vs reaction cycles (Starch – 0.5 g; HSiW/C – 0.5 g; H_2O – 20 mL; 423 K, 4 h).

absence of leaching of HSiW into the reaction medium. The reaction products obtained from each of the five reaction runs were analyzed by ^{13}C NMR (Fig. S6). Peaks characteristic of glucose alone were observed in the hydrolyzate with the fresh as well as the catalyst regenerated for four times. Moreover, the starch conversion was complete. Thus a reusable, active and selective catalyst for the hydrolysis of starch to glucose was designed. Heteropoly acid based industrial processes like hydration of olefins, oxidation of methacrolein and polymerization of tetrahydrofuran have already been commercialized [38]. Since the current process of glucose production from starch utilizes carbon supported heteropoly acids at modest loadings (≈ 20 wt. %) of active component (HSiW), the catalyst is cost effective. Activated carbon is abundantly available and relatively cheap. In addition, the use of activated carbon as support for HSiW facilitated selective production of glucose from starch. Owing to these specific features of the catalytic process industrial adoptability of the catalyst for practical utility is possible.

4. Conclusion

Industrial scale conversion of biomass to glucose is much awaited. Successful conversion of starch exclusively to glucose in an atom and energy efficient way using a heteropoly acid catalyst is demonstrated. The yield of glucose (94 wt. %) obtained is close to the theoretical yield (111 wt. %) possible from starch. The new catalyst (HSiW/C) designed and demonstrated for starch conversion could be a possible substitute to enzymes for glucose production from starch. The selectivity of the catalyst is demonstrated with the absence of products such as HMF, levulinic acid and formic acid.

Acknowledgments

Gedanken thanks the Israel Science Foundation (ISF) for supporting the research via a grant 12/586 and the Ministry of Science and Technology (MOST) for grant number 3-9802.

Appendix A. Supplementary data

Supplementary data related to this article can be found at <http://dx.doi.org/10.1016/j.renene.2014.12.070>.

References

- [1] Pulidindi IN, Kimchi BB, Gedanken A. Can cellulose be a sustainable feedstock for bioethanol production? *Renew Energy* 2014;71:77–80.
- [2] Hermiatia E, Azum J, Tsubaki S, Mangunwidjaj D, Sunarti CT, Suparno O, et al. Improvement of microwave-assisted hydrolysis of cassava pulp and tapioca flour by addition of activated carbon. *Carbohydr Polym* 2012;87:939–42.
- [3] Kobayashi H, Yabushita M, Komanoya T, Hara K, Fujita I, Fukuoka A. High-yielding one-pot synthesis of glucose from cellulose using simple activated carbons and trace hydrochloric acid. *ACS Catal* 2013;3:581–7.
- [4] Divya Nair MP, Padmaja G, Moorthy SN. Biodegradation of cassava starch factory residue using a combination of cellulases, xylanases and hemicellulases. *Biomass Bioenergy* 2011;35:1211–8.
- [5] Orozco RL, Redwood MD, Leeke GA, Bahari A, Santos RCD, Macaskie LE. Hydrothermal hydrolysis of starch with CO_2 and detoxification of the hydrolysates with activated carbon for bio-hydrogen fermentation. *Int J Hydrogen Energy* 2012;37:6545–53.
- [6] Namchot W, Panyacharay N, Jonglertjunya W, Sakdaronnarong C. Hydrolysis of delignified sugarcane bagasse using hydrothermal technique catalyzed by carbonaceous acid catalysts. *Fuel* 2014;116:608–16.
- [7] Yamaguchi D, Hara M. Starch saccharification by carbon-based solid acid catalyst solid state sciences, 12; 2010. p. 1018–23.
- [8] Díaz MJ, Cara C, Ruiz E, Pérez-Bonilla M, Castro E. Hydrothermal pre-treatment and enzymatic hydrolysis of sunflower stalks. *Fuel* 2011;90(11):3225–9.
- [9] Baum A, Agger J, Meyer AS, Egebo M, Mikkelsen JD. Rapid near infrared spectroscopy for prediction of enzymatic hydrolysis of corn bran after various pretreatments. *New Biotechnol* 2012;29:293–301.

- [10] Cinelli BA, Lopez JA, Castilho LR, Freire DMG, Castro AM. Granular starch hydrolysis of babassu agroindustrial residue: a bioprocess within the context of biorefinery. *Fuel* 2014;124:41–8.
- [11] de Freitas AC, Escaramboni B, Carvalho AFA, de Lima VMG, de Oliva-Neto P. Production and application of amylases of *Rhizopus oryzae* and *Rhizopus microsporus* var. oligosporus from industrial waste in acquisition of glucose. *Chem Pap* 2014;68:442–50.
- [12] Duvernay WH, Chinn MS, Yencho GC. Hydrolysis and fermentation of sweet potatoes for production of fermentable sugars and ethanol. *Ind Crop Prod* 2013;42:527–37.
- [13] Wu L, Gau M, Takai T, Kasuga S, Yun MS, Okuyasu K. Sorghum as whole-crop feedstock for integrated production of fermentable sugars. *Ind Crop Prod* 2013;49:645–7.
- [14] Binod P, Kuttiraja M, Archana M, Janu KU, Sindhu R, Sukumaran RK, et al. High temperature pretreatment and hydrolysis of cotton stalk for producing sugars for bioethanol production. *Fuel* 2012;92(1):340–5.
- [15] Jiang Y, Li K, Cao Q, Mu XJ. Acid functionalized, highly dispersed carbonaceous spheres: an effective solid acid for hydrolysis of polysaccharides. *J Nanopart Res* 2011;13:463–9.
- [16] Rogalinski T, Liu K, Albrecht T, Brunner GJ. Hydrolysis kinetics of biopolymers in subcritical water hydrolysis kinetics of biopolymers in subcritical water. *J Supercrit Fluid* 2008;46:335–41.
- [17] Sugano MK, Katoh H, Komatsu A, Kobayashi H, Okado K, Kakuta Y, et al. Additive effects of acetic acid upon hydrothermal reaction of amylopectin. *Biomass Bioenergy* 2012;44:130–4.
- [18] Amarasekara AS, Wiredu B. Aryl sulfonic acid catalyzed hydrolysis of cellulose in water. *Appl Catal A Gen* 2012;417–418:259–62.
- [19] Mukai SR, Sugiyama T, Tamon H. Immobilization of heteropoly acids in the network structure of carbon gels. *Appl Catal A Gen* 2003;256:99–105.
- [20] Chimienti ME, Pizzio LR, Cáceres CV, Blanco MN. Tungstophosphoric and tungstosilicic acids on carbon as acidic catalysts. *Appl Catal A Gen* 2001;208:7–19.
- [21] Lee JH, Choi HW, Kim BY, Chung MS, Kim DS, Choi SW, et al. Non-thermal starch hydrolysis using ultra high pressure: I. Effects of acids and starch concentrations. *Food Sci Technol* 2006;39:1125–32.
- [22] Tasic MB, Konstantinovic BV, Lazic ML, Veljkovic VB. The acid hydrolysis of potato tuber mash in bioethanol production. *Biochem Eng J* 2009;43:208–11.
- [23] Kamio E, Takahashi S, Noda H, Fukuhara C, Okamura T. Liquefaction of cellulose in hot compressed water under variable temperatures. *Ind Eng Chem Res* 2006;45:4944–53.
- [24] Nagamori M, Funazukuri TJ. Glucose production by hydrolysis of starch under hydrothermal conditions. *Chem Technol Biotechnol* 2004;79:229–33.
- [25] Su F, Wu Q, Song D, Zhang X, Wang M, Guo Y. Pore morphology-controlled preparation of ZrO₂-based hybrid catalysts functionalized by both organo-silica moieties and Keggin-type heteropoly acid for the synthesis of levulinate esters. *J Mater Chem A* 2013;1:13209–21.
- [26] Okuhara T, Mizuno N, Misono M. Catalysis by heteropoly compounds – recent developments. *Appl Catal A Gen* 2001;222:63–77.
- [27] Ghanbari-Siahkali A, Philippou A, Dwyer J, Anderson MW. The acidity and catalytic activity of heteropoly acid on MCM-41 investigated by MAS NMR, FTIR and catalytic tests. *Appl Catal A Gen* 2000;192:57–69.
- [28] Hou Z, Okuhara T. Synthesis of diphenyl methane from formalin and benzene in a biphasic system with 12-tungstophosphoric acid. *Chem Commun* 2001:1686–7.
- [29] Izumi Y, Iida K, Usami K, Nagata T. An efficient method for acetolysis of cyclic ethers catalyzed by heteropoly acid. *Appl Catal A Gen* 2003;256:199–202.
- [30] Pulidindi IN. Development and exploitation of carbon materials from plant sources. Ph. D. Thesis. Madras: Indian Institute of Technology; 2009.
- [31] Klein M, Pulidindi IN, Perkas N, Ella MM, Gruzman A, Gedanken A. Direct production of glucose from glycogen under microwave irradiation. *RSC Adv* 2012;2:7262–7.
- [32] Pulidindi IN, Gedanken A. Carbon nanoparticles based nonenzymatic glucose sensor. *Int J Environ Anal Chem* 2014;94:28–35.
- [33] Lunkenbein T, Kamperman M, Schieder M, Li SWZ, Sai H, Forster S, et al. Towards mesoporous Keggin-type polyoxometalates – systematic study on organic template removal. *J Mater Chem A* 2013;1:6238–48.
- [34] Berry BF, Derrick GR, Marco JF, Mortimer M. Silica-supported silicotungstic acid: a study by X-ray photoelectron spectroscopy. *Mater Chem Phys* 2009;114:1000–3.
- [35] Moffat JB. Metal-oxygen clusters: the surface and catalytic properties of heteropoly, XV. Springer; 2001. p. 1–308.
- [36] Kumar R, Rao GR. Synthesis and characterization of hybrid molecular material prepared by ionic liquid and silicotungstic acid. *Mater Chem Phys* 2008;112:853–7.
- [37] Kunlan L, Lixin X, Jun L, Jun P, Guoying C, Zuwei X. Salt-assisted acid hydrolysis of starch to D-glucose under microwave irradiation. *Not Found In Database* 2001;331:9–12.
- [38] Kozhevnikov IV. Catalysis by heteropoly acids and multicomponent polyoxometalates in liquid-phase reactions. *Chem Rev* 1998;98:171–98.