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Glucose production from potato peel waste under microwave irradiation

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ABSTRACT

Potato starch was chemically hydrolyzed to glucose using silicotungstic acid ($H_4SiW_{12}O_{40}\cdot nH_2O$, HSiW) as catalyst under microwave irradiation in a short duration (5 min). Potato starch was completely converted to glucose, levulinic acid and formic acid. The methodology was further used for the conversion of potato peel waste (PPW), a zero value waste to glucose. A glucose yield of 59 wt.% was obtained upon the microwave irradiation (15 min) of PPW. The combined use of solid acid catalyst and microwave irradiation offers a fast and green process for glucose production from starch based waste materials.

1. Introduction

Renewable energy sources are being investigated vigorously [1]. Bioethanol is an alternative to non-renewable transportation fuels [2]. Sustainability of bioethanol production is dependent on the availability of feedstock. Starch is a vital component of agricultural and kitchen wastes which is a cheap and abundant feedstock for the production of fermentable sugars, a precursor to bioethanol. Biomass is being explored intensively as a feedstock for the production of bioethanol [3–7].

Conversion of agricultural and food wastes to fuels is attractive from economic and environmental aspects [8,9] and this has been the objective of many researchers [10–14]. Commercialization of bioethanol is dependent on the availability of the feedstock as well as the economic feasibility of the conversion. Typical challenges involved in the production of bioethanol in an economically feasible way include: (1) identifying appropriate feedstock; (2) developing suitable pretreatment methods; and (3) developing fast and efficient methods of hydrolysis for the release of glucose and the subsequent fermentation of the sugars [15–19]. Solid waste crops and kitchen wastes (potato peels) could be potential feedstock for the production of renewable energy [20,21]. Khawla et al. used enzymatic saccharification to obtain the fermentable sugars from potato peel waste [22].

The transformation of starch into glucose is generally carried out by its hydrolysis with mineral acids or with amylase [23]. The use of mineral acids is environmentally unfriendly and the use of enzymes makes the process costlier as well as longer in terms of time. Heteropoly acids (HPA's) are environmentally friendly and reusable [24]. Tsubaki et al., reported the use of solid acid catalyst and microwave irradiation for the starch hydrolysis which is limited to corn starch [25]. Heteropoly acid (HPA) catalysts are being investigated as possible substitute to mineral acids for the hydrolysis of starch and cellulose [26]. Sonication and microwave based technologies accelerate the depolymerization of starch [27]. Thus, the focus of the current investigation is to develop a fast and environmentally friendly chemical process for the production of glucose from starch-based wastes using a HPA catalyst and microwave irradiation. The primary motivation for the synthesis of glucose lies in the fact that glucose could be subsequently converted to several fine chemicals and fuels (ethanol in particular) as depicted in Scheme 1.

2. Experimental

Potato peels were obtained, from our kitchen, generated as waste during cooking. All reagents were used without further purification. Double distilled water was used as a solvent. The starch hydrolysis was carried out in a domestic microwave oven

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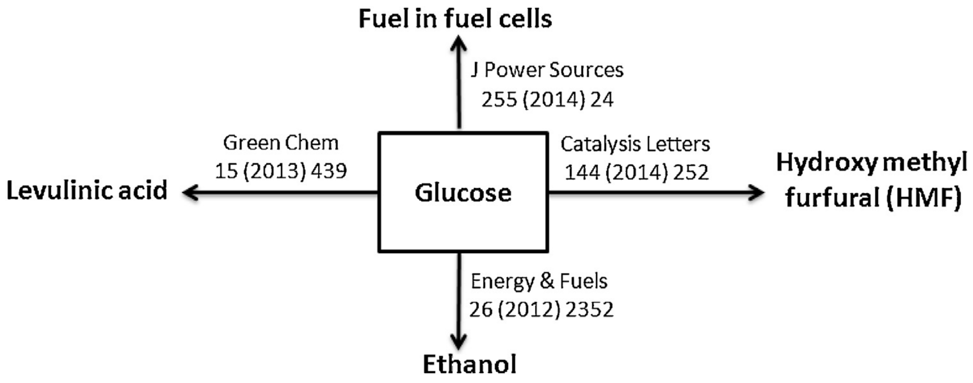
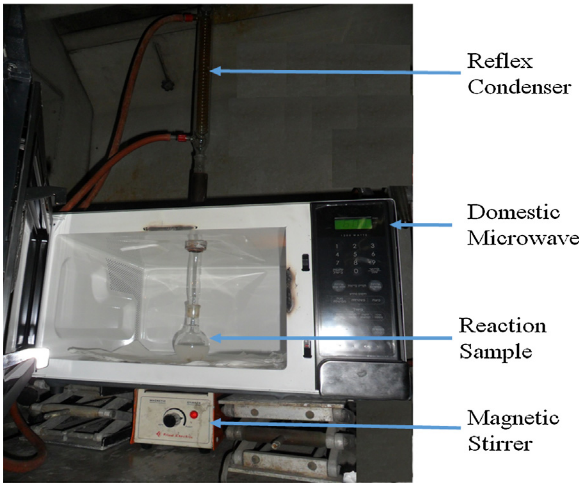


Scheme 1. Schematic representation of potential uses of glucose.



Scheme 2. Experimental set-up used for the hydrolysis of potato peel waste.

(DMWO, SHARP R-390F) operated at 2.45 GHz in a batch mode under atmospheric pressure in the presence of air and cooling condenser attached to the reaction vessel. The output of the microwave oven was 1100 W and was operated at 100% power. The microwave oven was so modified as to have stirring provision at the bottom of the oven (depicted in Scheme 2), by replacing the turntable and the turner [26]. In addition, the reaction process is presented in the form of a movie (video 1).

Typical potato starch (99.98%, commercial sample procured from Sigma Aldrich Ltd., Israel; Product Number: S4251; CAS-No.: 9005-25-8) hydrolysis process comprise of taking a known amount of potato starch (0.1–0.5 g), catalyst (0.5–2.5 g, HSiW) and water (10–50 mL) in a round bottom flask followed by microwave irradiation (2–5 min). The reaction conditions, like the microwave irradiation time, wt./wt.% ratio of the reactant and the catalyst, were optimized so as to enhance the yield of glucose. The reaction temperature attained (109 °C) after 5 min, as a result of microwave irradiation was evaluated using a pyrometer (Fluke, 65 Infrared thermometer) just after the completion of the reaction. Experiments related to potato peel wastes deals with 20 wt.% aqueous suspensions (prepared using a blender) of potato peels. Typical hydrolysis process of potato peel waste comprises of taking 10 mL of potato peel waste suspension (20 wt.%) and 1 g HSiW catalyst and irradiating the same for different periods of time (2–15 min) in a microwave oven. The hydrolysate thus generated from starch and potato peels were analyzed by ^{13}C NMR (on a Bruker Avance DPX 300 instrument using D_2O as a solvent) to monitor the hydrolysis process and to examine the reaction products [1,27]. The catalyst (HSiW) is separated from the hydrolysate using solvent extraction (diethyl ether) method [28]. The crystalline structural stability of HSiW after microwave irradiation was evaluated using XRD analysis (on a Bruker D8 advanced X-ray diffractometer). HPLC analysis was carried out on a Shimadzu system with a refractive index detector (RID-10A). A strong cation-exchange column (Aminex HPX-87H, 300 × 7.8 mm) was used for the chromatographic separation and quantification of various components in the hydrolysate.

3. Results and discussion

Arapoglou et al., have reported the hydrolysis of potato peel waste, in a process based on enzymes which are not reusable and long process times are generally required [9,22]. Tsubaki et al., reported the use of solid acid catalyst and microwave irradiation for the starch hydrolysis which is limited to corn starch [25]. Hernoux-Villiere et al., reported the potential of combined use of microwave-sonochemical irradiation for glucose production from potato starch but using corrosive mineral acid (H_2SO_4) as catalyst [29]. To overcome the limitations of enzymes, mineral acids, feedstock availability, an improved process for glucose production from starch based waste materials is reported herewith.

3.1. *Effect of time of microwave irradiation*

The microwave irradiation time of the starch solution (0.1 g starch in 10 mL water) in the presence of the catalyst (0.5 g, HSiW) was varied from 2 to 5 min. The ^{13}C NMR Spectra of the hydrolysate obtained from the microwave irradiation of potato starch for 2, 3 and 5 min were shown in Fig. 1. The sharp and intense signals at 60.6 (C6), 69.5 (C4), 72.7 (C2), 75.7 (C3), 75.8 (C5) and 95.8 (C1β) were typical of glucose. The peaks at 27.9 (C5), 29.1 (C2), 37.7 (C3), 177.4 (C1) and 214.2 (C4) are characteristic of levulinic acid which is a by-product from glucose conversion.

Klein et al., also observed the formation of levulinic acid along with glucose in the depolymerisation of glycogen under microwave irradiation [30]. The peak at 99.6 ppm in the ^{13}C NMR spectra of the hydrolysate is typical of unreacted starch (Fig. 1(a) and (b)). In the case of 2 min and 3 min irradiated samples, traces of unreacted starch were still observed. Complete conversion of starch to glucose is achieved after 5 min of microwave irradiation (Fig. 1(c) where no peaks typical of starch were noticed. For comparison, the ^{13}C NMR spectrum of authentic sample of starch (1 wt.%) is shown in Fig. S1. The ^{13}C NMR spectra of authentic samples of glucose, levulinic acid and formic acid (165 ppm) were shown in Fig. S2. Thus the optimum time of irradiation for the complete conversion of starch is 5 min. The details of the conversion of starch and the distribution of the products in the hydrolysate as a function of microwave irradiation time are summarized in Table S1.

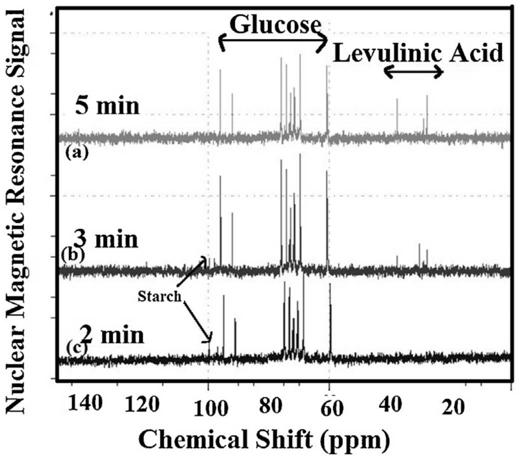


Fig. 1. ^{13}C NMR spectra of the hydrolysate obtained after (a) 2 min. (b) 3 min and (c) 5 min of microwave irradiation of starch solution (Starch, 0.1 g; HSiW, 0.5 g; water, 10 mL).

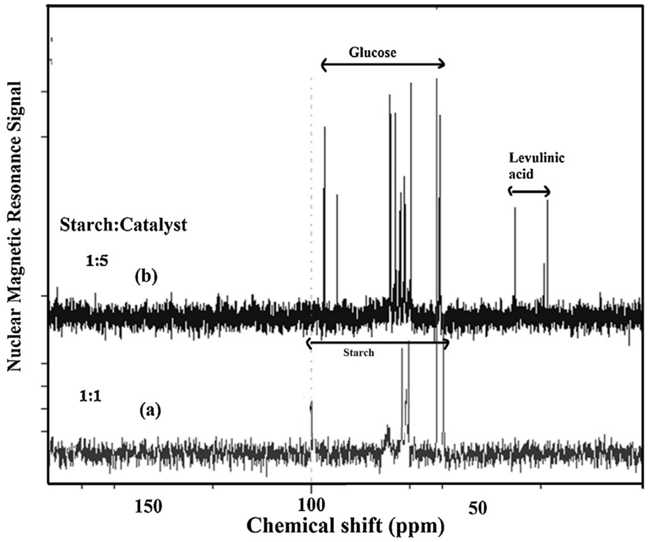


Fig. 2. ^{13}C NMR spectra of the hydrolysate obtained as a function of amount of catalyst, HSiW (wt./wt. ratio of starch and catalyst) (a) 1:1 and (b) 1:5.

3.2. Effect of the amount of catalyst (HSiW)

The ratio (wt./wt.%) of the reactant (starch) and the catalyst (HSiW) was varied from 1:1, 1:3 to 1:5 and the starch hydrolysis was carried out for 5 min. It was observed that at a ratio of 1:1, the starch is unreacted and no trace of glucose is observed (Fig. 2(a)). The conversion of starch is incomplete even at a ratio of 1:3. As expected at a higher catalyst concentration (at a ratio of 1:5) a complete conversion of starch is observed (Fig. 2(b)). In addition to glucose, by-products such as levulinic acid and formic acid were also observed. Details of the conversion of starch and the product distribution as a function of the amount of catalyst were shown in Table S2. It is observed that the optimum amount of catalyst should be at least five times in excess by weight to that of the reactant and only with this amount of catalyst, a complete conversion of starch could be accomplished. Li et al., made similar observations of the requirement of highly concentrated catalyst for the conversion of cellulose to glucose under microwave irradiation [28]. Tsubaki et al., reported an increase in the glucose yield with an increase in the HPA concentration (from 1.4 to 14. 6 mM) in the hydrolysis of corn starch at 160 °C [25]. The starch hydrolysis reaction has been scaled up to 0.5 g batch under optimized reaction conditions (5 min irradiation; 50 mL water and 2.5 g HSiW). Complete conversion of starch to glucose is observed (Fig. S3). In addition to glucose side products such as levulinic acid and formic acid were also observed.

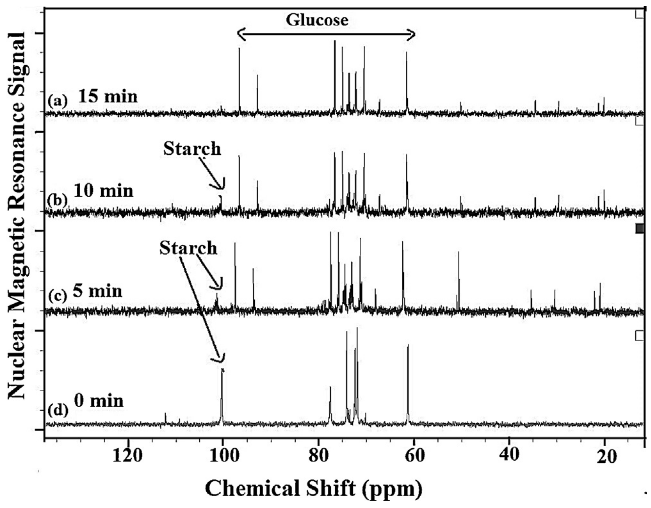


Fig. 3. ^{13}C NMR spectra of the hydrolysate obtained from potato peels as a function of irradiation time (0, 5 10, 15 min) (aqueous suspension of potato peels 10 mL, 20 wt.%, 1.0 g HSiW).

3.3. Stability of the catalyst under microwave irradiation conditions

The catalyst (HSiW) was separated from the reaction product after microwave irradiation by solvent extraction method using diethyl ether [28]. The X-ray diffraction pattern of the regenerated catalyst was found to be similar to that of the fresh silico tungstic acid (Fig. S4). The crystal structure of the HPA remained unaffected even after the microwave irradiation for 5 min.

3.4. Glucose production from waste potato peel

After successfully converting the potato starch (commercial sample) to glucose, the microwave irradiation based methodology was extrapolated to raw biomass (potato peel wastes). ^{13}C NMR spectra of the reaction products obtained after subjecting the aqueous potato peel suspension (20 wt.%) and the catalyst to microwave irradiation for 0, 5, 10 and 15 min was shown in Fig. 3.

As expected, signals typical of starch alone were seen in the aq. suspension of potato peel waste (Fig. 3(d)). As the irradiation time increased from 5 to 15 min the starch was gradually and completely converted to glucose (Fig. 3(a–c)). Longer irradiation time (15 min) was required for the complete conversion of potato peel waste to glucose unlike the commercial starch sample which required only 5 min. This difference could be attributed to the complex structure of potato peel waste comprising of 52.1 wt.% starch and other components being proteins, fats and other soluble and reducing sugars [31]. Analogous by-products (levulinic and formic acids) are observed in the case of commercial starch sample. Peaks typical of levulinic acid (in the range of 25–40 ppm) and formic acid (165 ppm not shown in the figure) (Fig. 3(a–c)) are observed. XRD measurements of the catalyst after 15 min of reaction demonstrated that the crystal structure is unchanged.

3.5. Determination of yield of glucose from HPLC analysis

The final quantification of glucose was determined by HPLC. HPLC analysis indicated the presence of glucose in the hydrolysate from potato peel waste. Presence of glucose was observed in the

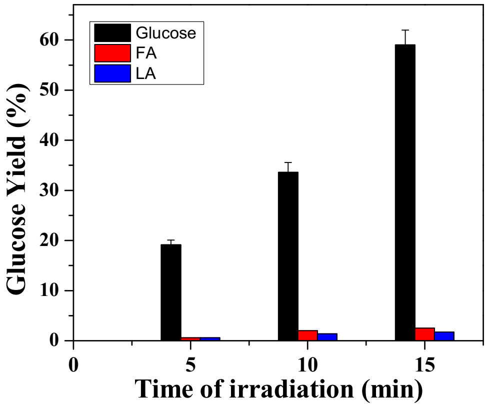


Fig. 4. HPLC analysis of hydrolysate from potato peels carried out at different microwave irradiation times. (FA—formic acid and LA—levulinic acid).

hydrolysate obtained in 5 min microwave irradiation (Fig. S5). In addition, levulinic and formic acids are observed as the reaction by products. A steady increase in the yield of glucose from 20 to 59 wt.% with an increase in irradiation time from 5 to 15 min was noticed (Fig. 4**)**. Another advantage of using the microwave irradiation for the process is that, even though the energy consumed in the batch microwave process is same as that of conventional heating, but for a continuous flow microwave process, the energy consumption is three times lower [32]. Moreover, microwave irradiation has been applied in organic chemistry for spectacular acceleration, higher yields under milder reaction conditions and higher product purities [33,34].

4. Conclusions

A microwave irradiation based process using a solid acid catalyst was developed for the production of glucose from potato peel waste (PPW). The hydrolysis process was fast owing to the use of microwave irradiation. HSiW catalyst was found to be stable even after microwave irradiation for 15 min. Complete conversion of starch to glucose could be achieved in 5 min with HSiW as a catalyst. Levulinic acid and formic acid were found to be the by-products of starch hydrolysis. Thus a fast process is suggested for the conversion of cheap, abundant and renewable carbohydrate, potato peel waste into glucose (yield, 59%). Glucose could be a potential starting material to a variety of fuels and fine chemicals. Use of solid acid catalyst made the process environmentally friendly. Currently, our focus is on converting the batch process to a continuous flow process in a microwave wave reactor to demonstrate the feasibility of the process for large-scale applications. Another advantage of using the microwave irradiation for the process is that, even though the energy consumed in the batch microwave process is same as that of conventional heating, but for a continuous flow microwave process, the energy consumption is three times lower.

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Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at http://dx.doi.org/10.1016/j.molcata.2016.03.025.

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