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# Selective Glucose Isomerization to Fructose via Nitrogen-doped Solid Base Catalyst Derived from Spent Coffee Grounds

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# Selective Glucose Isomerization to Fructose via Nitrogen-doped Solid Base Catalyst Derived from Spent Coffee Grounds

## Abstract

In this work, glucose isomerization to fructose was conducted via a solid base biochar catalyst derived from spent coffee grounds and melamine. The X-ray photoelectron spectroscopy (XPS) spectra identified the majority of pyridinic nitrogen on the biochar surface, which imparted the strong base character of the catalyst. Activity of the catalyst was evidenced by fast conversion of glucose (12%) and high selectivity to fructose (84%) in 20 min at a moderate temperature (120 °C) compared to recently reported immobilized tertiary amines at comparable N concentrations (10-15 mol% relative to glucose). By increasing the reaction temperature to 160 °C, fructose yield achieved 14% in 5 min. The base biochar catalyst showed superior selectivity (>80%) to commonly used homogeneous base catalysts such as aqueous hydroxides and amines (50-80%) and comparable catalytic activity (~20 mol% conversion within 20 min). Moreover, co-solvent of acetone in the reaction system may increase the overall basicity by stabilizing protonated water clusters via hydrogen bonding, which led to faster conversion and higher fructose selectivity than those in water. Approximately 19% fructose was obtained at 160 °C, and the basic sites on the biochar catalyst were stable in hydrothermal environment as indicated by acid-base titration test. Therefore, nitrogen-doped engineered biochar can potentially serve as solid base catalyst for biorefinery processes.

## Disciplines

Catalysis and Reaction Engineering | Organic Chemistry | Sustainability

## Comments

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**Abstract**

In this work, glucose isomerization to fructose was conducted via a solid base biochar catalyst derived from spent coffee grounds and melamine. The X-ray photoelectron spectroscopy (XPS) spectra identified the majority of pyridinic nitrogen on the biochar surface, which imparted the strong base character of the catalyst. Activity of the catalyst was evidenced by fast conversion of glucose (12%) and high selectivity to fructose (84%) in 20 min at a moderate temperature (120 °C) compared to recently reported immobilized tertiary amines at comparable N concentrations (10-15 mol% relative to glucose). By increasing the reaction temperature to 160 °C, fructose yield achieved 14% in 5 min. The base biochar catalyst showed superior selectivity (>80%) to commonly used homogeneous base catalysts such as aqueous hydroxides and amines (50-80%) and comparable catalytic activity (~20 mol% conversion within 20 min). Moreover, co-solvent of acetone in the reaction system may increase the overall basicity by stabilizing protonated water clusters via hydrogen bonding, which led to faster conversion and higher fructose selectivity than those in water. Approximately 19% fructose was obtained at 160 °C, and the basic sites on the biochar catalyst were stable in hydrothermal environment as indicated by acid-base titration test. Therefore, nitrogen-doped engineered biochar can potentially serve as solid base catalyst for biorefinery processes.

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4 **Keywords:** biorefinery; glucose isomerization; engineered biochar; carbon-based catalyst;  
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6 biomass valorization; waste recycling.  
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## 10 11 12 13 **Introduction**

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17 Fructose is a key precursor for the production of platform chemicals such as  
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19 5-hydroxymethylfurfural (HMF), furfuryl alcohol, and levulinic acid (LA)<sup>1-4</sup>. In view of  
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21 lower cost of glucose than fructose and its facile production via cellulosic biomass hydrolysis  
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26 <sup>5-7</sup>, glucose isomerization to fructose represents an important step in industrial applications<sup>8,9</sup>.  
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29 Glucose isomerases are typically employed for fructose production in large scale at a yield  
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31 (42-45%) close to thermodynamic equilibrium<sup>10,11</sup>. However, this method suffers from  
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34 several drawbacks including narrow operating conditions (e.g., pH and temperature), high  
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37 cost, relatively short life cycle, and susceptibility to deactivation<sup>12,13</sup>. Therefore, substantial  
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40 efforts have been made to search for alternative catalysts for glucose isomerization.  
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44 Lewis acid catalysts such as chromium and aluminum in homogeneous form<sup>1,14</sup> and tin-beta  
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46 zeolites in heterogeneous form<sup>11,15</sup> are effective catalysts for glucose isomerization. However,  
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49 either the homogeneous catalyst itself or the synthesis materials of the heterogeneous catalyst  
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52 contain hazardous materials, which pose environmental challenges in practical applications.  
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55 Recent studies have proven that Brønsted base can also catalyze glucose isomerization  
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4 through a different mechanism involving hydrogen transfer <sup>8</sup> instead of hydride shift for  
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6 Lewis acids <sup>11</sup>.  
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10 Fructose yields obtained from various homogeneous base catalysts such as triethylamine <sup>8,16</sup>,  
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12 polyethylenimines <sup>17</sup>, and basic amino acids <sup>18</sup> are comparable to those from Lewis acid  
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14 catalysts (~30%). This suggests that base catalysis provides a promising alternative to Lewis  
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16 acids for glucose isomerization. On the basis of these homogeneous catalytic results, Brunelli  
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18 et al. synthesized heterogeneous base catalysts by immobilizing organosilanes with tertiary  
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20 amine onto porous silica <sup>19</sup>. The catalysts showed comparable fructose selectivity but lower  
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22 catalytic activity than homogeneous amines. Hence, fabrication of environmentally friendly  
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24 catalysts from renewable or waste biomass deserves more investigation. Biochar, an  
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26 economically feasible and green material, has been extensively studied in environmental  
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28 applications for pollution abatement and soil remediation in view of its versatile functional  
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30 groups and favorable structure for modification <sup>20,21</sup>. It is noted that various functional groups  
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32 on the surface of engineered biochar can be distinctive active sites for catalytic reactions <sup>22</sup>.  
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34 The oxygen-containing functional groups such as carboxyl groups, phenolic groups and  
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36 sulfonic groups generally contribute to weak/strong acidity of carbonaceous materials <sup>23,24</sup>.  
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38 For example, sulfonated biochar has been recently applied as Brønsted acid catalyst in bread  
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40 waste or glucose conversion to HMF <sup>25,26</sup>.  
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4 The basicity of carbon surface is related to basic surface functional groups, mainly  
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6 nitrogen-containing functional groups such as amine, pyrrole, and pyridine, or proton  
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8 attraction by delocalized electrons of carbon aromatic rings <sup>27</sup>. Therefore, nitrogen-enriched  
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10 (N-enriched) biochar was hypothesized to be a potential catalyst for glucose isomerization if  
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12 it presents intrinsic basicity and allows easy separation from the reaction stream. According  
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14 to previous studies, spent coffee grounds are a nitrogen-rich biomass feedstock (30 wt%  
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16 protein) <sup>28</sup>, where the derived products can be a potential soil amendment with fertilizer or  
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18 utilized in electrocatalytic application as an option for waste valorization <sup>29,30</sup>. However, poor  
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20 surface coverage by nitrogen could result from the thermal decomposition of  
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22 nitrogen-containing functional groups in the structure of carbon during biomass pyrolysis at  
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24 high temperatures above 700 °C <sup>31</sup>. Thus, melamine can serve as an additional nitrogen  
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26 source for nitrogen doping on various carbon supports (e.g., graphene and carbon  
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28 nanotubes/xerogels) to increase their nitrogen content <sup>32-34</sup>. In addition to the functional  
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30 groups on the catalyst surface, solvents also affect chemical reactivity and selectivity of  
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32 catalytic reactions <sup>35-36</sup>. Our previous work showed that co-solvent of acetone or acetonitrile  
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34 can enhance glucose isomerization under a Lewis acid catalyst <sup>37</sup>, however, it is unclear  
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36 whether base-catalyzed glucose isomerization can also be promoted.  
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52 Therefore, the present work aims to: (i) synthesize N-enriched biochar catalyst for glucose  
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54 isomerization to fructose; (ii) examine catalytic activity of resultant catalysts in relation to its  
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4 physicochemical properties; (iii) assess the effect of co-solvent on base-catalyzed conversion;  
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6 and (iv) evaluate the catalytic stability of the biochar catalyst in reuse.  
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## 10 **Materials and Methods**

### 11 *Catalyst preparation and chemical reagents*

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14 Spent coffee grounds obtained from a local coffee shop and melamine (99%, Sigma Aldrich,  
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16 USA) were used as carbon source and nitrogen sources, respectively. The spent coffee  
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18 grounds were oven-dried (90 °C) until the moisture content was less than 1% based on mass  
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20 balance. In the catalyst synthesis procedure, 5 g of melamine and 40 g of the prepared spent  
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22 coffee grounds were mixed homogeneously in deionized water, and then the solution was  
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24 evaporated at 80 °C to remove water from the mixture. Then the oven-dried composites were  
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26 thermally treated by a two-step N<sub>2</sub>-purged pyrolysis performed in a horizontal tubular furnace  
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28 (AsOne TMF-300N, Japan). The composites were first heated up from 200 to 700 °C for 50  
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30 min, and then held at 700 °C for 2 h. The reactor conditions were referred to Kwon et al.<sup>28</sup>  
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32 (e.g., stainless Ultra-Torr vacuum fitting, quartz tubing, and stainless tubing). The flow rate of  
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34 nitrogen feed gas was set as 500 mL min<sup>-1</sup>, and the temperature inside the furnace was  
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36 measured using a S-type thermocouple (Omega, USA). The intent of the 2-step process was  
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38 to remove any residual water that could cause gasification at 700 °C during the first step and  
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40 to carbonize the sample by pyrolysis under water- and oxygen-free conditions in the second  
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4 step. The resulting biochar catalysts were ground and sieved to 2 mm and stored in a  
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6 desiccator at room temperature for further use.  
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10 Standards of glucose (99%), cellobiose ( $\geq 98\%$ ), levulinic acid (98%) and formic acid (98%)  
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12 from Alfa Aesar; fructose ( $\geq 99\%$ ) and maltose monohydrate ( $\geq 98\%$ ) from Wako;  
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14 levoglucosan from Fluorochem; and 5-hydroxymethylfurfural (HMF) ( $\geq 99\%$ ) from Sigma  
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16 Aldrich, were used as received for the calibration of high-performance liquid chromatography  
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18 (HPLC, Hitachi, Japan) in this study. Acetone (99.5%, Duksan Pure Chemicals) was used to  
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20 investigate the catalytic effect of a polar aprotic co-solvent on glucose isomerization based on  
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22 our previous study <sup>37</sup>.  
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### 31 *Biochar catalyst characterization*

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35 Approximately 0.93 g of the catalyst was degassed in vacuum at 150 °C for 12 h, followed by  
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37 N<sub>2</sub> adsorption-desorption isotherms at -196 °C. The specific surface area and pore volume of  
38  
39 the catalyst were analyzed using Brunauer-Emmett-Teller (BET) surface analyzer  
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41 (Belsorp-mini II, USA), while the pore size distributions were derived from  
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43 Barrett-Joyner-Halenda (BJH) analysis. X-ray photoelectron spectroscopy (K-ALPHA+XPS  
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45 System, Thermo Fisher Scientific) was performed with monochromated Al K $\alpha$  radiation  
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47 (1486.6 eV) system to examine the surface chemistry of the biochar catalyst. Survey scans  
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49 from 0 to 1200 eV were obtained at 1 eV step<sup>-1</sup>, and narrow scan was set at 0.1 eV step<sup>-1</sup>. The  
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4 core level spectra of C 1s (280-294 eV), N 1s (390-411 eV) and O 1s (524-542 eV) were  
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6 recorded and fitted with Gaussian functions. The shift of binding energy due to the relative  
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8 surface charge was corrected by the C1s level at 284.5 eV as an internal standard. The  
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10 structure of the catalyst were evaluated by powdered X-ray diffraction (XRD, Rigaku  
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12 SmartLab) analysis using Cu K $\alpha$  radiation with a scanning degree from 5 to 50° at a rate of 3°  
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14 min<sup>-1</sup>. The morphology of the catalyst was examined using a scanning electron microscope  
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16 equipped with energy dispersive X-ray spectroscopy (SEM-EDX, JEOL Model JSM-6490) at  
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18 an accelerating 20 kV. Thermogravimetric analysis (TGA; Rigaku Thermo plus EVO2) was  
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20 performed at a heating rate of 10 °C min<sup>-1</sup> from 100 to 1000 °C to determine the thermal  
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22 stability of the biochar catalyst and any adsorbed species on the catalyst after catalytic  
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24 reaction.  
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36 The acid-base properties of the catalyst were thoroughly characterized. The basic sites were  
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38 measured by back titration (pH meter, Mettler Toledo). Approximately 0.4 g of solid was  
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40 added into 40 mL of 0.05 M HCl and shaken for 24 h. A blank titration (only HCl, no catalyst)  
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42 was conducted. The mixture was centrifuged at 5000 rpm for 15 min and filtered by a 0.22  
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44  $\mu$ m syringe filter. The filtrate was divided into two aliquots, of which the mass was recorded.  
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48 The aliquots were purged with N<sub>2</sub> gas for 2 h before starting titration with 0.05 M NaOH, and  
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50 N<sub>2</sub> flow was maintained throughout the titration process<sup>38</sup>. The acid sites were measured in a  
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52 similar way. Microwave-heated catalyst (without substrate) was water-washed, oven-dried,  
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4 and ground before elemental analysis (Flash2000, Thermo Scientific) to investigate the  
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6 stability of the catalyst under hydrothermal conditions. Fresh catalyst was examined as  
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8 control.  
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### 11 12 13 *Glucose conversion and chemical analysis* 14 15

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17 Stock glucose solution was prepared at 10 wt/wt%. In each catalytic reaction, 5 mL of stock  
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19 glucose solution and 5 mL of deionized water or acetone together with 1 wt/wt% of catalyst  
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21 relative to solution (equivalent to 15.4 N mol% relative to glucose) were added into a closed  
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23 100-mL microwave reactor vessel. The glucose isomerization reaction was conducted under  
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25 100-mL microwave reactor vessel. The glucose isomerization reaction was conducted under  
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27 microwave heating due to its virtue of fast kinetics and high heating efficiency, promoting  
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29 product yields in significantly shorter reaction time on the scale of minutes<sup>39-40</sup>. In a typical  
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31 experiment, the reaction was subject to a 1-min ramping time to reach 100, 120 or 160 °C for  
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33 desired reaction time (from 1 to 60 min) under continuous magnetic stirring (Ethos Up  
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35 Microwave Reactor, Milestone). The reaction temperature was directly monitored by an  
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37 in-situ temperature sensor in a reference vessel, and a contact-less pressure sensor was used  
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39 to prevent leakage or venting. The recorded reaction pressure was 8 bar when acetone was  
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41 used compared to 3 bar in water only. All experiments were conducted in duplicate. Liquid  
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43 and solid phases after the reaction were separated by centrifugation. Aqueous samples were  
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45 filtered through a 0.22- $\mu$ m pore-size membrane filter (ProMax™, DiKMA) before  
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4 quantifying the chemical products via HPLC analysis. In addition, reusability of the catalyst  
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7 was evaluated by testing the catalyst at the optimal condition of glucose isomerization. The  
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10 used catalyst was washed with alcohol and deionized water three times to remove the  
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12 remaining soluble products followed by centrifugation and decantation. The catalyst was  
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15 oven-dried at 80 °C overnight for reuse.

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18 Detailed HPLC analytical methods were documented in our previous studies <sup>41-42</sup>. The  
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21 conversion, yield and selectivity of chemical products were presented on a mole basis as  
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24 follows.

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$$26$$
$$27 \text{Glucose conversion (\%)} = \frac{n_{Glu}(\text{initial}) - n_{Glu}(\text{final})}{n_{Glu}(\text{initial})} \times 100 \quad (1)$$
$$28$$

$$29$$
$$30 \text{Product yield (\%)} = \frac{Conc_P (mg\ ml^{-1}) \times Vol (ml) / MW_P}{n_{Glu}(\text{initial})} \times 100 \quad (2)$$
$$31$$

$$32$$
$$33 \text{Product selectivity (\%)} = \frac{\text{Product yield (\%)}}{\text{Glucose conversion (\%)}} \times 100 \quad (3)$$
$$34$$

35  
36 where  $Conc_P$  represented the product concentration such as fructose, furfural, HMF, and  
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38 levulinic acid detected by HPLC;  $MW_P$  referred to the molecular mass in the corresponding  
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40 products;  $n_{GLU}(\text{initial})$  represented the initial moles of glucose in each reaction. Total product  
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43 yield was calculated as a summary of entire soluble products detectable by HPLC including  
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47 glucose.

## 51 **Results and Discussion**

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### 55 *Physicochemical characteristics of the N-enriched biochar catalyst*

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4 The N-enriched biochar displayed Type II N<sub>2</sub> adsorption-desorption isotherm (Fig. S1a), and  
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6 the BJH plot (Fig. S1b) showed a larger fraction of pore diameter ranging 50-200 nm than  
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8 2-50 nm, indicating the characteristics of a macroporous material. In contrast to surface areas  
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10 above 100 m<sup>2</sup> g<sup>-1</sup> in other studies, the N-enriched biochar in this study showed a low specific  
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12 surface area (S<sub>BET</sub> = 0.35 m<sup>2</sup> g<sup>-1</sup>) (Table 1), probably due to the aggregation of the biochar  
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14 after the N-doping process<sup>43</sup>. The SEM images revealed a layered morphology with irregular  
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16 aggregates on the surface of the biochar catalyst (Fig. S2), which may be responsible for its  
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18 low surface area. The biochar catalyst showed characteristic diffraction peaks at 2θ = 23.5°  
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20 (002) and 2θ = 43.6° (100) of carbon materials (Fig. S3), though not as sharp crystalline  
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22 peaks. The broadened (100) peak represents the disordering characteristic of non-graphitic  
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24 carbons<sup>44</sup>, and the (002) reflection shows the stacking of aromatic carbon layers within the  
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26 disordered crystallites<sup>45</sup>. Carbon (85.9 wt%) and oxygen (13.1 wt%) were the two main  
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28 elements identified from the EDS analysis (Fig. S2), while nitrogen was below the detection  
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30 limit in this case.  
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44 The atomic ratios of carbon, nitrogen and oxygen determined by the XPS analysis, and the  
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46 percentages of chemical species calculated by peak deconvolution were summarized in Table  
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48 1. In contrast to the EDS result, the XPS analysis indicated a nitrogen concentration of 5.59  
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50 wt%. This discrepancy is probably due to the scanning depth variation between the two  
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52 methods (1-3 μm in EDS vs. 10 nm in XPS)<sup>46</sup>, where a deeper detection in EDS analysis  
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4 might reduce the average concentration of nitrogen. In other words, this result might suggest  
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6 that nitrogen element was doped on the external surface of the biochar, which implied  
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8 favorable accessibility to the active sites. Deconvolution of the N 1s spectra (Fig. 1a)  
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10 distinguished three peaks at 398.2 eV, 400.3 eV, and 402.8 eV, which could be ascribed to  
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12 pyridinic N (bound to two C atoms), pyrrolic N (bound to two C atoms and one H atom), and  
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14 oxidized N, respectively <sup>47-48</sup>. These identified nitrogen species were aligned with those of  
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16 graphitic carbon nitride materials and nitrogen-doped carbon xerogels <sup>32,49</sup>, while quaternary  
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18 N was absent from the N-enriched biochar. Thus, the engineered biochar exhibited abundance  
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20 of edge-terminating nitrogen species, *i.e.*, pyridinic N (43.6%) and pyrrolic N (37.3%) (Table  
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22 1). In general, pyridinic N can be more favorable to support glucose isomerization compared  
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24 to pyrrolic N because the lone pair of pyridine is localized and free for donation whereas the  
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26 pyrrole is completely delocalized over five atoms.  
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38 The titration results confirmed that the biochar catalyst possessed certain concentration of  
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40 basic sites (0.247 mmol g<sup>-1</sup>) and negligible amount of acidic sites (Table 1). Given that the  
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42 high ratio of pyridinic N would display a strong basic character <sup>50</sup>, the results in this study  
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44 revealed that N-doping onto biochar was successful for the fabrication of carbon-based base  
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46 catalyst. In the O 1s spectra (Fig. 1b), the peak at 531.6 eV and 533 eV represented carbonyl  
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48 oxygen and ether-type oxygen (in esters and anhydrides) <sup>51</sup>. Oxygenated functional groups  
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50 predominantly contributed to the acidity of carbon surface <sup>20</sup>. The C 1s spectra exhibited two  
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4 major peaks at 284.5 eV and 285.3 eV, which were assigned to C-C and C-O bond,  
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6 respectively. A minor shoulder at 287.4 eV was associated with C=O bond.  
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10 The mass decay of the N-enriched biochar up to 1000 ° C heating in Ar gas was  
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12 approximately 23% (Fig. 2), which was consistent with the XPS analysis, and it was mainly  
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14 attributed to the loss of heteroatom (*i.e.*, N) and O (16 wt% in total according to XPS results).  
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18 A small reflection point at 250 °C in the DTG curve could result from the decomposition of  
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20 insignificant amount of carboxyl-related groups, while rapid degradation rates that occurred  
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22 from 560 to 740 °C were likely due to the decomposition of oxygen-containing groups such  
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24 as ketones and lactones, and nitrogen-related species such as lactame- and pyrrole-like  
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26 compounds, as suggested by a temperature-programmed desorption study equipped with  
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28 mass spectrometer<sup>38</sup>. In addition, the mass decay evolving at the latter stage of >750 °C  
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30 could be primarily associated with the decomposition of pyridinic N, which is more stable  
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32 than pyrrolic N<sup>52</sup>. The thermal degradation analysis was in line with the results of XPS  
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34 analysis and showed high thermal stability of N-enriched biochar catalyst.  
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#### 45 *Glucose isomerization catalyzed by N-enriched biochar in water medium*

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49 As shown in Fig. 3, a rapid conversion of 11% glucose was achieved in 1 min with a  
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51 selectivity close to 100% at 120 °C in water medium as a green solvent. The highest fructose  
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53 yield was achieved in 20 min with a high selectivity of 84%. The N-enriched biochar catalyst  
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4 demonstrated a catalytic activity for glucose isomerization to fructose that is comparable to  
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6 homogeneous tertiary amines at similar N concentrations <sup>8</sup>, and a conversion higher than  
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8 heterogeneous tertiary amines on porous materials <sup>19</sup>. Extending the reaction time to 60 min,  
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10 glucose conversion increased only slightly to 15%, which was still far from the equilibrium  
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12 of glucose conversion (~ 60%) <sup>8,11,53</sup>. Meanwhile, the selectivity to fructose decreased to 79%,  
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14 which could be due to the formation of soluble intermediate products undetectable by HPLC  
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16 along with the reaction at this temperature because insoluble humins were negligible over the  
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18 course of reaction. Control test using biochar synthesized without melamine showed glucose  
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20 conversion was 2.2% at 120 °C in water (Table S1).  
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30 Increasing the reaction temperature to 160 °C promoted glucose conversion to 19% in 20 min,  
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32 while fructose yield merely increased to 13% (Fig. 4). Selectivity to fructose decreased from  
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34 85 to 70% along with increasing reaction time, as a result of dehydration of fructose to HMF,  
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36 which was a reaction favored at moderately high temperature and weakly acidic environment  
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38 (solution pH was observed to decrease to 4.66 in 5 min) <sup>54</sup>. The catalytic activity of the  
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40 N-enriched biochar catalysts for glucose isomerization was confirmed because only a small  
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42 amount of glucose (~2%) was converted in the absence of the catalysts while HMF was the  
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44 major product.  
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54 It has been recognized that solution pH has a crucial effect on glucose isomerization,  
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3 especially for Brønsted base catalysis<sup>8</sup>. The pH value of the initial reaction solution (in the  
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6 presence of catalysts) measured at room temperature was 7.24, which ruled out the possibility  
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9 of catalysis via hydroxide ions in the bulk solution. Instead, this led to the presumption that  
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12 the catalytic effect of N-enriched biochar may be largely induced from the lone pair of  
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15 electrons in the nitrogen-terminated edge structures<sup>55</sup>, which could attract hydrogen atoms in  
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18 the vicinity of water molecules, and thus, increasing the basicity of the catalyst in the local  
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21 environment. The majority of pyridinic N, as indicated by XPS analysis (Fig. 1 and Table 1),  
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24 could facilitate the high conversion rate of glucose within a short reaction time due to its  
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27 strong basicity. In addition, the carbonyl group on carbon materials has been known to impart  
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30 certain basicity on the surface, where the electron-withdrawing ability induces partial  
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33 negative charge of a hydroxyl group in water molecules.  
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36 The N-enriched biochar acting as a base catalyst for glucose isomerization in this study can  
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39 explain stagnant production yield of fructose along with extending the reaction time (Fig  
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42 5&6), where the catalytic activity was inhibited due to the observed decrease of solution pH  
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45 value. In this work, part of the pyridinic N species present on the catalyst could be protonated  
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48 due to the decrease of pH from 7.24 to 6.58 in 20 min at 120 °C, thereby possibly decreasing  
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51 their catalytic functions as the lone pair electrons on the N atom of pyridinic sites were  
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54 donated to H<sup>+</sup> ions. It is noted that N-doped catalysts exhibit high sensitivity to acidic media  
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57 due to the decrease in catalytic activity caused by protonation of pyridinic N to pyridinium  
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4 cation ( $\text{pK}_a = 5.7$ )<sup>56</sup>. Consequently, the nitrogen-terminated edge species of the biochar  
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6 catalyst may be protonated by the acidic compounds in the solution over an extended reaction  
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9 time.

#### 10 11 12 13 *Enhanced glucose isomerization activity in acetone/H<sub>2</sub>O mixture*

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17 The use of acetone as an environmentally-friendly co-solvent increased the glucose  
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19 conversion rate compared to using water alone (Fig. 5). The fructose yield rapidly attained  
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21 14% in 5 min at 120 °C, and the selectivity reached 95%. Similar to the reaction in water,  
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23 14% in 5 min at 120 °C, and the selectivity reached 95%. Similar to the reaction in water,  
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25 increasing the reaction time to 20 min slightly increased the glucose conversion to 17%.  
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27 However, the fructose yield did not increase accordingly as a result of decreased fructose  
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29 selectivity to 83%, although it was still considered high. Increasing the reaction temperature  
30  
31 to 160 °C led to 22% of glucose conversion and 18% of fructose yield in 20 min (Fig. 6).  
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33 Trivial amount of HMF (~ 1%) was found in 5 min, which was subsequently rehydrated into  
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35 levulinic acid as can be seen in 20 min. The total carbon balance was between 96 and 102%  
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37 in the presence of acetone, therefore, aldol reactions were supposed to be insignificant in this  
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39 system. A recent study has shown that the presence of acid sites or nitro groups may be  
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41 needed to activate aldol condensation<sup>57</sup>.  
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52 On the contrary to water medium, the fructose selectivity in acetone/H<sub>2</sub>O mixture was not  
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54 compromised by high temperature (160 °C) in a short reaction period, which demonstrated an  
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4 attractive benefit of the mixture system to enhance the glucose conversion while maintaining  
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6 the high selectivity. Glucose conversion in acetone/H<sub>2</sub>O mixture in the absence of N-enriched  
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8 biochar catalyst was lower than that in aqueous solution (Fig. 5&6). Therefore, the advantage  
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10 of acetone as a co-solvent was partially attributed to interfacial interaction between the  
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12 biochar catalyst and solvent, in addition to solution-phase interaction between glucose and  
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14 solvent. The initial pH value of the reaction mixture was 8.24, however, one should be  
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16 prudent in pH comparison as organic solvents may have different pH scales. According to a  
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18 recent study, the addition of acetone may polarize in water and stabilize water hydration  
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20 clusters via hydrogen bonding, rendering the acetone-water mixture more basic than water or  
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22 acetone alone <sup>58</sup>.

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33 Apart from the effect of increased basicity in the solvent mixture, acetone as a co-solvent  
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35 may demonstrate multiple advantages in glucose isomerization. The equilibrium proportion  
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37 of fructose could increase in an exponential manner with increasing acetone (or ethanol)  
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39 concentration in the solution, and the tautomer distribution of glucose was also observed with  
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41 higher proportion of  $\alpha$ -pyranose form <sup>59</sup>. It has been revealed that pyranose glucose was the  
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43 active species partitioning into tin-beta zeolites <sup>15</sup>, yet the effect of a particular glucose  
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45 structure for a heterogeneous base catalyst worth more understanding for rational design of  
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47 superior solid catalyst. With the use of Lewis acid catalysts (Sn<sup>4+</sup>), glucose isomerization rate  
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49 could be faster in acetone (and acetonitrile) compared to other polar aprotic solvents such as  
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3 tetrahydrofuran and dimethyl sulfoxide <sup>37</sup>. Due to negligible metal content in the biochar  
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6 catalyst, Lewis acid site was less likely to contribute to glucose isomerization in this study.  
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9 However, future computational simulation studies are recommended for elucidating how the  
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12 mixture of acetone/H<sub>2</sub>O enhances glucose isomerization in different isomerization pathways  
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15 catalyzed by Lewis acid and Brønsted base, respectively.  
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### 18 19 *Recyclability of the N-enriched biochar catalysts*

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22 The N-enriched biochar catalyst was microwave-heated in the aforementioned conditions  
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25 without glucose, and then separated for elemental analysis for comparison with the unreacted  
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28 catalyst. The results showed that the elemental composition (Table 2) had little change after  
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31 microwave heating, indicating that the N-terminated edge species on the biochar catalysts  
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34 were stable in the aqueous environment and resistant to thermal decomposition and water  
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37 hydrolysis under the studied conversion conditions. In other words, the N-enriched biochar  
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40 preserved activities under microwave heat and aqueous environment. However, no fructose  
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43 was found in the recyclability tests in either water or acetone/water mixture at 120 °C for 1  
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46 min. The loss of activity was proposed to result from the neutralization of the basic sites by  
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49 acidic compounds in the reaction in a recent study <sup>19</sup>. The spent N-enriched biochar catalyst  
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52 was rinsed by 1 M NaOH for 3 h <sup>60</sup>. The catalytic activity for glucose conversion could be  
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55 retained at 85% in the second run and 64% in the third run of the recycling tests, respectively  
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4 (Table S2). The elemental analysis confirmed that the catalyst composition did not change  
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6 after hydrothermal condition (Table 2), indicating the active N sites were free from leaching.  
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9 In view of the high selectivity (>80%) of fructose and minimal formation of insoluble humins  
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11 during the reactions with fresh catalysts, these results suggest that retention of carbonaceous  
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13 materials on the catalyst surface may hinder regeneration by using alkaline solution. Future  
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15 work is required for understanding the significance of nitrogen/amine species on the catalyst  
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17 and tailoring the synthesis design for higher reusability.  
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## 24 **Conclusions**

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28 Waste-derived biochar from spend coffee grounds was doped with melamine as nitrogen  
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30 source to produce N-enriched biochar catalyst under the optimized pyrolysis conditions. The  
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32 XPS spectra showed the predominant formation of edge-terminating nitrogen functional  
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34 groups (*i.e.*, pyridinic N) at a high ratio, which were largely responsible for the observed  
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36 basicity in the acid-base titration test. The N-enriched biochar showed outstanding catalytic  
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38 performance for glucose isomerization to fructose with high selectivity, and the reaction  
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40 activity was comparable to that with homogeneous base. The use of acetone as a co-solvent  
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42 increased the glucose isomerization rate and 14% of fructose was obtained with a selectivity  
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44 of 95% at 120 °C in 5 min. The overall results of this study demonstrated that N-enriched  
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46 biochar could serve as an efficient solid catalyst for glucose isomerization owing to the  
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4 basicity of the functional groups. Further investigation efforts are deserved to distinguish the  
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6 important roles of specific nitrogen groups and effects of physicochemical properties of the  
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8 biochar on its catalytic efficiency, where  $^1\text{H}$  and  $^{13}\text{C}$  NMR can shed light on catalyst  
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10 reaction/deactivation mechanisms. Tailored synthesis is recommended for advanced biochar  
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12 catalyst in the future.  
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40 Supporting Information for Publication: Nitrogen adsorption-desorption isotherms and  
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42 SEM-EDX images of N-doped biochar catalyst  
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3 **Table 1.** Surface characterization of the catalyst  
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5 **Table 2.** Elemental analysis of the catalysts  
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10 **Figure 2.** Thermogravimetric analysis of N-doped biochar catalyst at a heating rate of  
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13 **Figure 3.** Activities of glucose isomerization in water at  $120\text{ }^{\circ}\text{C}$  with 1 wt % N-doped  
14 biochar catalyst (equals to 15.4 N mol% related to glucose) in a 5 wt% glucose  
15 solution.  
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17 **Figure 4.** Activities of glucose isomerization in water at  $160\text{ }^{\circ}\text{C}$  with 1 wt % N-doped  
18 biochar catalyst (equals to 15.4 N mol% related to glucose) in a 5 wt% glucose  
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**Table 1.** Surface characterization of the catalyst

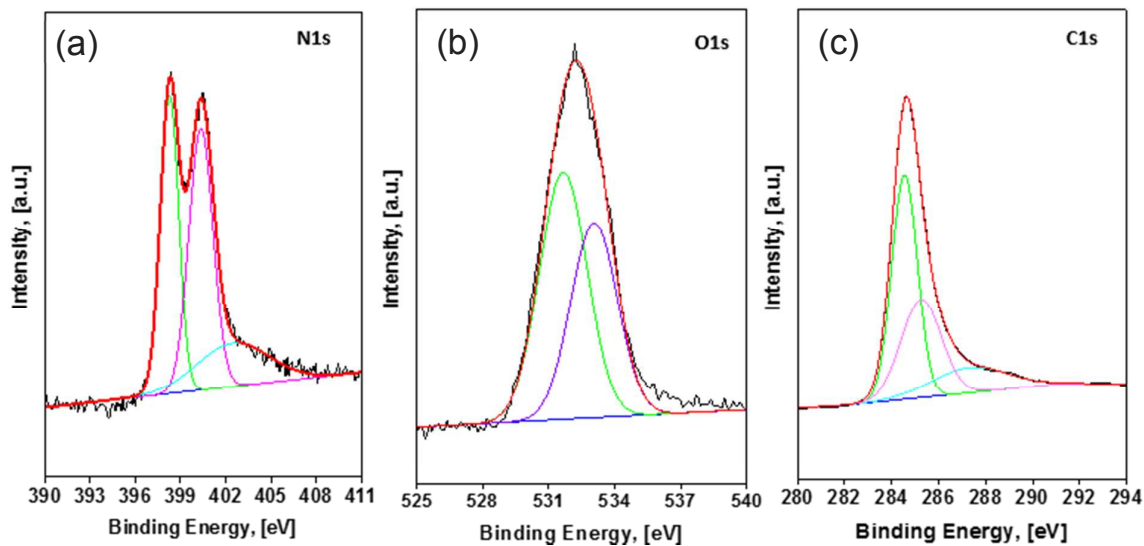
<b>BET Surface area (m<sup>2</sup> g<sup>-1</sup>)<sup>a</sup></b>	0.35					
<b>Composition (at. %)<sup>b</sup></b>	<b>C</b>		<b>N</b>		<b>O</b>	
	86.84		5.59		7.57	
<b>Core level (%)<sup>b</sup></b>	<b>C 1s</b>		<b>N 1s</b>		<b>O 1s</b>	
	C-C	46.2	C-N=C	43.6	C-O	56.5
	C-O	34.2	N-H	37.3	C=O	43.5
	C=O	19.6	=N-O	19.1		
<b>Basic /Acidic sites (mmol g<sup>-1</sup>)</b>	<b>Basic</b>			<b>Acidic</b>		
	0.247			0		

<sup>a</sup> Data derived from N<sub>2</sub> adsorption-desorption isotherms<sup>b</sup> Data obtained from XPS analysis

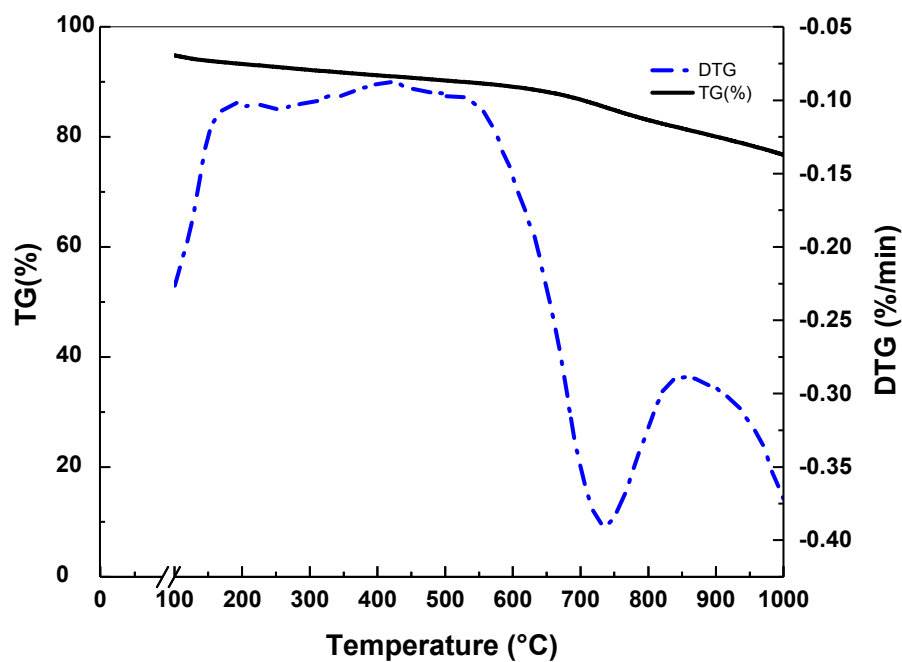
**Table 2.** Elemental analysis of the catalysts

<b>Composition (wt %)</b>	<b>N</b>	<b>C</b>	<b>H</b>	<b>O</b>	<b>Total</b>
Fresh Catalyst	10.42	77.47	2.39	7.29	97.57
Microwave-heated Catalyst <sup>a</sup>	11.13	74.91	2.08	7.30	95.42

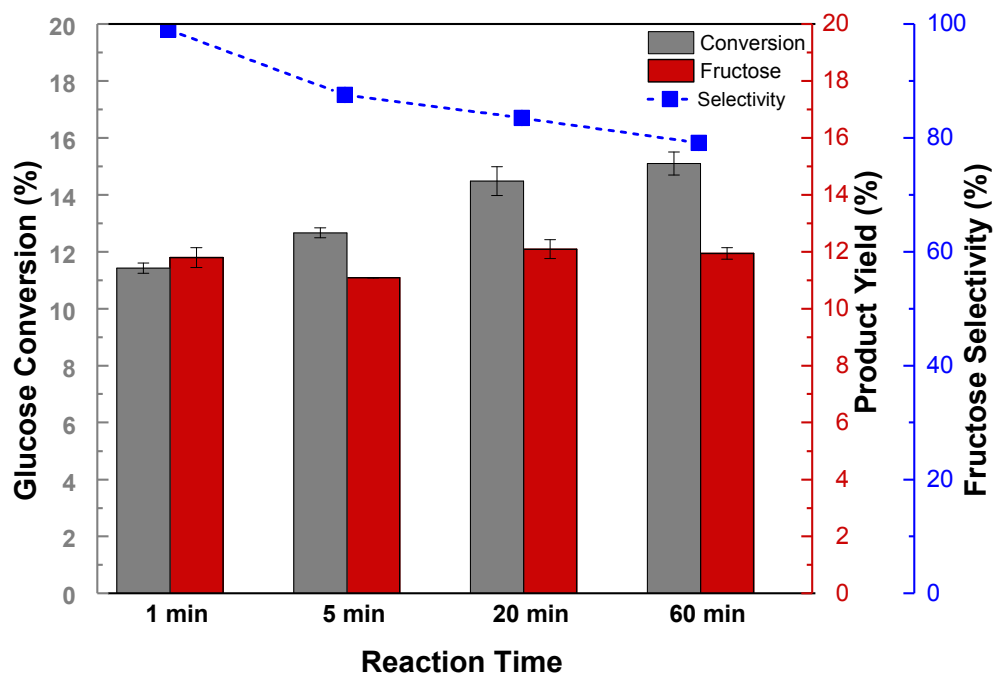
<sup>a</sup> The N-doped biochar catalyst was microwave-heated in acetone/water mixture without substrate at 120 °C for 1 min



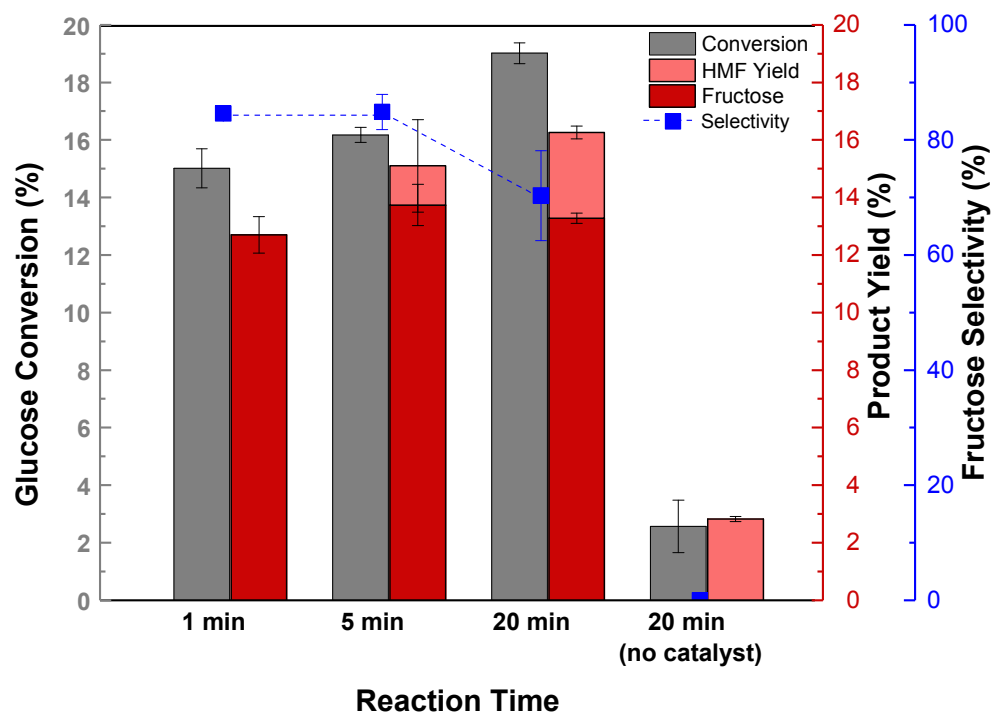
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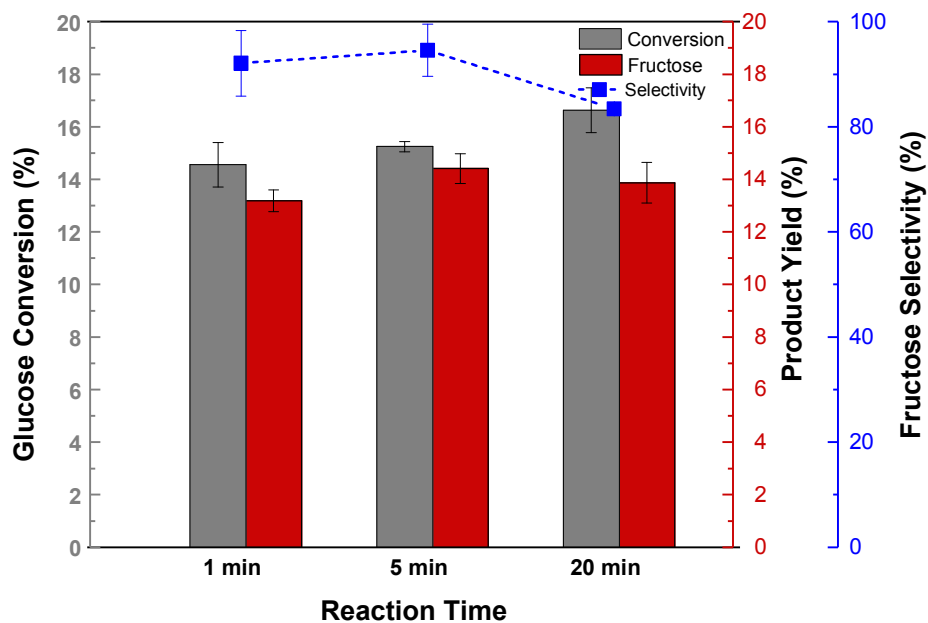


**Figure 3.** Activities of glucose isomerization in water at 120 °C with 1 wt % N-doped biochar catalyst (equals to 15.4 N mol% related to glucose) in a 5 wt% glucose solution.

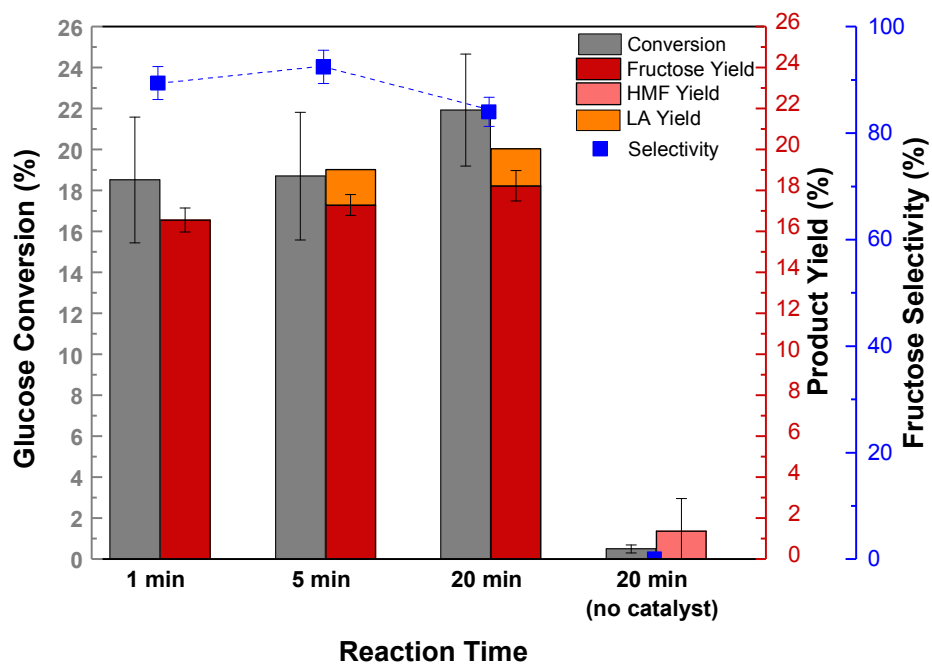


**Figure 4.** Activities of glucose isomerization in water at 160 °C with 1 wt % N-doped biochar catalyst (equals to 15.4 N mol% related to glucose) in a 5 wt% glucose solution.





**Figure 5.** Activities of glucose isomerization in acetone/water (1:1 v/v) at 120 °C with 1 wt % N-doped biochar catalyst (equals to 15.4 N mol% related to glucose) in a 5 wt% glucose solution.



**Figure 6.** Activities of glucose isomerization in acetone/water (1:1 v/v) at 160 °C with 1 wt % N-doped biochar catalyst (equals to 15.4 N mol% related to glucose) in a 5 wt% glucose solution.

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Nitrogen-doped coffee waste-derived biochar is a sustainable solid catalyst to achieve selective glucose isomerization, illustrating the capability of engineered biochars in catalysis for high-value product synthesis.

