

# 1Study of glucose isomerisation to fructose over three heterogeneous carbon-based 2Aluminium-impregnated catalysts

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15

## 16Abstract

17Driven by the worldwide demand for sustainable resources and renewable energy, the  
18synthesis of bio-based platform chemicals has attracted broad interest. The isomerisation of  
19glucose to fructose acts as a critical intermediate step among many chemical synthesis routes.  
20In this study, biochar (BC), graphitic oxide (GIO), and graphene oxide (GO) were used as  
21carbon supports to synthesize Al-impregnated heterogeneous catalysts, which were then used  
22for glucose isomerisation under microwave heating in the water at 140 °C. The kinetics model  
23with parameters was used to reveal the interplay of the active sites and compare the activity  
24of the three carbon-based catalysis systems. Catalyst characterisation results showed effective  
25aluminium (Al) impregnation onto the three types of catalysts, and it was found that GIO-  
26Al200 and GO-Al200 showed comparable catalytic activity (fructose yield of 34.3-35.0%)

27for glucose isomerisation. At the same time, BC-Al200 exhibited slightly lower catalytic  
28activity (fructose yield of 29.4%). The conversion kinetics suggested similar catalytic  
29mechanisms on the three catalysts while BC-Al200 manifested slower kinetics, possibly  
30implying higher activation energy. The fructose selectivity decreased with increasing time  
31due to the formation of side products, yet BC-Al200 resulted in less carbon loss than GIO-  
32Al200 and GO-Al200, probably attributed to its lower catalytic activity and higher pH  
33buffering capacity. A green synthesis route of this study promotes biomass valorisation and  
34makes engineered biochar a promising carbon-based catalyst for sustainable biorefinery.

35**Keywords:** engineered biochar, biomass valorisation, sustainable biorefinery, graphene  
36oxide, glucose isomerisation; waste management.

37

## 381. Introduction

39 The biorefinery based on biomass valorisation is currently drawing significant attention  
40among the scientific community as a strategy for the manufacture of a new generation of  
41various value-added chemicals and fuels with limited environmental footprints (Sudarsanam  
42et al., 2018; Clark, 2019). Cellulose- and starch-rich biomass can go through a range of  
43chemical processes including hydrolysis, isomerisation, dehydration, and rehydration to  
44generate various platform chemicals (Xiong et al., 2019), including 5-hydroxymethylfurfural  
45(5-HMF) (Yu and Tsang, 2017), levulinic acid (LA) (Chen et al., 2017; Chen et al., 2018),  
46and  $\gamma$ -valerolactone (GVL) (Dutta et al., 2019). These chemicals can play significant roles in  
47future industrial productions of many products such as pharmaceuticals, polymers, resins,  
48solvents, fungicides, and biodiesel. Fructose (ketohexose), is a crucial precursor in such

49 processes as well as a valuable product in its own right. It can be produced by the  
50 isomerisation of biomass-derived glucose (aldohexose) (Delidovich and Palkovits, 2016)  
51 using Lewis acid (through the intramolecular 1,2-hydride shift from the C2 to C1 position)  
52 (Li et al., 2017) or Brønsted base (through hydrogen transfer from O2 to O1 position) (Chen  
53 et al., 2018b) catalysis although yields are generally poor. The conventional biocatalytic  
54 process requires strict control of temperature (40–80 °C) and pH (5.8–8.0) as well as  
55 expensive enzymes (i.e., glucose isomerase) (Li et al., 2017). The synthesis of cost-effective  
56 and recyclable chemical catalysts that operate under mild conditions for this process is an  
57 important goal.

58 Biochar, a waste-derived carbonaceous material with relatively high surface area, porous  
59 structure, and stable characteristics, is prospective materials for catalyst synthesis (Li et al.,  
60 2020) and material engineering (Wang et al., 2019). Serving as a catalyst support (Lam et al.,  
61 2017), biochar can be functionalised by metallic pyrolysis (Lam et al., 2015) and physical  
62 and chemical activation (Liew et al., 2018). By the introduction of Brønsted or Lewis acidity  
63 into biochar (Xiong et al., 2018), the surface physicochemical properties can be tailored to  
64 manipulate the catalytic activity for various biomass valorisation reactions (Xiong et al.,  
65 2017). In recent studies, glucose isomerisation was shown to be catalysed by wood biochar  
66 impregnated with aluminium (Al) and tin (Sn) (Yu et al., 2019a; Yang et al., 2019). Besides,  
67 chemical oxidation of natural graphite powder can generate graphite oxide (GIO) with a  
68 layered structure. GIO could be exfoliated via ultrasonication, producing graphene oxide  
69 (GO) with one or a few layers of carbon atoms (Ray, 2015). GO and their derived materials  
70 are another group of promising carbon-based catalysts because of their superior properties

71such as two-dimensional hexagonal lattice structure, high stability, and large surface areas  
72(Bottari et al., 2017). The basal planes and hole defects of GO structure contain numerous  
73epoxides, hydroxyl groups, and carboxyl oxygen-bearing moieties, which may act as  
74hydrogen-bond donor and acceptor moieties (Georgakilas et al., 2016). These oxygen-  
75containing functional groups also account for the oxidative and weakly acidic properties of  
76GO (Antunes et al., 2014). Recent studies have intensively studied GO as a catalyst for  
77biomass conversion (Zhu et al., 2015), for example, GO without modification catalyses  
78fructose conversion to 5-HMF (Wang et al., 2014; Shaikh et al., 2018) and cellulose into  
79glucose (Mission et al., 2017). Metal modified GO such as graphene oxide–ferric oxide (GO-  
80Fe<sub>2</sub>O<sub>3</sub>) exhibited great catalytic activity in converting glucose into 5-HMF with 86% yield  
81(Zhang et al., 2015). Sulfonated graphene oxide achieved 94% 5-HMF yield from fructose  
82dehydration (Hou et al., 2016), whereas sulphur-modified GO acted as a catalyst for the  
83conversion of cellobiose to 5-HMF (Wang et al., 2016a).

84 Functionalization of these carbon materials with tailorable morphology and good chemical  
85stability shows great potential for catalyst synthesis. Aluminium is a promising Lewis acid  
86dopant for heterogeneous catalysis (Yu et al., 2016). It has been demonstrated that Al-biochar  
87composites, graphite oxide- and graphene oxide-supported catalysts are promising materials  
88for catalytic glucose isomerisation (Yu et al., 2019a; Yu et al., 2019b). Aluminium oxide-  
89silica/carbon composites (Al-Amsyar et al., 2017), N-graphene-modified Al<sub>2</sub>O<sub>3</sub> (Guo et al.,  
902016), graphene oxide/aluminium (GO/Al) mixed powders (Zhou et al., 2018) were  
91previously shown to be effective for catalysing biomass conversion and value-added  
92chemicals synthesis. However, different dosages and experimental conditions were often

93employed in previous studies, making it difficult to compare the effectiveness directly. A  
94proper comparison of the different heterogeneous carbon-based catalysts under the same  
95condition is needed to provide insights into the future design of sustainable and cost-effective  
96catalysts for glucose isomerisation.

97 In this study aluminium-doped carbon supports (i.e., biochar, graphite oxide, and graphene  
98oxide) are studied for green catalyst preparation to compare and explore the interplay as well  
99as the effect of the carbon on glucose isomerisation. The conversions were carried out via  
100microwave heating in the water at 140 °C (i.e., green solvent and moderate temperature),  
101which helps ensure the environmental suitability of the process for biorefineries. We then  
102compared the catalytic performance of three different carbon materials as support of Al  
103catalysts and addressed the kinetics of catalytic glucose isomerisation chemistry in water.  
104This work aims to explore the catalytic performances and interplays on different catalysts and  
105provide scientific insights into the design of engineered materials for biorefinery processes  
106and biomass valorisation.

107

## 1082. Materials and Methods

### 1092.1 Raw materials and chemical reagents

110 Graphite powder (AR, Accuchem) served as the precursor of synthesizing GIO and GO.  
111Sawdust collected from the Industrial Centre of the Hong Kong Polytechnic University was  
112the feedstock for producing wood biochar. The  $\text{AlCl}_3 \cdot 6\text{H}_2\text{O}$  (ACS grade) purchased from  
113Anaqua is the impregnation agent in this study. Standard compounds used in conversion  
114experiments as well as calibration of the analytical instrument were glucose ( $\geq 99.5\%$ ), 5-

115HMF ( $\geq 99\%$ ), and furfural (99%) from Sigma Aldrich; cellobiose ( $\geq 98\%$ ), levulinic acid  
116(98%), and formic acid (98%) from Alfa Aesar; levoglucosan from Fluorochem; and fructose  
117( $\geq 99\%$ ) and maltose monohydrate ( $\geq 98\%$ ) from Wako.

## 1182.2 Production of Al-impregnated catalysts

119 The GIO was prepared from graphite powder in accordance with the Hummers' method  
120(Hummers et al., 1958). Specifically, 10 g of graphite (G) and 5 g of sodium nitrate ( $\text{NaNO}_3$ )  
121were mixed with concentrated sulphuric acid ( $\text{H}_2\text{SO}_4$ ) (98 wt%, 230 mL) in an ice bath with  
122stirring and subsequently added 30 g of potassium permanganate ( $\text{KMnO}_4$ ) slowly. After  
123agitated at ca. 35 °C for 30 min, 460 mL water was added to the mixture, followed by  
124continuous stirring at 98 °C for 15 min. At the end of thermal treatment, water was added for  
125dilution, and residual  $\text{KMnO}_4$  was reduced using hydrogen peroxide ( $\text{H}_2\text{O}_2$ ). Afterwards,  
126repetitive centrifugation and decantation by deionised water were conducted to wash and  
127collect the solid residue. The washed residue after drying in an oven was collected as GIO.  
128For the production of GO, the dried GIO was suspended in deionised water and was subjected  
129to sonication for 5 h. The mixture was dried in an oven to collect all the solids as the GO.  
130Sawdust was used as the raw material to synthesize biochar (BC)-based catalysts directly.

131 For the Al modification, GIO, GO, and sawdust were placed in aqueous  $\text{AlCl}_3$  (200 mL)  
132for 4-h stirring, followed by oven-drying. The elemental Al loading, i.e., the mass ratio of Al  
133to the carbon supports, was 10 wt%. The  $\text{AlCl}_3$ -treated carbon supports were then activated in  
134a muffle furnace (Carbolite) with a heating rate of 10 °C  $\text{min}^{-1}$ . The target temperature (200 or  
135500 °C) was maintained for 2 h. The calcined materials are denoted as GIO-Al200, GO-  
136Al200, and BC-Al200 (i.e., the loading of Al species onto and the formation of biochar took

place simultaneously in a single step), in which 200 refers to the temperature of thermal activation.

### 2.3 Characterisation of the synthesized catalyst

The surface morphology was studied using scanning electron microscopy (SEM; TESCAN VEGA3). Brunauer-Emmett-Teller (BET) surface areas, pore volumes, and pore diameters were measured by nitrogen adsorption–desorption isotherm measurements at -196 °C with a gas sorption analyser (Micromeritics Accelerated Surface Area and Porosimetry system, ASAP 2020). Micro-Raman spectroscopy (Renishaw) of the biochar-based catalyst was performed with a 532 nm laser and 50× objective. Solid-state <sup>27</sup>Al nuclear magnetic resonance (NMR) spectroscopy was conducted using a 500 MHz JNM-ECZ500R (JEOL) with a scan number of 1301 and relaxation delay of 5 s.

### 2.4 Glucose conversion

The isomerisation of glucose to fructose was conducted in an Ethos Up Microwave Reactor (Milestone), according to the protocol in Yu et al. (2019b). Specifically, catalyst (0.25 g) and glucose (0.5 g) in deionised water (10 mL) were subjected to heating to 140 °C in a sealed Teflon vessel. The ramp time was 5 min and the temperature holding time was 1, 3, 5, 10, 15, 20, 30, or 40 min. Magnetic stirring was maintained throughout the heating. After that, the system was cool to room temperature by forced ventilation inside the reactor.

To evaluate the leaching of active sites, supplementary tests were carried out where the selected carbon samples were heated following the protocol as mentioned above except the addition of glucose. After heating, the solid and liquid phases were separated by centrifugation and decantation, and their respective catalytic performance was investigated by

159repeating the same thermal process adding glucose as the substrate. Water was also added as  
160the reaction medium for the catalytic conversion over the solid phase.

## 1612.5 Catalysis sample analysis

162 After dilution with deionised water (1:3 v/v) and filtration through a mixed cellulose ester  
163filter (0.22  $\mu\text{m}$ ), the liquid samples were analysed via high-performance liquid  
164chromatography (HPLC). A Chromaster instrument coupled with a refractive index detector  
165(Hitachi, Japan) and an Aminex HPX-87H column (Bio-Rad) was used. The temperature was  
166set at 50  $^{\circ}\text{C}$ , whereas 0.01 M  $\text{H}_2\text{SO}_4$  served as the mobile phase (0.5  $\text{mL min}^{-1}$ ). The product  
167yield and selectivity on a carbon mole basis were calculated using the equations (1) and (2).

$$168 \quad \text{Product yield (mol \%)} = \frac{P_f (\text{mg/ml}) \times n_p / MW_p}{Glu_i (\text{mg/ml}) \times n_{Glu} / MW_{Glu}} \times 100 \quad (1)$$

$$169 \quad \text{Product selectivity (mol \%)} = \frac{P_f (\text{mg/ml}) \times n_p / MW_p}{(Glu_i - Glu_f) (\text{mg/ml}) \times n_{Glu} / MW_{Glu}} \times 100 \quad (2)$$

170where  $P_f$  stands for the concentration of the products;  $n_p$  and  $n_{Glu}$  means the number of  
171carbons in the corresponding product and glucose, respectively;  $MW_p$  and  $MW_{Glu}$  represent the  
172molecular mass of the corresponding product and glucose, respectively; and  $Glu_i$  and  $Glu_f$   
173stand for the initial and final concentration of glucose, respectively.

174 The initial rate ( $r$ ) of glucose conversion is based on the concentration change of glucose  
175during the first 1-min reaction. According to Khajavi et al. (2005), degradation processes of  
176monosaccharides (e.g., glucose) is following the Weibull equation (3), where  $k$  and  $n$  stand  
177for rate constant and shape constant, respectively. These kinetic parameters were obtained by



178nonlinear regression analysis using the Solver of Microsoft Excel.

179 
$$C/C_0 = \exp[(-kt)^n] \quad (n < 1) \quad (3)$$

180The parameter  $n$  stands for the kinetic order of the reaction and describes the shape of kinetic  
181curves in this model. In particular, when  $n > 1$ , it exhibits a sigmoidal pattern; when  $n = 1$ , the  
182model represents simple first-order kinetics; when  $n < 1$ , the value of  $C/C_0$  steeply drops  
183during the early stage, and with time increasing, it presents a steady decrease (Khajavi et al.,  
1842005).

185

### 1863. Results and Discussion

#### 1873.1 Fructose yield change with time

188 All of the synthesized BC-Al200, GIO-Al200, and GO-Al200 materials showed useful  
189catalytic activity in the isomerisation of glucose in the water with maximum fructose yields  
190of 29%-35% after microwave heating at 140 °C. The product profiles of the catalytic  
191conversion with increasing time over the three Al-impregnated carbon catalysts showed a  
192similar trend (Figure 1a-c) in terms of fructose yields, where the curves rose steadily at the  
193expense of glucose and then levelled off after approximately 20 min.

194 For both GIO-Al200 and GO-Al200 catalysts, fructose yields increased to ~35% after 20  
195min of reaction. The carbon support GO was derived from GIO by ultrasonic exfoliation. As  
196indicated by Table 1, the surface area (13.2 m<sup>2</sup>/g) and total pore volume (0.064 cm<sup>3</sup>/g) of GO-  
197Al200 were higher than that of GIO-Al200 (3.38 m<sup>2</sup>/g; 0.015 cm<sup>3</sup>/g). In the SEM image  
198(Figure 2a), the surface of GIO-Al200 shows a multi-layer stacking structure, which is absent  
199from the surface morphology of GO-Al200 (Figure 2b). The rough surfaces with more porous

structures were possibly beneficial to the adsorption of fructose for catalysis. Although ultrasonication exfoliated the carbon structure by increasing the surface area and enlarging the pores, changes in these physical properties did not induce noticeable differences in catalytic activities between GIO- and GO-Al<sub>2</sub>O<sub>3</sub> catalysts. Although the enhanced physical structure assisted the bonding of AlCl<sub>3</sub> onto the surface of carbon supports in this study (surface Al content increasing from 5.9% of GIO-Al<sub>2</sub>O<sub>3</sub> to 12.5% of GO-Al<sub>2</sub>O<sub>3</sub>, based on previous XPS results (Yu et al., 2019b)), such improvement did not increase the catalytic activity. The critical determinant of catalytic activity is probably related to the distribution and speciation of Al on the surface, which vary with the conditions of synthesis and modification processes.

In comparison, when using BC as the support material (BC-Al<sub>2</sub>O<sub>3</sub>), the maximum fructose yield reached 29.4% after 40 min, which was slightly lower than that of GIO-Al<sub>2</sub>O<sub>3</sub> (35.0%) and GO-Al<sub>2</sub>O<sub>3</sub> (34.3%) under the same conditions (Figure 1). Less glucose (49.3%) was consumed after 40 min in the BC-Al<sub>2</sub>O<sub>3</sub> system than that for GIO-Al<sub>2</sub>O<sub>3</sub> and GO-Al<sub>2</sub>O<sub>3</sub> (67.6% and 66.3%, respectively), suggesting higher catalytic activities of the graphene-based catalysts than the biochar-based one (the corresponding selectivity will be further discussed in Section 3.3). BC-Al<sub>2</sub>O<sub>3</sub> was derived from wood waste, in which lignin and cellulose could have retained their structure and crystallinity at the relatively low pyrolysis temperature adopted in this study (200 °C) (Keiluweit et al., 2010). The graphitisation of materials was examined by calculating the ratio of D peak to G peak ( $I_D/I_G$ ) in Raman spectra. The  $I_D/I_G$  ratio for BC-Al<sub>2</sub>O<sub>3</sub> was 0.52 (Figure 8a), which was lower than that for GIO-Al<sub>2</sub>O<sub>3</sub> and GO-Al<sub>2</sub>O<sub>3</sub> at 0.95 and 0.93, respectively (Yu et al., 2019b). The discrepancy in surface

morphology of carbon support may lead to the varying extent of Al bonding during impregnation and heating processes, which subsequently resulted in the observed difference in the structures of materials. The GIO and GO catalysts tended to be more disordered, which could be favourable to their catalytic activities. In comparison, there was no clear trend in the fructose yield with the different surface areas and surface Al contents of BC-, GIO-, and GO-Al<sub>2</sub>O<sub>3</sub>, suggesting that these properties were not the most critical determinant of catalytic activity (Figures 1&2; Table 1).

The highest fructose yield (29.4-35.0 mol%) of glucose isomerisation over the three synthesized carbonaceous catalysts in the current study showed greater catalytic activities than the other biochar-based catalysts reported in the recent literature. For example, 10 wt% Al impregnated biochars pyrolysed at 500, 600, and 700 °C as catalysts for glucose isomerisation achieved 14–16 mol% fructose yields at 160 °C (Yu et al., 2019a) and tin-modified biochar catalyst obtained 12.1 mol% fructose yield at 150 °C (Yang et al., 2019), although the temperature used in this study was lower (140 °C).

### 3.2 Conversion kinetics and rate comparison

The kinetics parameters (n and k) of the three catalysts are shown in Table 2. The Weibull equation was employed in this study to fit the kinetics of glucose isomerisation (Figure 3). As for GIO-Al<sub>2</sub>O<sub>3</sub>, GO-Al<sub>2</sub>O<sub>3</sub>, and BC-Al<sub>2</sub>O<sub>3</sub> in the current research, the order constants (n) were in the narrow range of 0.57-0.73 under the studied condition, indicating similar catalytic mechanisms despite using different carbon supports. The other constant k in the kinetic model characterises the reaction rate. According to the Arrhenius equation,  $k = k_0 \exp$

243(-E/RT), the variation in  $k$  value at constant temperature (140 °C) indicates the difference in  
 244activation energies in the catalytic systems studied. As shown in Figure 3 and Table 2, the  
 245GIO-Al200 and GO-Al200 presented very similar kinetic parameters, e.g., initial rate ( $r$ ) =  
 24630.99 mmol/L-min for GIO-Al200 and 28.47 mmol/L-min for GO-Al200). Given their  
 247comparable catalytic activities, GIO was more advantageous in terms of its simpler synthesis  
 248procedure compared to GO. In comparison, BC-Al200 displayed lower activity than the GIO/  
 249GO-based catalysts, as the initial rate of BC-Al200 (14.49 mmol/L-min) was also lower than  
 250that of GIO-Al200 and GO-Al200. The faster kinetics of the latter were probably due to the  
 251more amorphous structures as discussed above. The aqueous  $\text{AlCl}_3$ -catalysed glucose  
 252isomerisation at 140 °C (Choudhary et al., 2013; Tang et al., 2016) has been shown to mostly  
 253follow the first-order reaction ( $n = 1$ ), and the reaction rates of  $0.014 \text{ min}^{-1}$  and  $0.0048 \text{ min}^{-1}$   
 254were respectively reported in these studies. The rate constant of glucose to fructose in a  
 255subcritical aqueous ethanol system at 180 °C was observed to be less than  $0.06 \text{ min}^{-1}$  (Gao et  
 256al., 2015), while another Brønsted base-catalysed (triethylamine) glucose isomerisation at 60  
 257°C achieved the rate constant at  $0.0096 \text{ min}^{-1}$  (Carraher et al., 2015). Currently, available  
 258kinetics studies on glucose conversion over heterogeneous catalysis are limited. The  
 259comparable kinetic constants of the carbon-supported GIO-Al200, GO-Al200, and BC-Al200  
 260catalysed systems in the current research prove the effectiveness and competitive advantages  
 261of the heterogeneous catalysts.

### 2623.3 Fructose selectivity and side reactions

263 Fructose selectivity varying with time on the three catalysts showed a similar trend (Figure  
 2644a), where fructose selectivity decreased from 87-97% at 1 min to 51-50% at 40 min. It

implied that the highest selectivity appeared within 1 min. While fructose was the main product from glucose in this Lewis-acid catalysed system, a small amount of 5-HMF (up to 6.38% yield) was formed by dehydration of fructose under the Al-impregnated catalysts (Figure 1a-c). When the fructose selectivity is plotted against the glucose conversion (Figure 4b), the relative positions among the three curves of GIO-Al200, GO-Al200, and BC-Al200 were quite close, implying similar balance between the desirable fructose formation and side reactions. Besides, the three catalysts exhibited an almost identical selectivity pattern to fructose, suggesting a similar nature of active sites. Differences in the reaction rates were probably due to the numbers and forms of accessible Al sites on the carbon supports.

Prolonged reaction time promoted the formation of other side products, which was revealed by the increasing loss of total carbon over time (Figure 5). For example, a small amount (less than 1.25%) of levoglucosan (LG) was observed over the reaction time of 40 min. When reaction time reached 40 min, the carbon loss to unidentified products was 22.9%, 21.3%, and 11.8% for GIO-Al200, GO-Al200, and BC-Al200, respectively. BC-Al200 produced fewer side products and carbon loss than GIO-Al200 and GO-Al200, probably attributed to its lower catalytic activity. The unavoidable carbon loss may be due to undesirable reactions such as polymerization and hexose internal condensation (Yu et al., 2016). After glucose is converted to fructose, it can further dehydrate to 5-HMF if there is an acid environment. Carbohydrate products and other intermediates that formed from this reaction system may polymerise through aldol addition and condensation, thus forming oligosaccharides, which more easily occurs under Lewis acidity than Brønsted acidity (Yu et al., 2016; Yu et al., 2017).

#### 2873.4 Roles of active sites and leaching

288 Additional tests on glucose conversion over solid and liquid phases separately at 140 °C for  
28920 min were performed by hydrothermal treatment of the original catalyst. As illustrated in  
290Figure 6, the catalytic activity of both liquid and solid phase after hydrothermal treatment of  
291GIO-Al200 and BC-Al200 implied that active species leached from the solid catalyst to the  
292solution to some extent during heating. To explore the potential role of pyrolysis temperature  
293on the active sites of the catalysis, we produced GIO-Al at 500 °C (GIO-Al500) and  
294evaluated its catalytic performance in supplementary tests. The fructose yield from the solid  
295phase of GIO-Al500 after hydrothermal treatment was approximately twice higher than that  
296from the liquid phase. The substantially lower contribution of liquid fraction than solid phase  
297suggested that a higher activation temperature of catalyst production would stabilise the  
298active sites and allow less subsequent leaching. However, GIOAl-500 achieved a lower  
299overall fructose yield compared to its counterpart calcinated at 200 °C.

300 The final pH of the solution decreased over time (Figure 7), ranging from 3.89 to 2.68  
301between 1 and 40 min. This observation is probably because acid products (e.g., formic acid)  
302formed over time and the leaching of active Al species from the carbon support. Leaching of  
303Al decreased the solution pH with time thus increasing the number of protons that could  
304promote side reactions such as dehydration and polymerization, which accounted for the  
305observed decrease of fructose selectivity over time (Figure 4). This phenomenon became less  
306significant when BC-Al200 was applied, as the final pH was higher than with GIO-Al200 and  
307GO-Al200. As mentioned in Section 3.3, BC-Al200 gave fewer side products with higher  
308fructose selectivity (60.4%) than GIO-Al200 and GO-Al200 (51.0% and 51.8%) at 40 min.

309 For instance, the 5-HMF yield from using BC-Al200 at 40 min was 3.48%, which was lower  
310 than 6.38% and 5.97% of GIO-Al200 and GO-Al200. This result can be explained by the  
311 presence of alkali minerals in sawdust and its derived biochar (Wang et al., 2016b), which  
312 buffered the decrease of solution pH. Therefore, the pH buffering capacity of biochar catalyst  
313 can help to moderate the catalytic activity and reduce the undesirable side reactions.

#### 314 3.5 Active sites of BC-Al200

315 In the Al-impregnated carbon catalysis system, aluminium species coordinated in the  
316 carbon support catalyse glucose isomerisation in a Lewis acid-driven pathway, where hydride  
317 shift occurred in different carbon positions of glucose in conjunction with an electron pair  
318 acceptor. It has been reported that the Lewis acidic active sites for glucose isomerisation  
319 might be Al species in the amorphous phase including aluminium carbide ( $\text{Al}_4\text{C}_3$ ) and four-,  
320 five-, six- coordinated Al species (e.g.,  $\beta\text{-Al}(\text{OH})_3$ ,  $\gamma\text{-Al}(\text{OH})_3$ ,  $\text{Al-O-C}$ ,  $\text{AlO}(\text{OH})$ , and  $\gamma\text{-}$   
321  $\text{AlO}(\text{OH})$ ) that are impregnated on the carbon supports (Yu et al., 2019a, Yu et al., 2019b),  
322 and also probably from hydrolysed Al(III) complex  $[\text{Al}(\text{H}_2\text{O})_4(\text{OH})_2]^{1+} / [\text{Al}(\text{OH})_2(\text{aq})]^+$  (Tang  
323 et al., 2015; Norton et al., 2018; Cao et al., 2019). Such Al-coordinated complexes played an  
324 active role in shortening the hydrogen transfer distance during glucose isomerisation, thus  
325 overcoming the energy barrier and facilitating the rate-determining hydride shift (Ju et al.,  
326 2019). Moreover, the oxygen-containing functionalities can further facilitate glucose  
327 isomerisation by enhancing reflection, transmission, and absorption of microwave in the  
328 oxygen moieties intensified hotspots (Yu et al., 2019b).

329 As for biochar catalyst in the current study, the amorphous phase of BC-Al200 was shown

330 in the Raman spectra with  $I_D/I_G$  at 0.52 (Figure 8a). Effective impregnation of Al species was  
 331 confirmed by XPS (Figure 8b) and NMR spectra (Figure 8c). According to XPS fitting, it can  
 332 be seen that  $\beta$ -Al(OH)<sub>3</sub>,  $\gamma$ -Al(OH)<sub>3</sub> / Al-O-C, and  $\gamma$ -AlO(OH) are the main Al components in  
 333 the BC-Al200 catalyst, constituting approximately 67.8%, 15.3%, and 17% of the total Al  
 334 species. These species might be present in the configurations of four-, five-, and six-  
 335 coordinated aluminium, (Al[4], Al[5], and Al[6]) as shown in Figure 8c. Diverse oxygen-  
 336 containing groups on the biochar surface, such as hydroxyl and epoxy groups can facilitate  
 337 the impregnation of Al and promote the formation of an Al-O matrix (Yu et al., 2019a).  
 338 Similar chemical features of BC-Al200 suggested similar pathways when using graphite-  
 339 derived and biomass-derived materials as carbon support to synthesize active catalysts for  
 340 glucose isomerisation. Nevertheless, when comparing the Al species of the three catalysts,  
 341 Al<sub>4</sub>C<sub>3</sub> was present in GIO-Al200 but was absent from GO-Al200 and BC-Al200. The  
 342 contents of Al[6] (including Al[6]<sup>\*</sup> and Al[6]<sup>#</sup>) of all the three catalysts were between 70%  
 343 and 80%, while Al[4] of BC-Al200 was only slightly lower than those of GIO-Al200 and  
 344 GO-Al200 (8.8% and 10.5%) (Yu et al., 2019b). The Al[5] (five-coordination) content  
 345 constituted 16.8% of BC-Al200, while the corresponding figures in GIO-Al200 and GO-  
 346 Al200 were only 5.9% and 1.1% (Yu et al., 2019b). Such differences of Al species may act as  
 347 significant factors in determining the active site distributions, the roles of which are expected  
 348 to be further explored with computational simulation of molecular geometry and energy  
 349 barriers. The more amorphous surface of graphite and graphene oxide may present more  
 350 abundant and evenly distributed microwave-sensitive functionalities and active sites  
 351 rendering faster kinetics as well as greater catalytic activities than the biochar support.



352 These findings provide key information about conversion kinetics and catalytic activity,  
353 and hence contribute to further optimising the synthesis process of carbon-based catalysts for  
354 sustainable biorefinery. As summarised in Figure 9, the synthesis method of metal-doped  
355 carbonaceous catalysts was facile and green, which reduced the use of costly and potentially  
356 hazardous chemicals as well as minimised the release of secondary pollutants into the  
357 environment. The carbon supports acted as the skeleton with diverse functionalised moieties,  
358 while the metal doping introduced the active species with catalytic sites. Comparatively,  
359 biochar-based catalysts showed a similar catalytic performance and kinetics mode with  
360 graphite/graphene oxide-based catalysts. Biochar derived from waste biomass is a renewable  
361 and sustainable material, and its simple one-step production process through pyrolysis with  
362 metal doping seems economically competitive for large-scale production. The utilisation of  
363 engineered biochar can relieve greenhouse gas emissions and waste disposal burdens. Further  
364 optimisation of synthesis design can improve the catalytic performance of engineered biochar  
365 for producing valuable platform chemicals in a cost-effective and environmentally friendly  
366 way.

367

#### 3684. Conclusions and future prospects

369 This study compared the performances of three carbon materials (GIO, GO, and BC) as  
370 supports to synthesize heterogeneous catalysts by impregnation with 10 wt% Al for the  
371 catalytic isomerisation of glucose to fructose for sustainable biorefinery. By using microwave  
372 heating at 140 °C in water as a green solvent, Al-impregnated carbon-based catalysts showed  
373 considerable catalytic activities for glucose isomerisation with maximum fructose yields of

37429-35%. GIO-Al200 showed similar catalytic activities as GO-Al200, while BC-Al200  
375presented slightly slower kinetics with less carbon loss as side products. Engineered biochar  
376catalyst could be synthesized in a low-cost and sustainable manner with less resource  
377consumption and carbon emission to the environment. From the results of this study, the  
378design of cost-effective and environment-friendly carbon-based catalysts to optimise the  
379catalytic activity could be further investigated. For example, adjusting the pyrolysis  
380temperature or purging gas to tailor the oxygenated functionality of biochar surface, and  
381changing the concentration or speciation of impregnation agent to improve the dispersion of  
382active sites, are promising directions for future design of catalysts for sustainable biorefinery.  
383More explorations on integrated biorefinery to make full use of the biomass feedstock and  
384exploit the chain reactions with various value-added products are expected to achieve high  
385carbon efficiency. The insights revealed in this work contribute to the green design of Al-  
386impregnated biochar catalyst for biorefinery process and biomass valorisation.

387

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### 394**References**

395 1. Al-Amsyar, S. M., Adam, F., Ng, E. P., 2017. Aluminium oxide-silica/carbon composites

- 396 from rice husk as a bi-functional heterogeneous catalyst for the one-pot sequential  
397 reaction in the conversion of glucose. *Surf. Interfaces* 9, 1-8.
- 398 2. Antunes, M. M., Russo, P. A., Wiper, P. V., Veiga, J. M., Pillinger, M., Mafra, L.,  
399 Evtuguin, D. V., Pinna, N., Valente, A. A., 2014. Sulfonated graphene oxide as effective  
400 catalyst for conversion of 5-(Hydroxymethyl)-2-furfural into Biofuels. *ChemSusChem*,  
401 7, 804-812.
- 402 3. Bottari, G., Herranz, M. Á., Wibmer, L., Volland, M., Rodríguez-Pérez, L., Guldi, D. M.,  
403 Hirsch, A., Martín, N., D'Souza, F., Torres, T., 2017. Chemical functionalization and  
404 characterization of graphene-based materials. *Chem. Soc. Rev.* 46, 4464-4500.
- 405 4. Cao, J., Ma, M., Liu, J., Yang, Y., Liu, H., Xu, X., Huang, J., Yue, H., Tian, G., Feng, S.,  
406 2019. Highly effective transformation of carbohydrates to 5-Hydroxymethylfurfural with  
407 Al-montmorillonite as catalyst. *Appl. Catal.* 571, 96-101.
- 408 5. Carraher, J. M., Fleitman, C. N., Tessonnier, J. P., 2015. Kinetic and mechanistic study of  
409 glucose isomerisation using homogeneous organic Brønsted base catalysts in water. *ACS*  
410 *Catal.* 5, 3162-3173.
- 411 6. Clark, J. H., 2019. Green biorefinery technologies based on waste biomass. *Green*  
412 *Chem.* 21, 1168-1170.
- 413 7. Chen, S. S., Maneerung, T., Tsang, D. C., Ok, Y. S., Wang, C. H., 2017. Valorization of  
414 biomass to hydroxymethylfurfural, levulinic acid, and fatty acid methyl ester by  
415 heterogeneous catalysts. *Chemical Engineering Journal*, 328, 246-273.
- 416 8. Chen, S. S., Wang, L., Iris, K. M., Tsang, D. C., Hunt, A. J., Jérôme, F., Zhang, S., Ok, Y.  
417 S., Poon, C. S., 2018a. Valorization of lignocellulosic fibres of paper waste into levulinic  
418 acid using solid and aqueous Brønsted acid. *Bioresour. Technol.* 247, 387-394.
- 419 9. Chen, S. S., Yu, I. K., Cho, D. W., Song, H., Tsang, D. C., Tessonnier, J. P., Ok, Y. S.,  
420 Poon, C. S., 2018b. Selective Glucose Isomerisation to Fructose via a Nitrogen-doped  
421 Solid Base Catalyst Derived from Spent Coffee Grounds. *ACS Sustainable Chem. Eng.*  
422 6, 16113-16120.
- 423 10. Choudhary, V., Mushrif, S. H., Ho, C., Anderko, A., Nikolakis, V., Marinkovic, N. S.,  
424 Frenkel, A. I., Sandler, S.I., Vlachos, D. G., 2013. Insights into the interplay of Lewis  
425 and Brønsted acid catalysts in glucose and fructose conversion to 5-(hydroxymethyl)  
426 furfural and levulinic acid in aqueous media. *J. Am. Chem. Soc.* 135, 3997-4006.
- 427 11. Delidovich, I., and Palkovits, R., 2016. Catalytic Isomerisation of Biomass-Derived  
428 Aldoses: A Review. *ChemSusChem*, 9, 547-561.
- 429 12. Dutta, S., Yu, I. K. M., Tsang, D. C., Ng, Y. H., Ok, Y. S., Sherwood, J., Clark, J. H.,  
430 2019. Green synthesis of gamma-valerolactone (GVL) through hydrogenation of  
431 biomass-derived levulinic acid using non-noble metal catalysts: A critical review. *Chem.*  
432 *Eng. J.* 372, 992-1006.
- 433 13. Gao, D. M., Kobayashi, T., Adachi, S., 2015. Kinetic analysis for the isomerisation of

- 434 glucose, fructose, and mannose in subcritical aqueous ethanol. *Biosci. Biotechnol.* 79,  
435 1005-1010
- 436 14. Georgakilas, V., Tiwari, J. N., Kemp, K. C., Perman, J. A., Bourlinos, A. B., Kim, K. S.,  
437 Zboril, R., 2016. Noncovalent functionalization of graphene and graphene oxide for  
438 energy materials, biosensing, catalytic, and biomedical applications. *Chem. Rev.* 116,  
439 5464-5519.
- 440 15. Guo, W., Liu, H., Zhang, S., Han, H., Liu, H., Jiang, T., Han, B., Wu, T., 2016. Efficient  
441 hydrogenolysis of 5-hydroxymethylfurfural to 2, 5-dimethylfuran over a cobalt and  
442 copper bimetallic catalyst on N-graphene-modified Al<sub>2</sub>O<sub>3</sub>. *Green Chem.* 18, 6222-  
443 6228.
- 444 16. Hou, Q., Li, W., Ju, M., Liu, L., Chen, Y., Yang, Q., 2016. One-pot synthesis of  
445 sulfonated graphene oxide for efficient conversion of fructose into HMF. *RSC*  
446 *Advances*, 6, 104016-104024.
- 447 17. Hummers, W. S., and Offeman, R. E., 1958. Preparation of graphitic oxide. *J. Am. Chem.*  
448 *Soc.* 80, 1339-1339.
- 449 18. Ju, Z., Zhang, Y., Zhao, T., Xiao, W., Yao, X., 2019. Mechanism of Glucose–Fructose  
450 Isomerization over Aluminum-Based Catalysts in Methanol Media. *ACS Sustainable*  
451 *Chem. Eng.* 7, 14962-14972.
- 452 19. Keiluweit, M., Nico, P.S., Johnson, M.G., Kleber, M., 2010. Dynamic molecular  
453 structure of plant biomass-derived black carbon (biochar). *Environ. Sci. Technol.* 44,  
454 1247.
- 455 20. Khajavi, S. H., Kimura, Y., Oomori, T., Matsuno, R., Adachi, S., 2005. Degradation  
456 kinetics of monosaccharides in subcritical water. *J. Food Eng.* 68, 309-313.
- 457 21. Lam, S. S., Liew, R. K., Cheng, C. K., Chase, H. A., 2015. Catalytic microwave  
458 pyrolysis of waste engine oil using metallic pyrolysis char. *Applied Catalysis B:*  
459 *Environmental*, 176–177, 601-617.
- 460 22. Lam, S. S., Liew, R. K., Wong, Y. M., Azwar, E., Jusoh, A., Wahi, R., 2017. Activated  
461 carbon for catalyst support from microwave pyrolysis of orange peel. *Waste Biomass*  
462 *Valor.* 8, 2109–2119
- 463 23. Li, H., Yang, S., Saravanamurugan, S., Riisager, A., 2017. Glucose isomerisation by  
464 enzymes and chemo-catalysts: Status and current advances. *ACS Catal.* 7, 3010-3029.
- 465 24. Li, Z., Sun, Y., Yang, Y., Han, Y., Wang, T., Chen, J., Tsang, D. C. W., 2020. Biochar-  
466 supported nanoscale zero-valent iron as an efficient catalyst for organic degradation in  
467 groundwater. *J. Hazard. Mater.*, 383, 121240.
- 468 25. Liew, R.K., Chong, M.Y., Osazuwa, O.U., Nam, W. L., Phang, X. Y., Su, M. H., Cheng,  
469 C. K., Chong, C. T., Lam, S.S., 2018. Production of activated carbon as catalyst support  
470 by microwave pyrolysis of palm kernel shell: a comparative study of chemical versus  
471 physical activation. *Res Chem Intermed* 44, 3849–3865.

- 472 26. Mission, E. G., Quitain, A. T., Sasaki, M., Kida, T., 2017. Synergizing graphene oxide  
473 with microwave irradiation for efficient cellulose depolymerization into glucose. *Green*  
474 *Chemistry*, 19, 3831-3843.
- 475 27. Norton, A. M., Nguyen, H., Xiao, N. L., Vlachos, D. G., 2018. Direct speciation methods  
476 to quantify catalytically active species of  $\text{AlCl}_3$  in glucose isomerisation. *RSC Adv.* 8,  
477 17101-17109.
- 478 28. Ray, S. C., 2015. Applications of Graphene and Graphene-Oxide Based Nanomaterials  
479 (Chapter 2), *Application and Uses of Graphene Oxide and Reduced Graphene Oxide*.  
480 page 39-55. Elsevier Inc.
- 481 29. Shaikh, M., Singh, S. K., Khilari, S., Sahu, M., Ranganath, K. V., 2018. Graphene oxide  
482 as a sustainable metal and solvent free catalyst for dehydration of fructose to 5-HMF: A  
483 new and green protocol. *Catal. Commun.* 106, 64-67.
- 484 30. Sudarsanam, P., Zhong, R., Van den Bosch, S., Coman, S. M., Parvulescu, V. I., Sels, B.  
485 F., 2018. Functionalised heterogeneous catalysts for sustainable biomass  
486 valorisation. *Chem. Soc. Rev.* 47, 8349-8402.
- 487 31. Tang, J., Guo, X., Zhu, L., Hu, C., 2015. Mechanistic study of glucose-to-fructose  
488 isomerisation in water catalyzed by  $[\text{Al}(\text{OH})_2(\text{aq})]^+$ . *ACS Catal.* 5, 5097-5103.
- 489 32. Tang, J., Zhu, L., Fu, X., Dai, J., Guo, X., Hu, C., 2016. Insights into the Kinetics and  
490 Reaction Network of Aluminum Chloride-Catalyzed Conversion of Glucose in  $\text{NaCl}$ -  
491  $\text{H}_2\text{O}/\text{THF}$  Biphasic System. *ACS Catal.* 7, 256-266.
- 492 33. Wang, H., Kong, Q., Wang, Y., Deng, T., Chen, C., Hou, X., Zhu, Y., 2014. Graphene  
493 oxide catalyzed dehydration of fructose into 5-hydroxymethylfurfural with isopropanol  
494 as cosolvent. *ChemCatChem*, 6, 728-732.
- 495 34. Wang, L., Chen, L., Tsang, D. C. W., Kua, H. W., Yang, J., Ok, Y. S., Ding, S., Hou, D.,  
496 Poon, C. S., 2019. The roles of biochar as green admixture for sediment-based  
497 construction products. *Cem. Concr. Compos.*, 104, 103348.
- 498 35. Wang, L., Chen, S. S., Tsang, D. C., Poon, C. S., Shih, K., 2016b. Value-added recycling  
499 of construction waste wood into noise and thermal insulating cement-bonded  
500 particleboards. *Constr. Build. Mater.* 125, 316-325.
- 501 36. Wang, X., Su, K., Li, Z., Cheng, B., 2016a. Formation of larger-area graphene from  
502 small GO sheets in the presence of basic divalent sulfide species and its use in biomass  
503 conversion. *RSC Adv.* 6, 11176-11184.
- 504 37. Xiong, X., Yu, I. K. M., Cao, L., Tsang, D. C. W., Zhang, S., Ok, Y. S., 2017. A review of  
505 biochar-based catalysts for chemical synthesis, biofuel production, and pollution  
506 control. *Bioresour. Technol.* 246, 254-270.
- 507 38. Xiong, X., Yu, I. K. M., Tsang, D. C. W., Bolan, N. S., Ok, Y. S., Igalavithana, A. D.,  
508 Kirkham, M.B., Kim, K.H., Vikrant, K., 2019. Value-added Chemicals from Food Supply  
509 Chain Wastes: State-of-the-art Review and Future Prospects. *Chem. Eng. J.* 121983.

- 510 39. Xiong, X., Yu, I. K. M., Chen, S. S., Tsang, D. C. W., Cao, L., Song, H., Kwon, E. E.,  
511 Ok, Y. S., Zhang, S., Poon, C. S., 2018. Sulfonated biochar as acid catalyst for sugar  
512 hydrolysis and dehydration. *Catal. Today* 314, 52-61.
- 513 40. Yang, X., Yu, I. K. M., Cho, D. W., Chen, S. S., Tsang, D. C. W., Shang, J., Yip, A. C. K.,  
514 Wang, L., Ok, Y. S., 2019. Tin-Functionalized Wood Biochar as a Sustainable Solid  
515 Catalyst for Glucose Isomerisation in Biorefinery. *ACS Sustainable Chem. Eng.* 7, 4851-  
516 4860.
- 517 41. Yu, I. K. M., Tsang, D. C. W., 2017. Conversion of biomass to hydroxymethylfurfural: A  
518 review of catalytic systems and underlying mechanisms. *Bioresour. Technol.* 238, 716-  
519 732.
- 520 42. Yu, I. K. M., Tsang, D. C., Yip, A. C., Chen, S. S., Ok, Y. S., Poon, C. S., 2016.  
521 Valorization of food waste into hydroxymethylfurfural: dual role of metal ions in  
522 successive conversion steps. *Bioresour. Technol.* 219, 338-347.
- 523 43. Yu, I. K. M., Tsang, D. C. W., Yip, A. C. K., Chen, S. S., Wang, L., Ok, Y. S., Poon, C.  
524 S., 2017. Catalytic valorization of starch-rich food waste into hydroxymethylfurfural  
525 (HMF): controlling relative kinetics for high productivity. *Bioresour. Technol.* 237, 222-  
526 230.
- 527 44. Yu, I. K. M., Xiong, X., Tsang, D. C. W., Wang, L., Hunt, A. J., Song, H., Shang, J., Ok,  
528 Y.S., Poon, C. S., 2019a. Aluminium-biochar composites as sustainable heterogeneous  
529 catalysts for glucose isomerisation in a biorefinery. *Green Chem.* 21, 1267-1281.
- 530 45. Yu, I. K. M., Xiong, X., Tsang, D. C. W., Ng, Y. H., Clark, J., Fan, J., Zhang, S., Hu, C.,  
531 Ok, Y. S., 2019b. Graphite Oxide-and Graphene Oxide-supported Catalysts for  
532 Microwave-assisted Glucose Isomerisation in Water. *Green Chem.* 21, 4341-4353.
- 533 46. Zhang, M., Su, K., Song, H., Li, Z., Cheng, B., 2015. The excellent performance of  
534 amorphous  $\text{Cr}_2\text{O}_3$ ,  $\text{SnO}_2$ ,  $\text{SrO}$  and graphene oxide–ferric oxide in glucose conversion into  
535 5-HMF. *Catal. Commun.* 69, 76-80.
- 536 47. Zhou, W., Fan, Y., Feng, X., Kikuchi, K., Nomura, N., Kawasaki, A., 2018. Creation of  
537 individual few-layer graphene incorporated in an aluminum matrix. *Composites Part A:  
538 Applied Science and Manufacturing.* 112, 168-177.
- 539 48. Zhu, S., Wang, J., Fan, W., 2015. Graphene-based catalysis for biomass  
540 conversion. *Catal. Sci. Technol.* 5, 3845-3858.
- 541