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1 **Valorization of Humins from Food Waste Biorefinery for Synthesis of Biochar-**
2 **supported Lewis Acid Catalysts**

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13

14 **Abstract**

15 To close the carbon loop of biomass waste valorization, it is imperative to utilize the
16 unavoidable by-products such as humins, a carbonaceous residue with complex and
17 heterogeneous composition. In this study, starch-rich rice waste was effectively converted into
18 value-added chemicals (e.g., 5-hydroxymethylfurfural) under microwave heating at 160 °C
19 using AlCl₃ as the catalyst. The solid by-products, i.e., humins, were then valorized as a raw
20 material for fabricating biochar-supported Lewis acid catalysts. The humins were collected and
21 pretreated by AlCl₃ as the impregnation agent, followed by carbonization. Detailed
22 characterization revealed several Al-O species on the biochar surface plausibly in the
23 amorphous state. The oxygen-containing functional groups of humins might serve as anchoring
24 sites for the Al species during impregnation. The humins-derived biochars exhibited good
25 catalytic activity toward glucose-to-fructose isomerization, a common biorefinery reaction
26 catalyzed by Lewis acids. A fructose yield of up to 14 Cmol% could be achieved under
27 microwave heating at 160 °C for 20 min in water as the greenest solvent. Such catalytic
28 performance was comparable with the previously reported Al-based catalysts derived from
29 wood waste and graphene/graphitic oxide. This study herein highlights humins as a low-cost
30 alternative source of carbon for the preparation of renewable solid catalysts, proposing a novel
31 practice for recycling by-products from food waste valorization to foster circular economy and
32 sustainable development.

33 **Keywords:** biomass valorization; food waste recycling; engineered biochar; sustainable
34 biorefinery; glucose isomerization; waste management.

35 **1. Introduction**

36 The global shortage of energy and resources has driven the urgent demand for innovative
37 technologies to seek renewable alternatives to fossil fuels. Waste biomass generated in
38 significant amounts has been promisingly serving as a sustainable and green resource for the
39 production of value-added products in recent years, which will play an important role in our
40 transition to circular economy (Mak et al., 2020). Food waste is one of the major waste biomass
41 streams receiving considerable public attention and research interest. Various valorization
42 options using physical, chemical, and biological processing technologies have been reported
43 (Xiong et al., 2019). The composition of food waste makes it suitable as a starting material for
44 the production of biofuels and chemicals. For instance, cellulose and starch, the major
45 components in food waste, are a source of versatile glucose molecules that can be converted to
46 fructose. The latter is a promising substrate for the synthesis of value-added chemicals, such
47 as 5-hydroxymethylfurfural (HMF), which is a critical and valuable building block for the
48 manufacture of pharmaceuticals, resins, solvents, and polymers (Mukherjee et al., 2015; Yu
49 and Tsang, 2017).

50 The chemical process of cellulose/starch conversion involves multiple reactions that are
51 often accelerated over different catalysts. For example, the hydrolysis of polysaccharides to
52 glucose is commonly catalyzed by Brønsted acid sites, whereas glucose isomerization to
53 fructose can be promoted over Lewis acids or Brønsted bases (Yu and Tsang, 2017). Most of
54 the reported catalytic conversions are accompanied by side reactions under hydrothermal
55 conditions, which generate heterogeneous solid residues, denoted as humins, via irreversible
56 aldol condensation among intermediates and products (Cheng et al., 2018; Filiciotto et al., 2018;

57 Pfab et al., 2019). Humins is insoluble and macromolecular substances composed of co-
58 products such as furanics, levulinates, and sugar-derived molecules (Filiciotto et al., 2019). The
59 cross-linked structure renders humins as a potential carbon matrix for catalyst support. To
60 achieve high carbon efficiency in the circular bioeconomy, it is desirable to explore value-
61 added application of the unavoidable humins. Previous studies investigated steam reforming of
62 humins to hydrogen (Hoang et al., 2013) and liquefaction/depolymerization of humins into
63 pyrolysis oil (Agarwal et al., 2017). These technologies focused on mineralization via selective
64 bond dissociation, yet high temperature and catalyst consumption may restrict its large-scale
65 valorization (Hoang et al., 2015). An alternative approach that might be more energy-efficient
66 is to exploit and modify the polycyclic aromatic structure of humins. Previous studies examined
67 humins as a prospective precursor of eco-friendly carbon materials, such as hydrophobic
68 humins/flax fibres composites and humins-based resins (Sangregorio et al., 2019; Sangregorio
69 et al., 2020).

70 There are, however, limited research studies on the synthesis of humins-derived biochar for
71 the application in green biorefinery processes. Biochar is an environmentally friendly, low-
72 cost, and renewable material produced from waste biomass by means of pyrolysis or
73 hydrothermal carbonization (Tang et al., 2013). They have been extensively tested in a range
74 of applications, including uses as potential catalysts or catalyst supports, because the porous
75 structure, surface area, and functional groups can be tuned to facilitate the impregnation of
76 active sites and adsorption of reactants (Xiong et al., 2017; Kumar et al., 2020). While raw
77 lignocellulosic biomass (forestry waste, agricultural residue, etc.) are typical feedstock in the
78 biochar production, humins could be an alternative carbon source, especially for applications

79 that would benefit from hydrophilic surface (van Zandvoort et al., 2013), such as catalyst
80 supports. Sulfonated humins-derived catalysts were studied for the esterification of levulinic
81 acid (LA) and n-butanol, hydroxyalkylation/alkylation of 2-methylfuran and furfural (Yang et
82 al., 2020), and cellulose conversion to LA (Wang et al, 2018). We conjecture that impregnation
83 of transition metals can introduce Lewis acid sites on humins-derived biochar surface, which
84 would enable its application in more diverse reactions. Our previous studies of Al-based
85 catalysts supported on wood waste biochar (Yu et al., 2019a) and graphene/graphite oxide (Yu
86 et al., 2019b; Xiong et al., 2020) revealed their good performance in glucose-fructose
87 isomerization.

88 In this study, we aim to recycle and valorize humins for the synthesis of renewable,
89 sustainable solid Lewis acids that can catalyze biorefinery processes. Cooked rice waste daily
90 generated in the Hong Kong International Airport (HKIA) was collected and used as the food
91 waste substrate in this work. A high-performance waste recycling system for valorization of
92 starch-rich waste from local enterprises is expected to bring environmental and economic
93 benefits to the society. Rice waste conversion was performed for HMF production and the
94 simultaneously produced humins were collected and modified by metal impregnation in $AlCl_3$
95 aqueous solutions. The prepared catalysts were characterized and evaluated for glucose
96 isomerization as a model reaction mediated by Lewis acids in biorefineries.

97

98 **2. Materials and methods**

99 2.1 Chemicals and raw materials

100 Cooked rice waste was collected from restaurants in the HKIA, and was subjected to drying
101 at 105 °C, grinding, and sieving (0.2 mm mesh), before storage in an airtight container at 4 °C.
102 The $\text{AlCl}_3 \cdot 6\text{H}_2\text{O}$ (ACS grade) purchased from Anaqua was used for impregnation in this study.
103 Standard compounds were used for catalytic glucose conversion and equipment calibration,
104 including glucose ($\geq 99.5\%$), HMF ($\geq 99\%$), and furfural (99%) from Sigma Aldrich;
105 cellobiose ($\geq 98\%$), LA (98%), and formic acid (FA) (98%) from Alfa Aesar; levoglucosan
106 from Fluorochem; and fructose ($\geq 99\%$) and maltose monohydrate ($\geq 98\%$) from Wako. All
107 the chemicals were used as received.

108

109 2.2 Rice waste and glucose catalytic conversion

110 The catalytic conversion of rice waste or glucose was performed following the procedures
111 reported in our previous studies (Yu et al., 2019a; Yu et al., 2019b). The mixture was placed
112 in a sealed Teflon vessel, followed by heating to 160 °C in the Ethos Up Microwave Reactor
113 (Milestone, maximum power 1900 W). Various rice waste loading (0.1, 0.15, and 0.2 g mL⁻¹)
114 and AlCl_3 catalyst dosage (Al concentration = 10 or 20 wt%) were tested at 160 °C with a ramp
115 time of 5 min and holding time ranging from 0 to 40 min. Vigorous magnetic stirring was
116 maintained throughout the whole process. After the reaction, the vessel was cooled to room
117 temperature under continuous mechanical ventilation for 40 min in the reactor. The soluble
118 samples were prepared for product analysis, while the solid residues were collected for the
119 synthesis of humins-derived biochar catalysts. The catalysts were evaluated for glucose
120 isomerization, which was performed following the abovementioned procedure. The biochar

121 catalyst (0.25 g) and glucose (0.5 g) were added to 10 mL deionized water or water/acetone
122 (1:1 v/v) solvent, followed by microwave heating at 140 °C and 160 °C for 5, 20, and 40 min,
123 respectively. All trials were carried out in duplicate.

124

125 2.3 Synthesis of humins-derived biochar catalysts

126 Based on the results of rice waste conversion achieving the maximal HMF yield, the
127 conditions for batch production of humins were determined at 0.15 g mL⁻¹ rice waste in 10 wt%
128 AlCl₃ aqueous solution at a temperature of 160 °C. The holding time was 0 and 15 min,
129 producing residues denoted as Humins0 and Humins15, respectively. The residues were
130 recovered by centrifugation and decantation, followed by multiple washing with deionized
131 water. For Al impregnation, 10 g residues were suspended in a 200 mL solution of 10 wt%
132 AlCl₃ with stirring for 4 h. After oven-drying the mixture at 105 °C, the AlCl₃-treated humins
133 were placed in a ceramic boat for carbonization in a Carbolite muffle furnace at 500 °C for 2 h
134 (10 °C min⁻¹ ramping), which produced humins-derived biochars labelled as HB15-Al and
135 HB0-Al. It was reported that pyrolysis temperatures ranging from 500 to 700 °C are favourable
136 for biochar production in view of stable polycyclic aromatic carbon and overall yield for
137 common feedstock (Xiong et al., 2017). For an energy-efficient utilization and fair comparison
138 with our previous reports on biochar-based catalysts (Yu et al., 2019a; Xiong et al., 2020), we
139 selected 500 °C as the carbonization temperature in this study (**Fig. 1**). As for control
140 experiments, humins without AlCl₃ treatment were subjected to the same pyrolysis treatment,
141 and the resultant biochars were denoted as HB15 and HB0. All prepared catalysts were stored
142 in a sealed container in a desiccator before characterization and catalytic activity evaluation.

143

144 2.4 Biochar catalyst characterization

145 The morphology, topography, and elemental distribution of the humins-based biochar
146 catalysts were revealed by scanning electron microscopy (SEM) with energy dispersive X-ray
147 analysis (EDX) [TESCAN VEGA3]. Brunauer-Emmett-Teller (BET) surface area and pore
148 volume were measured by nitrogen adsorption–desorption isotherm measurement at -196 °C
149 using a gas sorption analyser (Micromeritics Accelerated Surface Area and Porosimetry system,
150 ASAP 2020). The crystalline and amorphous phases were revealed by X-ray diffraction
151 analysis (XRD; Rigaku SmartLab) in a scanning range of 10–80° 2 θ at a rate of 5° min⁻¹ at 45
152 kV and 200 mA. The surface functionalities were studied using micro-Raman spectroscopy
153 (Renishaw) with a laser source at a wavelength of 532 nm and an objective of 50 \times . X-ray
154 photoelectron spectroscopy (XPS; ESCALAB 250Xi spectrometer, USA) with
155 monochromated Al K α radiation was performed with a pass energy of 187.85 eV at 1.6 eV per
156 step for survey scans (0 to 1200 eV). Curve fitting was performed for the obtained spectra of
157 Al 2p using XPSPEAK41.

158

159 2.5 Catalysis product analysis

160 Liquid samples collected after microwave-assisted conversion were diluted with deionized
161 water (1:3 v/v) and filtered through a mixed cellulose ester filter (0.22 μ m) before analysis.
162 High-performance liquid chromatography (HPLC) was performed using a Chromaster
163 instrument equipped with a refractive index detector (Hitachi, Japan) and an Aminex HPX-
164 87H column (Bio-Rad) at an analytical temperature of 50 °C. The mobile phase was 0.01 M

165 H₂SO₄ at a flow rate of 0.5 mL min⁻¹. The yield and selectivity of the products were calculated
166 in terms of the carbon content.

$$167 \text{ Product yield (Cmol\%)} = \frac{P_f(\text{mg/ml}) \times n_p / MW_P}{Glu_i(\text{mg/ml}) \times n_{Glu} / MW_{Glu}} \times 100, \quad (1)$$

$$168 \text{ Product selectivity (Cmol\%)} = \frac{P_f(\text{mg/ml}) \times n_p / MW_P}{(Glu_i - Glu_f)(\text{mg/ml}) \times n_{Glu} / MW_{Glu}} \times 100 \quad (2)$$

169 where P_f represents the concentration of the products, n_p and n_{Glu} are number of carbons in the
170 corresponding product and glucose, MW_p and MW_{Glu} are molecular mass of the corresponding
171 product and glucose, and Glu_i and Glu_f represent the initial and final concentration of glucose,
172 respectively. One gram of starch (90.1 wt% in rice waste) is equivalent to 1.11 g glucose.

173

174 3. Results and discussion

175 3.1 HMF production from rice waste

176 The distribution of products from catalytic conversion of rice waste at various substrate and
177 catalyst loadings are shown in **Fig. 2** (160 °C, 15 min). The total yields of detectable products
178 were 32.6-58.6 Cmol%, in which the major species were glucose, fructose, and HMF, along
179 with LA, FA, and levoglucosan in small quantities. The aqueous AlCl₃ provided Brønsted acids
180 as the cation underwent partial hydrolysis in water, releasing protons promoting the cleavage
181 of C-O-C linkages in rice starch. The produced glucose was then isomerized over the Lewis
182 acid site of Al³⁺ ions to form fructose, which could undergo dehydration to yield HMF in the
183 presence of Brønsted acids. Increasing the rice waste loading from 0.1 to 0.15 g mL⁻¹ did not
184 affect the HMF yield (16.6 to 15.4 Cmol%; **Fig. 2**). However, a further increase to 0.2 g mL⁻¹
185 rice waste resulted in a drop of HMF production (8.6 Cmol%) and a decrease in the fructose-
186 to-glucose molar ratio from ~1.1 to ~0.73. Lewis acid site density might be insufficient to

187 maintain the isomerization rate at a high feedstock loading, and the reduced concentration of
188 fructose might slow down the subsequent dehydration step. The following experiments adopted
189 the rice waste loading of 0.15 g mL^{-1} for a high-throughput HMF generation.

190 The time-dependent product yields from rice waste conversion are shown in **Fig. 3a&b** (rice
191 waste 0.15 g mL^{-1} , $160 \text{ }^{\circ}\text{C}$). At 10 wt% catalyst loading, rapid starch hydrolysis was promoted
192 and the glucose yield peaked at 33.2 Cmol% within 5 min of microwave-assisted conversion.
193 During this period, the fructose yield of 24.6 Cmol% was obtained, and the fructose-to-glucose
194 ratio of 0.74:1 was close to the thermodynamic equilibrium of 1:1, suggesting efficient
195 isomerization. As the reaction time increased, the yield of HMF increased to 15.4 Cmol% and
196 reached a plateau after 15 min. Increasing the catalyst loading to 20 wt% shortened the reaction
197 time from 15 min to 5 min for reaching the peak of HMF yield (**Fig. 3b**). Nevertheless, the
198 product profiles at both catalyst loadings remained similar, when considering glucose, fructose,
199 and HMF as the major products.

200 The hydrothermal catalytic conditions also facilitated side reactions such as rehydration of
201 HMF to LA ($\sim 5\text{-}13 \text{ Cmol\%}$; **Fig. 3**). A carbon loss of $32\text{-}75 \text{ Cmol\%}$ was estimated (**Fig. 3**)
202 while $7.1\text{-}8.4 \text{ wt\%}$ insoluble, dark solid residues were observed after the conversion, which
203 could be attributed to the polymerization among intermediates and HMF through aldol addition
204 and condensation. Such residues, broadly named as humins, are carbonaceous, heterogeneous
205 materials with a furan-rich polymer network containing different oxygen functional groups
206 (van Zandvoort et al., 2013). Our screening experiments showed that the condition at 0.15 g
207 mL^{-1} rice waste, 10 wt% catalyst loading, and heating at $160 \text{ }^{\circ}\text{C}$ for 15 min could generate 15.4
208 Cmol\% HMF and 25.9 Cmol\% sugars with considerable humins production when using water

209 as the greenest solvent. While HMF and the sugars are attractive platform chemicals, the low-
210 value humins residues were collected for the synthesis of biochar-supported catalysts to achieve
211 carbon-efficient biorefinery, which is discussed in the following sections.

212

213 3.2 Biochar catalyst characterization

214 As shown in **Fig. 4**, the SEM image of the solid residues generated after 15-min conversion
215 of rice waste (Humins15) shows a rougher surface compared to that collected at 0 min
216 (Humins0) (methods in **Section 2.3**). HB0 resulting from the pyrolysis of Humins0 presented
217 macropores (5-40 μm), which might collapse when Al impregnation was performed prior to
218 pyrolysis (i.e., HB0-Al). This observation is substantiated by the evidence that the BET surface
219 area significantly decreased from $125 \text{ m}^2 \text{ g}^{-1}$ for HB0 to $23 \text{ m}^2 \text{ g}^{-1}$ for HB0-Al (**Table 1**). Such
220 difference was smaller in the case of HB15 vs. HB15-Al ($201 \text{ vs. } 150 \text{ m}^2 \text{ g}^{-1}$). This suggests
221 that precursor Humins15 had a more stable structure compared to Humins0, probably due to
222 the higher degree of condensation associated with a longer reaction time. It is noted that the
223 measured surface area might be higher if the probing gas is changed from N_2 to CO_2 due to
224 higher kinetic energy and smaller kinetic diameter of the latter one (Weber and Quicker, 2018).

225 Successful incorporation of Al species on the biochars was evidenced by the EDX mapping
226 (**Fig. 5**). It is noted that Humins0 carried more oxygen-containing functional groups (34.7% O)
227 than Humins15 (28.6% O), which might facilitate the impregnation of Al species (Yu et al.,
228 2019a). This was corroborated by the observation that HB0-Al had a higher Al content (3.47%)
229 compared to HB15-Al (2.99%) (**Table 2**). Such elemental comparison based on the EDX
230 results was consistent with the XPS analysis, although the latter revealed a higher proportion

231 of Al (8.7-9.2%; **Table 2**). Given that XPS has a smaller depth of analysis (3-5 nm) than EDX
232 (μm) (Hantsche, 1989; Kerber et al., 1998), the difference in Al% measurement suggests that
233 the Al species were mainly located on the surface of the humins-derived biochar catalyst. Curve
234 fitting of the XPS spectra of Al 2p indicated the possible Al species as $\text{Al}(\text{OH})_3$, $\text{AlO}(\text{OH})$, and
235 Al-O-C in HB0-Al and HB15-Al (**Fig. 6**). This is in agreement with the profiles of Al-
236 impregnated wood waste-derived biochar and graphene/graphite oxide in our previous studies
237 (Yu et al., 2019a; Yu et al., 2019b; Xiong et al., 2020). The XRD patterns of HB0-Al and HB15-
238 Al display no distinct peaks assigned to any Al-based minerals, suggesting that the Al species
239 were primarily in amorphous structures and/or short-range crystalline order (Lawrinenko et al.,
240 2017; Yu et al., 2019a) (**Fig. 7a**).

241 Pyrolysis of humins tends to generate aromatic structures such as furans, arenes, and
242 phenolics (Shen et al., 2020). The broad XRD peak at $20\text{-}30^\circ$, which was characteristic of
243 amorphous carbon (Rajan et al., 2014; Shang et al., 2015), had a higher intensity in HB0
244 compared to HB15 (**Fig. 7a**). The graphitization of humins-derived biochar catalyst was further
245 examined by calculating the ratios of D peak to G peak (I_D/I_G) in Raman spectra (**Fig. 7b**).
246 Biochar derived from Humins15 (with and without Al impregnation) presented lower I_D/I_G
247 values (0.62-0.74) than those from Humins0 (0.96-0.98), indicating a lower proportion of
248 disorder fraction in the former sample. The prolonged conversion process of rice waste
249 valorization consumed the amorphous polysaccharide and promoted the condensation reactions
250 among the intermediates and HMF. This could have reduced the amount of defects on the
251 humins surface, which was reflected by the decrease in the O content from 34.7% in Humins0
252 to 28.6% in Humins15 (**Table 2**).

253

254 3.3 Glucose isomerization over humins-derived biochar catalysts

255 The catalytic activity of the humins-derived biochar catalysts was evaluated for the
256 isomerization of glucose to fructose under microwave heating at 160 °C for 20 min in water
257 (**Fig. 8**). The HB0-Al and HB15-Al successfully achieved 14.1 and 10.4 Cmol % fructose
258 yields, respectively. This performance was comparable with the Al-impregnated wood waste-
259 derived biochar (14% fructose, 160 °C, 20 min; Yu et al., 2019a) and Al-impregnated graphite
260 oxide (15% fructose, 140 °C, 20 min; Yu et al., 2019b), which were synthesized following a
261 similar protocol. The use of humins herein, a biorefinery by-product, presents a more
262 economical option for fabricating the carbon-supported heterogeneous catalysts. The use of
263 humins and humins-derived biochar without Al modification (Humins0, Humins15, HB0,
264 HB15) resulted in negligible fructose yields (< 3 Cmol%), confirming that the catalytic activity
265 was associated with the available Al sites impregnated in the biochar catalysts as revealed in
266 the characterization (**Section 3.2**).

267 The catalytic performance of HB0-Al and HB15-Al was further studied under various
268 conditions. As shown in **Fig. 9**, increasing the reaction temperature from 140 to 160 °C
269 increased the fructose yield over both catalysts from 4 to 10-14 Cmol%, after 20-min
270 microwave-assisted reaction in water as the medium. At 160 °C, a longer reaction time of 40
271 min marginally increased the fructose yield to 13.8-15.6 Cmol%. The reduced rate of fructose
272 formation may imply the deactivation of catalysts, plausibly due to metal leaching and
273 agglomeration and/or carbon intermediate/byproduct deposit on the biochar catalyst surface
274 during the conversion process. Changing the reaction medium from water only to a mixture of

275 water and acetone (1:1 v/v) achieved similar fructose yields (~14 Cmol%) yet enhanced the
276 selectivity by 10-15% after microwave heating at 160 °C for 20 min. It has been suggested that
277 solvation of intermediates/products in organic solvents may suppress the side reactions and
278 improve the selectivity (Yu and Tsang, 2017). Overall, these results suggest that the humins-
279 derived biochar can serve as a useful support for Al species to catalyze glucose isomerization
280 in green solvent systems (water and acetone/water). The low-value humins generated during
281 the waste-to-chemical process could be further valorized into sustainable solid catalysts for
282 sustainable biorefinery applications, making a step forward to achieve circular bioeconomy
283 with a closed carbon loop.

284

285 **4. Conclusions**

286 This study proposed the valorization of humins, a biorefinery by-product, for the synthesis
287 of biochar-supported Lewis acid catalysts. Effective catalytic conversion of rice waste into
288 useful platform chemicals (HMF and sugars) was achieved by microwave heating, using AlCl₃
289 as the catalyst in aqueous medium. The co-produced humins were subjected to Al impregnation
290 and carbonization, which produced biochar catalysts carrying Al-O species on the surface and
291 plausibly in amorphous state. The oxygen-containing functional groups on humins could serve
292 as the anchoring sites for the impregnation agent. The humins-derived biochar catalysts were
293 active toward the isomerization of glucose to fructose under microwave heating at 160 °C in
294 both water and water/acetone medium. Their catalytic performance was comparable with
295 previously reported carbon-based materials, suggesting that humins is a potentially competitive,
296 low-cost precursor of carbon supports. Our findings reveal an innovative practice of integrated

297 biorefinery, by recycling the unavoidable solid residues into renewable catalysts useful for a
298 typical biorefinery chemical process. Such an emerging application of humins can facilitate
299 value-added waste recycling and promote a closed carbon loop to achieve circular economy
300 and sustainable development.

301

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307

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