1 Valorization of Humins from Food Waste Biorefinery for Synthesis of Biochar-

2 supported Lewis Acid Catalysts

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14**Abstract**

15   To close the carbon loop of biomass waste valorization, it is imperative to utilize the

16unavoidable by-products such as humins, a carbonaceous residue with complex and

17heterogeneous composition. In this study, starch-rich rice waste was effectively converted

18into value-added chemicals (e.g., 5-hydroxymethylfurfural) under microwave heating at 160

19°C using AlCl$_3$ as the catalyst. The solid by-products, i.e., humins, were then valorized as a

20raw material for fabricating biochar-supported Lewis acid catalysts. The humins were

21collected and pretreated by AlCl$_3$ as the impregnation agent, followed by carbonization.

22Detailed characterization revealed several Al-O species on the biochar surface plausibly in

23the amorphous state. The oxygen-containing functional groups of humins might serve as

24anchoring sites for the Al species during impregnation. The humins-derived biochars

25exhibited good catalytic activity toward glucose-to-fructose isomerization, a common

26biorefinery reaction catalyzed by Lewis acids. A fructose yield of up to 14 Cmol% could be

27achieved under microwave heating at 160 ^{o}C for 20 min in water as the greenest solvent.

28Such catalytic performance was comparable with the previously reported Al-based catalysts

29derived from wood waste and graphene/graphitic oxide. This study herein highlights humins

30as a low-cost alternative source of carbon for the preparation of renewable solid catalysts,

31proposing a novel practice for recycling by-products from food waste valorization to foster

32circular economy and sustainable development.

33**Keywords:** biomass valorization; food waste recycling; engineered biochar; sustainable

34biorefinery; glucose isomerization; waste management.

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1. Introduction

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

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

2018; Pfab et al., 2019). Humins is insoluble and macromolecular substances composed of co-products such as furanics, levulinates, and sugar-derived molecules (Filiciotto et al., 2019). The cross-linked structure renders humins as a potential carbon matrix for catalyst support. To achieve high carbon efficiency in the circular bioeconomy, it is desirable to explore value-added application of the unavoidable humins. Previous studies investigated steam reforming of humins to hydrogen (Hoang et al., 2013) and liquefaction/depolymerization of humins into pyrolysis oil (Agarwal et al., 2017). These technologies focused on mineralization via selective bond dissociation, yet high temperature and catalyst consumption may restrict its large-scale valorization (Hoang et al., 2015). An alternative approach that might be more energy-efficient is to exploit and modify the polycyclic aromatic structure of humins. Previous studies examined humins as a prospective precursor of eco-friendly carbon materials, such as hydrophobic humins/flax fibres composites and humins-based resins (Sangregorio et al., 2019; Sangregorio et al., 2020).

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

79that would benefit from hydrophilic surface (van Zandvoort et al., 2013), such as catalyst

80supports. Sulfonated humins-derived catalysts were studied for the esterification of levulinic

81acid (LA) and n-butanol, hydroxyalkylation/alkylation of 2-methylfuran and furfural (Yang et

82al., 2020), and cellulose conversion to LA (Wang et al, 2018). We conjecture that

83impregnation of transition metals can introduce Lewis acid sites on humins-derived biochar

84surface, which would enable its application in more diverse reactions. Our previous studies of

85Al-based catalysts supported on wood waste biochar (Yu et al., 2019a) and graphene/graphite

86oxide (Yu et al., 2019b; Xiong et al., 2020) revealed their good performance in glucose-

87fructose isomerization.

88 In this study, we aim to recycle and valorize humins for the synthesis of renewable,

89sustainable solid Lewis acids that can catalyze biorefinery processes. Cooked rice waste daily

90generated in the Hong Kong International Airport (HKIA) was collected and used as the food

91waste substrate in this work. A high-performance waste recycling system for valorization of

92starch-rich waste from local enterprises is expected to bring environmental and economic

93benefits to the society. Rice waste conversion was performed for HMF production and the

94simultaneously produced humins were collected and modified by metal impregnation in

95$AlCl_3$ aqueous solutions. The prepared catalysts were characterized and evaluated for glucose

96isomerization as a model reaction mediated by Lewis acids in biorefineries.

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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

101 drying at 105 $^{\circ}$C, grinding, and sieving (0.2 mm mesh), before storage in an airtight container

102 at 4 °C. The AlCl$_3$·6H$_2$O (ACS grade) purchased from Anaqua was used for impregnation in

103 this study. Standard compounds were used for catalytic glucose conversion and equipment

104 calibration, including glucose ($\geq$ 99.5%), HMF ($\geq$ 99%), and furfural (99%) from Sigma

105 Aldrich; cellobiose ($\geq$ 98%), LA (98%), and formic acid (FA) (98%) from Alfa Aesar;

106 levoglucosan from Fluorochem; and fructose ($\geq$ 99%) and maltose monohydrate ($\geq$ 98%)

107 from Wako. All the chemicals were used as received.

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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 $^{\circ}$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 $^{\circ}$C with a

115 ramp time of 5 min and holding time ranging from 0 to 40 min. Vigorous magnetic stirring

116 was maintained throughout the whole process. After the reaction, the vessel was cooled to

117 room temperature under continuous mechanical ventilation for 40 min in the reactor. The

118 soluble samples were prepared for product analysis, while the solid residues were collected

119 for the synthesis of humins-derived biochar catalysts. The catalysts were evaluated for

120 glucose isomerization, which was performed following the abovementioned procedure. The

121biochar catalyst (0.25 g) and glucose (0.5 g) were added to 10 mL deionized water or

122water/acetone (1:1 v/v) solvent, followed by microwave heating at 140 $^\circ$C and 160 $^\circ$C for 5,

12320, and 40 min, respectively. All trials were carried out in duplicate.

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1252.3 Synthesis of humins-derived biochar catalysts

126   Based on the results of rice waste conversion achieving the maximal HMF yield, the

127conditions for batch production of humins were determined at 0.15 g mL^{-1} rice waste in 10 wt

128% AlCl$_3$ aqueous solution at a temperature of 160 $^\circ$C. The holding time was 0 and 15 min,

129producing residues denoted as Humins0 and Humins15, respectively. The residues were

130recovered by centrifugation and decantation, followed by multiple washing with deionized

131water. For Al impregnation, 10 g residues were suspended in a 200 mL solution of 10 wt%

132AlCl$_3$ with stirring for 4 h. After oven-drying the mixture at 105 $^\circ$C, the AlCl$_3$-treated humins

133were placed in a ceramic boat for carbonization in a Carbolite muffle furnace at 500 $^\circ$C for 2

134h (10 $^\circ$C min^{-1} ramping), which produced humins-derived biochars labelled as HB15-Al and

135HB0-Al. It was reported that pyrolysis temperatures ranging from 500 to 700 $^\circ$C are

136favourable for biochar production in view of stable polycyclic aromatic carbon and overall

137yield for common feedstock (Xiong et al., 2017). For an energy-efficient utilization and fair

138comparison with our previous reports on biochar-based catalysts (Yu et al., 2019a; Xiong et

139al., 2020), we selected 500 $^\circ$C as the carbonization temperature in this study (**Fig. 1**). As for

140control experiments, humins without AlCl$_3$ treatment were subjected to the same pyrolysis

141treatment, and the resultant biochars were denoted as HB15 and HB0. All prepared catalysts

142were stored in a sealed container in a desiccator before characterization and catalytic activity

143evaluation.

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1452.4 Biochar catalyst characterization

146 The morphology, topography, and elemental distribution of the humins-based biochar

147catalysts were revealed by scanning electron microscopy (SEM) with energy dispersive X-ray

148analysis (EDX) [TESCAN VEGA3]. Brunauer-Emmett-Teller (BET) surface area and pore

149volume were measured by nitrogen adsorption−desorption isotherm measurement at -196 °C

150using a gas sorption analyser (Micromeritics Accelerated Surface Area and Porosimetry

151system, ASAP 2020). The crystalline and amorphous phases were revealed by X-ray

152diffraction analysis (XRD; Rigaku SmartLab) in a scanning range of 10–80° 2θ at a rate of 5°

153min^{-1} at 45 kV and 200 mA. The surface functionalities were studied using micro-Raman

154spectroscopy (Renishaw) with a laser source at a wavelength of 532 nm and an objective of

15550×. X-ray photoelectron spectroscopy (XPS; ESCALAB 250Xi spectrometer, USA) with

156monochromated Al Kα radiation was performed with a pass energy of 187.85 eV at 1.6 eV

157per step for survey scans (0 to 1200 eV). Curve fitting was performed for the obtained spectra

158of Al 2p using XPSPEAK41.

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1602.5 Catalysis product analysis

161 Liquid samples collected after microwave-assisted conversion were diluted with deionized

162water (1:3 v/v) and filtered through a mixed cellulose ester filter (0.22 µm) before analysis.

163High-performance liquid chromatography (HPLC) was performed using a Chromaster

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164 instrument equipped with a refractive index detector (Hitachi, Japan) and an Aminex HPX-

165 87H column (Bio-Rad) at an analytical temperature of 50 $^{\circ}$C. The mobile phase was 0.01 M

166 H_2SO_4 at a flow rate of 0.5 mL min^{-1}. The yield and selectivity of the products were

167 calculated in terms of the carbon content.

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

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$$Product\ selectivity\,(Cmol\%) = \frac{P_f(mg/ml) \times n_p/MW_P}{(Glu ¿ ¿ i - Glu_f)(mg/ml) \times n_{Glu}/MW_{Glu} \times 100 ¿} \qquad (2)$$

170 where P_f represents the concentration of the products, n_p and n_{Glu} are number of carbons in the

171 corresponding product and glucose, MW_p and MW_{Glu} are molecular mass of the corresponding

172 product and glucose, and Glu_i and Glu_f represent the initial and final concentration of glucose,

173 respectively. One gram of starch (90.1 wt% in rice waste) is equivalent to 1.11 g glucose.

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175 **3. Results and discussion**

176 3.1 HMF production from rice waste

177   The distribution of products from catalytic conversion of rice waste at various substrate

178 and catalyst loadings are shown in **Fig. 2** (160 $^{\circ}$C, 15 min). The total yields of detectable

179 products were 32.6-58.6 Cmol%, in which the major species were glucose, fructose, and

180 HMF, along with LA, FA, and levoglucosan in small quantities. The aqueous AlCl$_3$ provided

181 Brønsted acids as the cation underwent partial hydrolysis in water, releasing protons

182 promoting the cleavage of C-O-C linkages in rice starch. The produced glucose was then

183 isomerized over the Lewis acid site of Al^{3+} ions to form fructose, which could undergo

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184dehydration to yield HMF in the presence of Brønsted acids. Increasing the rice waste

185loading from 0.1 to 0.15 g mL^{-1} did not affect the HMF yield (16.6 to 15.4 Cmol%; **Fig. 2**).

186However, a further increase to 0.2 g mL^{-1} rice waste resulted in a drop of HMF production

187(8.6 Cmol%) and a decrease in the fructose-to-glucose molar ratio from ~1.1 to ~0.73. Lewis

188acid site density might be insufficient to maintain the isomerization rate at a high feedstock

189loading, and the reduced concentration of fructose might slow down the subsequent

190dehydration step. The following experiments adopted the rice waste loading of 0.15 g mL^{-1}

191for a high-throughput HMF generation.

192   The time-dependent product yields from rice waste conversion are shown in **Fig. 3a&b**

193(rice waste 0.15 g mL^{-1}, 160 $^{\circ}$C). At 10 wt% catalyst loading, rapid starch hydrolysis was

194promoted and the glucose yield peaked at 33.2 Cmol% within 5 min of microwave-assisted

195conversion. During this period, the fructose yield of 24.6 Cmol% was obtained, and the

196fructose-to-glucose ratio of 0.74:1 was close to the thermodynamic equilibrium of 1:1,

197suggesting efficient isomerization. As the reaction time increased, the yield of HMF increased

198to 15.4 Cmol% and reached a plateau after 15 min. Increasing the catalyst loading to 20 wt%

199shortened the reaction time from 15 min to 5 min for reaching the peak of HMF yield (**Fig.**

200**3b**). Nevertheless, the product profiles at both catalyst loadings remained similar, when

201considering glucose, fructose, and HMF as the major products.

202   The hydrothermal catalytic conditions also facilitated side reactions such as rehydration of

203HMF to LA (~5-13 Cmol%; **Fig. 3**). A carbon loss of 32-75 Cmol% was estimated (**Fig. 3**)

204while 7.1-8.4 wt% insoluble, dark solid residues were observed after the conversion, which

205could be attributed to the polymerization among intermediates and HMF through aldol

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206addition and condensation. Such residues, broadly named as humins, are carbonaceous,

207heterogeneous materials with a furan-rich polymer network containing different oxygen

208functional groups (van Zandvoort et al., 2013). Our screening experiments showed that the

209condition at 0.15 g mL^{-1} rice waste, 10 wt% catalyst loading, and heating at 160 $^{\circ}$C for 15 min

210could generate 15.4 Cmol% HMF and 25.9 Cmol% sugars with considerable humins

211production when using water as the greenest solvent. While HMF and the sugars are

212attractive platform chemicals, the low-value humins residues were collected for the synthesis

213of biochar-supported catalysts to achieve carbon-efficient biorefinery, which is discussed in

214the following sections.

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216 3.2 Biochar catalyst characterization

217   As shown in **Fig. 4**, the SEM image of the solid residues generated after 15-min

218conversion of rice waste (Humins15) shows a rougher surface compared to that collected at 0

219min (Humins0) (methods in **Section 2.3**). HB0 resulting from the pyrolysis of Humins0

220presented macropores (5-40 µm), which might collapse when Al impregnation was performed

221prior to pyrolysis (i.e., HB0-Al). This observation is substantiated by the evidence that the

222BET surface area significantly decreased from 125 m^2 g^{-1} for HB0 to 23 m^2 g^{-1} for HB0-Al

223(**Table 1**). Such difference was smaller in the case of HB15 vs. HB15-Al (201 vs. 150 m^2 g^{-1}).

224This suggests that precursor Humins15 had a more stable structure compared to Humins0,

225probably due to the higher degree of condensation associated with a longer reaction time. It is

226noted that the measured surface area might be higher if the probing gas is changed from N$_2$ to

227CO$_2$ due to higher kinetic energy and smaller kinetic diameter of the latter one (Weber and

228Quicker, 2018).

229   Successful incorporation of Al species on the biochars was evidenced by the EDX mapping

230(**Fig. 5**). It is noted that Humins0 carried more oxygen-containing functional groups (34.7%

231O) than Humins15 (28.6% O), which might facilitate the impregnation of Al species (Yu et

232al., 2019a). This was corroborated by the observation that HB0-Al had a higher Al content

233(3.47%) compared to HB15-Al (2.99%) (**Table 2**). Such elemental comparison based on the

234EDX results was consistent with the XPS analysis, although the latter revealed a higher

235proportion of Al (8.7-9.2%; **Table 2**). Given that XPS has a smaller depth of analysis (3-5

236nm) than EDX (µm) (Hantsche, 1989; Kerber et al., 1998), the difference in Al%

237measurement suggests that the Al species were mainly located on the surface of the humins-

238derived biochar catalyst. Curve fitting of the XPS spectra of Al 2p indicated the possible Al

239species as $Al(OH)_3$, AlO(OH), and Al–O–C in HB0-Al and HB15-Al (**Fig. 6**). This is in

240agreement with the profiles of Al-impregnated wood waste-derived biochar and

241graphene/graphite oxide in our previous studies (Yu et al., 2019a; Yu et al., 2019b; Xiong et

242al., 2020). The XRD patterns of HB0-Al and HB15-Al display no distinct peaks assigned to

243any Al-based minerals, suggesting that the Al species were primarily in amorphous structures

244and/or short-range crystalline order (Lawrinenko et al., 2017; Yu et al., 2019a) (**Fig. 7a**).

245   Pyrolysis of humins tends to generate aromatic structures such as furans, arenes, and

246phenolics (Shen et al., 2020). The broad XRD peak at 20-30°, which was characteristic of

247amorphous carbon (Rajan et al., 2014; Shang et al., 2015), had a higher intensity in HB0

248compared to HB15 (**Fig. 7a**). The graphitization of humins-derived biochar catalyst was

249further examined by calculating the ratios of D peak to G peak (I_D/I_G) in Raman spectra (**Fig.**

250**7b**). Biochar derived from Humins15 (with and without Al impregnation) presented lower I_D/

251I_G values (0.62-0.74) than those from Humins0 (0.96-0.98), indicating a lower proportion of

252disorder fraction in the former sample. The prolonged conversion process of rice waste

253valorization consumed the amorphous polysaccharide and promoted the condensation

254reactions among the intermediates and HMF. This could have reduced the amount of defects

255on the humins surface, which was reflected by the decrease in the O content from 34.7% in

256Humins0 to 28.6% in Humins15 (**Table 2**).

257

2583.3 Glucose isomerization over humins-derived biochar catalysts

259　The catalytic activity of the humins-derived biochar catalysts was evaluated for the

260isomerization of glucose to fructose under microwave heating at 160 $^\circ$C for 20 min in water

261(**Fig. 8**). The HB0-Al and HB15-Al successfully achieved 14.1 and 10.4 Cmol % fructose

262yields, respectively. This performance was comparable with the Al-impregnated wood waste-

263derived biochar (14% fructose, 160 $^\circ$C, 20 min; Yu et al., 2019a) and Al-impregnated

264graphite oxide (15% fructose, 140 $^\circ$C, 20 min; Yu et al., 2019b), which were synthesized

265following a similar protocol. The use of humins herein, a biorefinery by-product, presents a

266more economical option for fabricating the carbon-supported heterogeneous catalysts. The

267use of humins and humins-derived biochar without Al modification (Humins0, Humins15,

268HB0, HB15) resulted in negligible fructose yields (< 3 Cmol%), confirming that the catalytic

269activity was associated with the available Al sites impregnated in the biochar catalysts as

270revealed in the characterization (**Section 3.2**).

271　The catalytic performance of HB0-Al and HB15-Al was further studied under various

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272conditions. As shown in **Fig. 9**, increasing the reaction temperature from 140 to 160 $^{\circ}$C

273increased the fructose yield over both catalysts from 4 to 10-14 Cmol%, after 20-min

274microwave-assisted reaction in water as the medium. At 160 $^{\circ}$C, a longer reaction time of 40

275min marginally increased the fructose yield to 13.8-15.6 Cmol%. The reduced rate of fructose

276formation may imply the deactivation of catalysts, plausibly due to metal leaching and

277agglomeration and/or carbon intermediate/byproduct deposit on the biochar catalyst surface

278during the conversion process. Changing the reaction medium from water only to a mixture

279of water and acetone (1:1 v/v) achieved similar fructose yields (~14 Cmol%) yet enhanced

280the selectivity by 10-15% after microwave heating at 160 $^{\circ}$C for 20 min. It has been

281suggested that solvation of intermediates/products in organic solvents may suppress the side

282reactions and improve the selectivity (Yu and Tsang, 2017). Overall, these results suggest

283that the humins-derived biochar can serve as a useful support for Al species to catalyze

284glucose isomerization in green solvent systems (water and acetone/water). The low-value

285humins generated during the waste-to-chemical process could be further valorized into

286sustainable solid catalysts for sustainable biorefinery applications, making a step forward to

287achieve circular bioeconomy with a closed carbon loop.

288

289**4. Conclusions**

290   This study proposed the valorization of humins, a biorefinery by-product, for the synthesis

291of biochar-supported Lewis acid catalysts. Effective catalytic conversion of rice waste into

292useful platform chemicals (HMF and sugars) was achieved by microwave heating, using

293AlCl$_3$ as the catalyst in aqueous medium. The co-produced humins were subjected to Al

294impregnation and carbonization, which produced biochar catalysts carrying Al-O species on

295the surface and plausibly in amorphous state. The oxygen-containing functional groups on

296humins could serve as the anchoring sites for the impregnation agent. The humins-derived

297biochar catalysts were active toward the isomerization of glucose to fructose under

298microwave heating at 160 $^{\circ}$C in both water and water/acetone medium. Their catalytic

299performance was comparable with previously reported carbon-based materials, suggesting

300that humins is a potentially competitive, low-cost precursor of carbon supports. Our findings

301reveal an innovative practice of integrated biorefinery, by recycling the unavoidable solid

302residues into renewable catalysts useful for a typical biorefinery chemical process. Such an

303emerging application of humins can facilitate value-added waste recycling and promote a

304closed carbon loop to achieve circular economy and sustainable development.

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