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1 Life-Cycle Greenhouse Gas- and Water-Intensity of Cellulosic Biofuel Production Using 2 Cholinium Lysinate Ionic Liquid Pretreatment

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11

12Abstract:

13

14 Cellulosic biofuels present an opportunity to meet a significant fraction of liquid
15transportation fuel demand with renewable, low-carbon alternatives. Certain ionic liquids (ILs)
16have proven effective at facilitating hydrolysis of lignocellulose to produce fermentable sugars
17with high yields. Although their negligible vapor pressure and low flammability make ILs
18attractive solvents at the point of use, their life-cycle environmental impacts have not been
19investigated in the context of cellulosic biorefineries. This study provides the first life-cycle
20greenhouse gas (GHG) and water use inventory for biofuels produced using IL pretreatment. We
21explore two corn stover-to-ethanol process configurations: conventional water-wash (WW) route
22and the more recently developed integrated high gravity (iHG) route, which eliminates washing
23steps after pretreatment. Our results are based on the use of a representative IL, cholinium
24lysinate ([Ch][Lys]). We find that the WW process results in unacceptably high GHG emissions.
25The iHG process has the potential to reduce GHG emissions per MJ fuel by ~45% relative to
26gasoline if [Ch][Lys] is used. Use of a protic IL with comparable performance to [Ch][Lys] could
27achieve GHG reductions up to 70-85%. The water-intensities of the WW and iHG processes are
28both comparable to other cellulosic biofuel technologies.

29

30**Keywords:** *Biomass pretreatment; Cholinium lysinate; Ionic liquid; Life-cycle assessment; Water
31intensity*

32

33

34Introduction:

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36 The success of biological routes to producing biofuels hinges on the ability to efficiently
37deconstruct biomass into fermentable sugars. Pretreatment of lignocelluloses is critical to
38overcoming biomass recalcitrance and facilitating hydrolysis¹⁻². Commonly used pretreatment
39methods include dilute sulfuric acid (DA)³⁻⁴, ammonia fiber expansion (AFEX)⁵⁻⁶, and steam-
40explosion⁷⁻⁸. The use of certain ILs for pretreatment has been shown to offer several advantages
41over other pretreatment processes, including high delignification, production of a clean lignin
42stream, reduced processing time for enzymatic hydrolysis, and high surface area in the recovered
43biomass, and higher sugar yields at low enzyme loadings^{9,10-11}. Certain ionic liquids (ILs) are

44considered “green” solvents because of their low vapor pressure, low flammability, and low
45toxicity, and several have been extensively studied over the last decade as alternative solvents for
46biomass pretreatment^{2, 12-13}.

47

48 A variety of ILs, including 1-ethyl 1-methylimidazolium acetate ([C₂MIM][OAc])¹⁴⁻¹⁶, 1-
49ethyl 1-methylimidazolium chloride ([C₂MIM][Cl])¹⁷, and cholinium lysinate ([Ch][Lys])¹⁸⁻²⁰,
50have been explored for the pretreatment of various lignocellulosic biomass feedstocks including
51corn stover^{14, 21-22}, switchgrass^{9, 12}, pine²³, miscanthus^{15, 24} and mixed feedstock²⁵. Choline-based
52ILs, sometimes referred to as “bionic liquids” because they are bio-derived, are particularly
53attractive because they can be produced using cheaper raw materials and simpler synthesis
54methods than [C₂MIM]-based ILs²⁰. Among these, [Ch][Lys] has demonstrated promising levels
55of delignification and generated high glucose yields after saccharification of the pretreated
56substrates. Hou *et al* (2012)¹⁸ found choline-based ILs to be effective pretreatment solvents with
57high polysaccharide digestibility and sugar yields. Sun *et al*¹⁹ reported that [Lys] anions provided
58greater delignification (70-80% vs. 16-50%) and higher glucose yields (78-96% vs. 56-90%)
59compared to [OAc] anions. ILs containing the lysinate anion afforded greater delignification and
60higher glucose yields than other anions such as carboxyl, hydroxyl, and aromatic groups²⁶.

61

62 The life-cycle assessment (LCA) research community has only recently begun to
63investigate the environmental impacts of ILs, although the focus has been on other applications
64such as carbon capture, aerospace²⁷, and chemical production²⁸⁻²⁹. The results have been largely
65negative, when ILs are compared to more conventional alternatives. For instance, Zhang *et al.*
66(2008)²⁹ assessed the life-cycle impacts of 1-butyl-3-methyl-imidazolium tetrafluoroborate
67[C₄MIM][BF₄] as a solvent for the manufacture of cyclohexane and in a Diels–Alder reaction,
68compared with conventional synthesis methods, and concluded that processes that use ILs are
69likely to perform comparatively worse in most environmental impact categories. Past studies
70highlight the fact that solvents with environmentally preferable properties do not necessarily
71translate to reduced system-wide impacts³⁰. Previous studies also highlight the diversity of ILs
72and their applications, and the need for comprehensive analysis specific to the IL(s) and
73application of interest. Using LCA early on to guide the selection of ILs and design of IL
74pretreatment-based biorefineries is critical to achieving sustainability goals. Scarcity of relevant
75data for industrial-scale IL manufacturing processes is a key barrier to the quantitative
76assessment of environmental impacts - many are simply not yet produced at a large scale³⁰. In the
77absence of such data, some studies have qualitatively assessed the environmental aspects of
78different ILs based on strengths, weaknesses, opportunities and threats (SWOT) analysis³¹, and
79eco-toxicological risk profile³².

80

81 This is the first study to assess the life-cycle implications of using ILs in a biorefinery
82context. We selected two metrics: GHG emissions and water use (withdrawals and consumption).
83Water use is less frequently studied relative to GHG emissions, but is particularly critical for
84biofuels, which can be more water-intensive than petroleum-derived fuels^{33,34}. A number of

85 studies have quantified the water-intensity of producing biofuels via more conventional
 86 processes, and we use those results as a basis for comparison³⁴⁻³⁸. Our specific objectives are
 87 three-fold: (1) to quantify life-cycle GHG emissions-intensity of a commercially relevant
 88 production process for [Ch][Lys]; (2) to evaluate the GHG emissions- and water-intensity of
 89 biofuel production using IL pretreatment; and (3) to identify opportunities to improve the
 90 environmental performance of cellulosic biorefineries with IL pretreatment. Given the
 91 uncertainty with the data and the early state nature of these processes, sensitivity analysis is an
 92 integral part of our analysis. Our modeled biorefineries produce ethanol, although the methods
 93 and data can be used to evaluate an array of microbial routes to advanced biofuels. For
 94 benchmarking purposes, we compare our results with conventional gasoline.

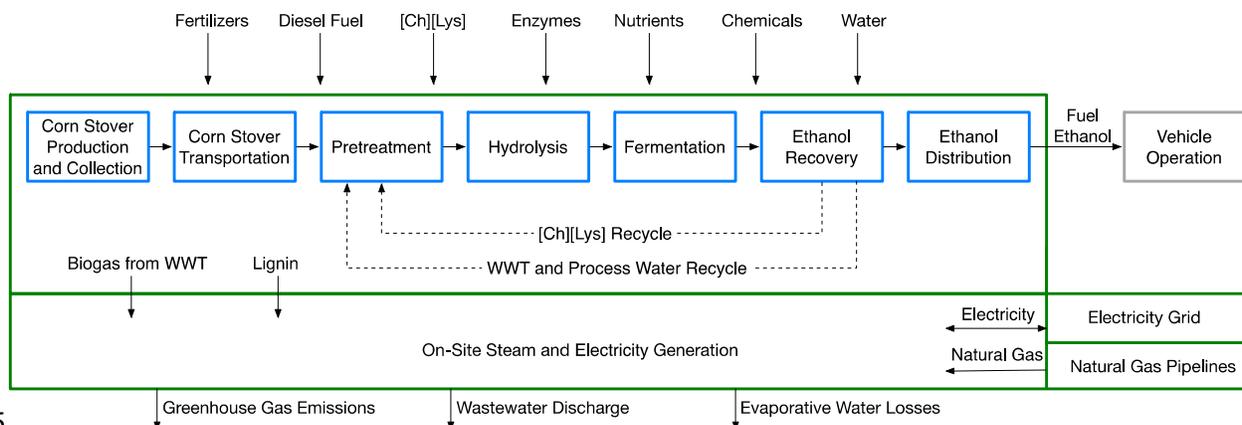
95

96 **Methodology:**

97

98 **Scope of the study:** The system boundary includes all stages of ethanol production
 99 including feedstock production and collection, transportation, fuel production, and fuel
 100 distribution (Figure 1). The vehicle operation stage is excluded because the biogenic CO₂ emitted
 101 during combustion is offset by the CO₂ sequestered during feedstock growth (this assumption is
 102 consistent with the Environmental Protection Agency’s Renewable Fuel Standard (RFS2)³⁹ and
 103 California’s Low Carbon Fuel Standard (LCFS)⁴⁰).

104



105

106 **Figure 1:** System boundaries for life-cycle GHG emissions and water analysis used in this study

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108

109 **Biomass Production, and Logistics:** In this study, we considered corn stover as a
 110 representative feedstock for biofuel production. We assume that farmers replace the nutrient
 111 content of harvested corn stover by applying additional fertilizers, as is common practice in the
 112 most widely-cited models and studies⁴¹⁻⁴³. Assumptions for corn stover yield, energy demand for
 113 harvesting, and additional fertilizer requirements are presented in Supplementary Information A
 114 (Table S1). We did not consider land use change impact as corn stover was treated using a
 115 consequential approach where only changes to business as usual corn harvesting practices were

116allocated to stover. When this consequential approach is used, land use impacts are minimal
117(about 1 g CO₂e/MJ) in the case of corn stover⁴³. As suggested by a number of studies^{44, 45, 41}, we
118assumed that approximately two thirds of corn stover can be removed without impacting soil
119carbon. The distance between the farm and biorefinery is assumed to be 80 km. We assume
120ethanol is distributed to fueling stations via truck and rail (Table 2), with an average total
121transportation distance of 300 kilometers (more details in Table S1).

122

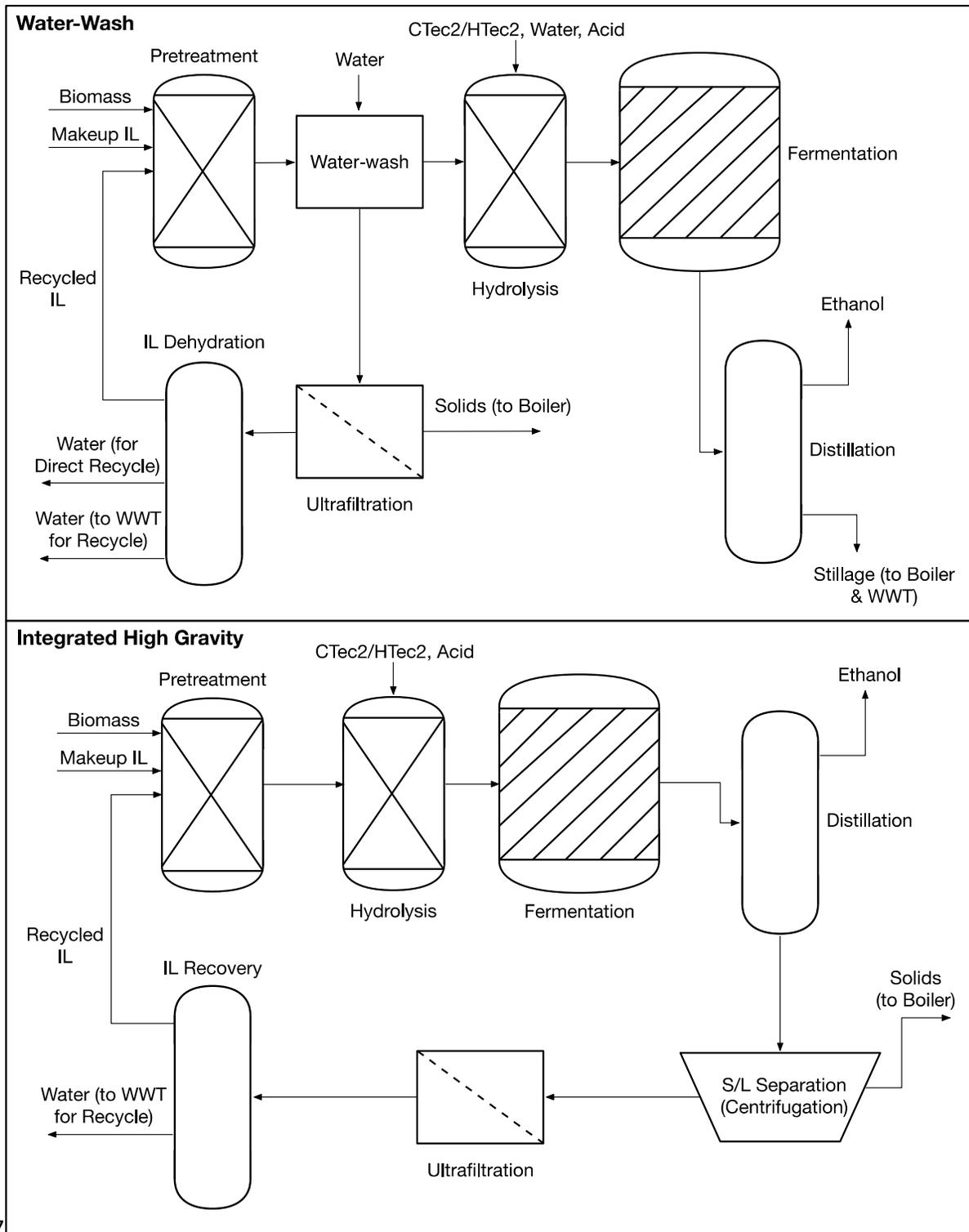
123 **Ionic Liquid Production:** Since most IL production is not well documented in existing
124literature or databases, these processes must be modeled to understand mass and energy balances,
125and to quantify the resulting emission and water use. We have selected [Ch][Lys] as a
126representative solvent for biomass pretreatment in the biorefinery scenarios investigated here
127(discussed in the following section) because of its effectiveness in pretreating biomass and
128compatibility with cellulase enzymes. [Ch][Lys] is produced by reacting choline hydroxide with
129lysine (Supplementary Info). The choline hydroxide synthesis is adapted from Li et al (2013)⁴⁶
130and Moonen et al (2016)⁴⁷ and requires ethylene oxide (EO) and trimethylamine (TMA). EO is
131produced through the oxidation of ethylene, while TMA is produced by reacting ammonia and
132methanol. The lysine production process is based on Marinussen and Kool (2010)⁴⁸ and is
133produced via aerobic fermentation where *Corynebacterium glutamicum* produces the amino acid
134using glucose as carbon source. More details on the synthesis processes and respective mass and
135energy data for [Ch][Lys] synthesis are presented in Supplementary Information A (Table S2 and
136Table S3). The geographic location where the reactants are produced affects the environmental
137impacts because of differing electricity grid mixes. Over 50% lysine in the global market is
138currently produced in China. To account for the possibility of growth in domestic lysine
139production, we considered two scenarios by varying the source of electricity used in the process
140– i.e., the U.S. electricity mix and Chinese electricity mix. We considered US based lysine
141production for the GHG and water intensity calculations associated with the biofuel in this study.

142

143 **Biofuel Production with IL Pretreatment:** Two different process configurations are
144modeled for biofuel production: 1) water-wash (WW) and, 2) integrated high gravity (iHG).
145These configurations are shown in Figure 2 and have been demonstrated experimentally in Xu *et*
146*al.* (2016)²⁰ and Sun *et al.* (2014)¹⁹. Mass and energy data for the WW and iHG processes are
147generated using integrated biorefinery models built in commercial software platform SuperPro
148Designer. The primary difference between these two configurations is the point at which IL is
149recovered in the process (i.e., immediately after pretreatment in the WW route vs. after
150fermentation in the iHG route). Our biorefinery models include sections for feedstock handling,
151biomass pretreatment and hydrolysis, fermentation, product recovery, wastewater treatment
152(WWT), and utilities. A simplified representation of the process is given in Figure 2. The product
153recovery, WWT, and co-generation sections are based on NREL's design report³. Unlike the
154widely-used WW process, the iHG configuration is in early stages of development. To better
155understand the impact of potential improvements to the iHG process, we have considered two
156different scenarios: 1) iHG-Current (85% IL recovery, due to losses during electro dialysis) and 2)

157iHG-Projected (99% IL recovery). The iHG-Projected scenario requires a protic IL. Protic ILs
158are made up of ions derived from simple amino bases (e.g., ethanolamine, cholinium hydroxide)
159and acids (e.g., acetic acid, sulfuric acid, phosphoric acid, hydrochloric acid and formic acid) –
160for example, the effectiveness of triethylammonium hydrogen sulfate has been tested, and this IL
161could be produced at-scale for as little as \$1.24/kg⁴⁹. Using protic ILs eliminates the need for pH
162adjustment and subsequent IL regeneration step in the downstream⁴⁹ (see Table 2 and SI for more
163details). In this paper, we do not presume a specific protic IL because the technology is very
164early-stage and requires further empirical data to demonstrate performance. Instead, we assume a
165hypothetical protic IL that achieves performance in-line with that of [Ch][Lys].

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Figure 2. Simplified block flow diagram of the biorefinery process: water wash route (top) and integrated high gravity route (bottom).

172 More process related details and other key parameters associated with all the three
173 scenarios studied (i.e., WW, iHG-Current, and iHG-Projected) are given in Supplementary
174 Information A (Table S4). Where possible, all three scenarios are based on identical assumptions
175 to facilitate a comparative analysis. For example, enzymes are sourced from an off-site location
176 (e.g., a third-party vendor) rather than being produced on-site. Sugar yields during hydrolysis
177 and fuel yields in fermentation are based on NREL's n^{th} biorefinery targets³ (~93% conversion of
178 glucan and xylan to monomeric sugars in hydrolysis, followed by 95% conversion of glucose
179 and 85% conversion of xylose to produce ethanol). Our sensitivity analysis explores variations in
180 key parameters, including fuel yield.

181

182 **Co-products:** The biorefinery design influences its energy balance, which determines
183 whether it is a net electricity importer or exporter, and how much (if any) primary fuel must be
184 imported. Electricity co-product credits can have a significant impact on net GHG emissions and
185 water use. In this regard, the three scenarios discussed above are very different (as indicated in
186 the electricity import/export data provided in Table 2). The WW process requires more thermal
187 energy than could be generated from residual solids and biogas, so there is no excess energy to
188 generate electricity on-site and natural gas must be imported (primarily to satisfy energy needs in
189 the IL dehydration step) in addition to grid electricity. Conversely, the iHG processes (both
190 current and projected) result in surplus steam, so those facilities co-generate electricity with an
191 on-site multi-stage turbo-generator. However, the two iHG configurations do not generate the
192 same quantities of surplus electricity. The iHG-Current process requires an electricity-intensive
193 IL regeneration step, so nearly all the electricity produced is consumed on-site. The iHG-
194 Projected scenario does not require IL regeneration, and can export a significant quantity of
195 electricity to the grid. In all cases, we assume exported electricity will displace an average U.S.
196 electricity mix. We considered Midwest Reliability Organization (MRO) and Northeast Power
197 Coordinating Council (NPCC) regions to account for the variations in emission intensity of
198 different electricity grid mixes, which is captured by the uncertainty bars. We also considered a
199 +/- 10% variation in net electricity demand at the facility in the sensitivity analysis to account for
200 uncertainty in the energy balance that may be achieved in a commercial-scale facility.

201

202 **Life-Cycle Inventory:**

203

204 Direct biorefinery inputs and outputs are shown in Table 2. Upstream life-cycle inventory
205 data were collected from widely-used life-cycle assessment databases/tools⁵⁰⁻⁵² and peer-
206 reviewed literature^{34, 46-48}. Lysine production data were obtained from Marinussen and Kool
207 (2010)⁴⁸, who completed a comprehensive study of lysine production in Europe using glucose
208 from corn as a source of carbon. We modified this data to represent the U.S. corn and electricity
209 production. Life-cycle emissions data for chemicals, fertilizers, and transportation were obtained
210 from sources including USLCI⁵⁰, GREET⁵¹ and EcoInvent⁵². Where available, we used U.S.-
211 specific values (e.g., USLCI and GREET). When no U.S.-based data was available, we used
212 European values and modified them based on U.S. grid mixes. We used a hybrid life cycle

213assessment approach that utilizes process-based and input-output (IO) based LCA. We developed
 214an input-output vector based on physical units and used the method originally employed for LCA
 215by Hendrickson et al. (and later used widely in LCA studies) to compute the total requirements
 216vector and convert those requirements to GHG emissions and water use^{36, 53-54}. We chose to use a
 217customized input-output vector and physical units-based impact vectors for this study to avoid
 218the uncertainties associated with sector aggregation in the U.S. national level input-output tables.
 219A functional/physical unit-based input-output (IO) table for all relevant materials, energy
 220sources, and services is presented in Supplementary Information B. This input-output table forms
 221the basis for our model, which was originally used to generate results in Balakrishnan *et al.*
 2222015⁵⁵.

223

224**Table 2:** Life-cycle input data per kg of ethanol produced

Product/Processes	Unit	Pretreatment Methods		
		Water-wash	iHG-Current	iHG-Projected
<i>Inputs</i>		Nominal values		
Diesel in harvesting machine	MJ/kg	0.24	0.24	0.24
Corn stover (20% moisture)	kg	5.47	4.7	4.7
Transportation	km	80	80	80
[Ch][Lys]	kg	0.17	0.16	0.03
Corn liquor	kg	0.06	0.05	0.05
Hydrolase	kg	0.03	0.03	0.03
DAP (diammonium phosphate)	kg	0.01	0.01	0.01
NG (natural gas)	kg	1.31	-	-
HCl	kg	-	0.18	-
H ₂ SO ₄	kg	0.002	-	-
Electricity	kWh	1.4	-	-
Fuel distribution	km	300	300	300
<i>Outputs</i>				
Ethanol	kg	1	1	1
Electricity	kWh	-	0.07	0.85

225

226 We present water use in two metrics: (a) consumption, and (b) withdrawals and is
 227calculated using an impact vector, applied to the input-output results generated by our model.
 228Water consumption refers to the water that is taken from the surface or groundwater sources
 229which is not directly returned - for example, evaporative losses in a closed loop cooling system³⁵.
 230Water withdrawals refers to the water that is taken from the surface or groundwater, used in a
 231process, and discharged back to the original source - for example, water discharged from an
 232open-loop cooling system³⁴. Consistent with methodologies used in previous studies, we do not
 233assume that additional irrigation is required for corn stover as a result of partial residual
 234removal^{34, 36}. Water consumption and withdrawals for the production of chemicals, fertilizers, and
 235other material inputs are included in our analysis. The direct water consumption at the
 236biorefinery is largely due to evaporative losses from the cooling towers^{36, 56}. Since the boiler
 237blowdown water and process water are treated in the WWT section and recycled in our processes

238(consistent with the NREL model³), the direct consumption and withdrawal are essentially equal.
239Most of the life-cycle water consumption and withdrawal data are taken from Scown *et al.*
240(2011)³⁴ and updated as appropriate, based on more recent literature. The Scown *et al.* database
241was updated to represent the 2015 electricity mix. The water intensity of cholinium hydroxide
242production was calculated based on the mass and energy balance. Life cycle water inventory data
243is presented in Supplementary Information A (Table S5).

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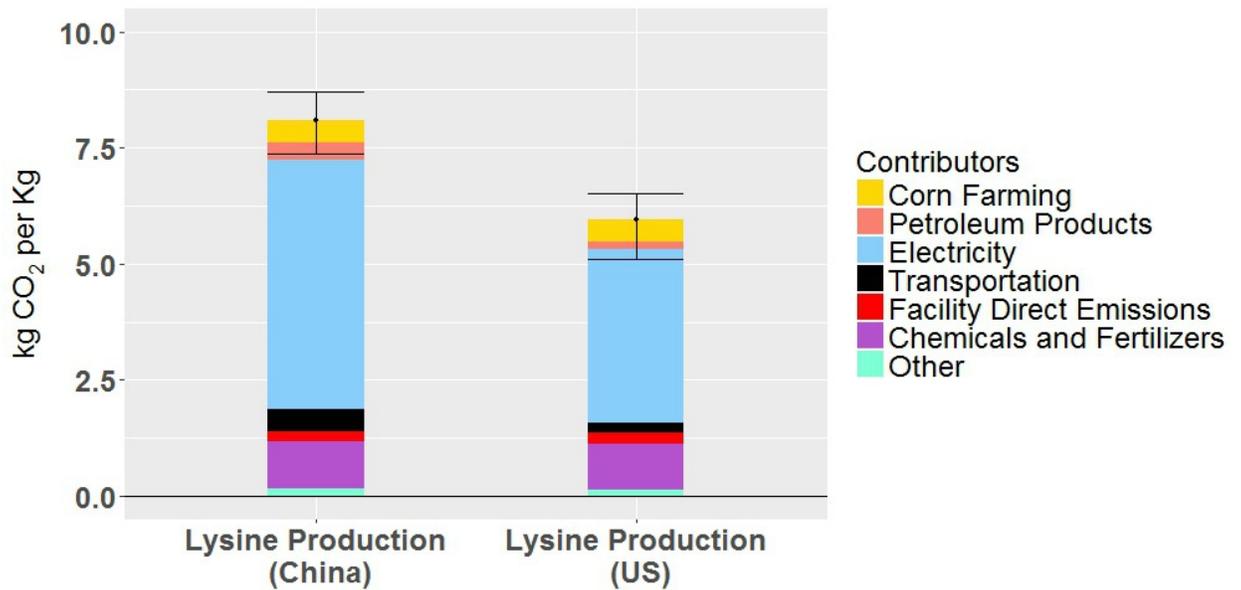
246**Results and Discussion:**

247

248 **Life-Cycle GHG Emissions for [Ch][Lys] Production:** The GHG-intensity of [Ch]
249[Lys] production was found to be between 6 and 8 kg CO₂e/kg (Figure 3), depending on whether
250lysine is produced in the U.S. or China. The contribution of choline hydroxide is ~1.5 kg
251CO₂e/kg -- ethylene input is responsible for about 50% of that total, followed by ammonia and
252electricity. The GHG-intensity of U.S.-produced lysine production is ~4.75 kg CO₂e/kg. Major
253contributors in lysine production include electricity (about 40%) and nutrients. Our GHG
254emission results for lysine production are comparable with those obtained in previous studies:
255Marinussen (2010)⁴⁸ estimated GHG emissions of 5.5, 5.4 and 5.5 kg CO₂e/kg of lysine produced
256in Germany, Denmark and France, respectively⁴⁸. Similar results were reported by a study in
257Japan on different amino acids including lysine⁵⁷. The study reported a weighted average GHG
258emissions from the production of lysine, threonine and tryptophan to be about 5.35 kg CO₂e/kg
259of amino acid produced. Different electricity mixes, and assumption about the sources of
260nutrients and feedstocks, are primarily responsible for the variations in results for lysine. The
261variation in our results for [Ch][Lys] using U.S.- and Chinese lysine is due to differences in
262electricity and transportation. The Chinese electricity mix is more carbon-intensive on average
263(0.6 g CO₂e/kWh in the U.S. vs. 0.9 g CO₂e/kWh in China), and because the aerobic
264fermentation step required to produce lysine is electricity-intensive, lysine produced in China has
265an appreciably larger GHG footprint. This highlights the potential benefits of sourcing
266domestically-produced lysine for IL production facilities in the U.S.

267

268 The performance and biocompatibility of [Ch][Lys] and other [Ch]-based amino acid
269ILs²⁶ means they are likely to remain a focal point for biomass pretreatment research. However,
270our results highlight the fact that simply because an IL is made with bio-derived inputs (as is the
271case with lysine) does not translate to a low or net zero GHG footprint unless. Energy-intensive
272aerobic fermentation and the nutrients required for amino acid production can result in
273substantial emissions. ILs with low-carbon inputs and simple methods for synthesis could result
274in reduced costs and environmental impacts. Early-stage efforts to achieve these goals are
275already underway.⁵⁸ Given the current and near-term state of technology, the most economically
276and environmentally-preferable strategy, is to minimize IL consumption by maximizing the
277recovery efficiency (>99%), even if the recovery is energy-intensive itself. This is particularly true
278in the case of biomass pretreatment as the IL-to-biomass mass ratio is typically greater than one.



280

281 **Figure 3:** Life-cycle GHG emissions-intensity of [Ch][Lys] production process. Uncertainty bars
 282 capture variation on all inputs by $\pm 10\%$.

283

284

285

Life-Cycle GHG Emissions for IL-Based Biofuel Production: Figure 4 (A) and 4 (B)
 286 show the life-cycle GHG emissions for all the three scenarios: WW, iHG-Current, and iHG-
 287 Projected scenarios. Consistent with standard LCA practice⁵⁹⁻⁶⁰, the emissions are divided into
 288 several important categories, including farming, petroleum products (i.e., diesel, crude oil, coal
 289 and natural gas), electricity, transportation, direct emissions (e.g., combustion of natural gas on-
 290 site), chemicals & fertilizers, and electricity credits (Fig 4A) and key life cycle stages of biofuel
 291 production supply chain, including feedstock production, processing and transportation, fuel
 292 conversion and fuel distribution (Fig 4B). The chemicals & fertilizers category aggregates
 293 several components including chemicals and fertilizers used in feedstock production, enzyme
 294 production, and other chemicals such as HCl and make-up IL (i.e., IL used to replenish
 295 unrecovered IL). Based on the process design considered in this study, the WW route has the
 296 highest GHG emissions (~198 g CO₂e/MJ). This GHG-intensity is more than double the GHG-
 297 intensity of gasoline (93 g CO₂e/MJ)⁵¹. Relative to the WW route, the iHG process reduces GHG
 298 emissions dramatically. The iHG-Current route achieves a reduction of ~45% relative to
 299 gasoline. If the improvements in iHG-Projected scenario can be realized, further reductions can
 300 be expected compared with gasoline: ~70% reduction without co-product credit for surplus
 301 electricity and as much as a 85% reduction with co-product credits for the surplus electricity.
 302 With these projected advances, bioethanol produced in the iHG-Projected scenario can qualify
 303 for the *cellulosic biofuels* category of RFS2 (this category requires at least a 60% emissions
 304 reduction compared to petroleum fuels⁶¹). In terms of life cycle stages, the fuel conversion stage
 305 is the major contributor to the total GHG emissions (~70% of the total) followed by feedstock

306production and processing stage (~30% of the total). The GHG emissions results for all three
307scenarios are discussed in detail in the following sections.

308

309***Water-wash (WW) configuration:***

310 In the WW route, 58% of the the total GHG emissions are attributed to the combustion of
311natural gas at the biorefinery (other important contributors include electricity, fertilizers, and
312chemicals). The dominance of on-site fuel use is because the WW route requires enormous
313thermal energy to dehydrate the IL after the water washing step. All steam generated from on-site
314combustion of residual solids and biogas is required, plus a substantial quantity of imported
315natural gas. Since this process requires that all water be evaporated, it is driven by the quantity of
316wash water used rather than the properties of the selected IL. Our model is optimized to
317minimize water usage during washing and energy input for vacuum evaporation, so dramatic
318improvements in the energy-intensity is unlikely. An ability to take advantage of otherwise
319unused renewable/low-carbon energy sources (overbuilt solar power capacity, stranded biogas, or
320waste heat from a co-located facility, for example) could provide modest emissions reductions.
321Nanofiltration has been proposed as an alternative strategy for IL dehydration⁶², but this will
322require further improvements with respect to IL recovery efficiency and fouling. Lower IL
323recoveries impact economic viability⁶³ as well as the GHG-intensity (since [Ch][Lys] and other
324amino acid-based IL production is CO₂-intensive to produce), so improving IL recovery is crucial
325to making nanofiltration, or any other technology, viable. Eliminating the need for the water-
326washing step by implementing an integrated processes such as iHG process considered in this
327study is the only clear path, given currently-available IL recovery technologies, to reducing the
328GHG-intensity of biofuels produced using IL pretreatment.

329

330***Integrated high gravity-Current configuration:***

331 The net GHG footprint for the iHG-Current route is about 51 g CO₂e/MJ (a ~45%
332reduction compared to gasoline). Although the iHG-Current scenario does not require imported
333natural gas to meet on-site energy needs, it does require nearly all steam generated from the
334combustion of biogas and residual solids to meet the biorefinery's heat and electricity needs.
335More conventional cellulosic biorefinery designs may export more electricity, resulting in a
336larger electricity offset credit (based on a co-product accounting strategy known as system
337expansion), although commonly-cited reports rely on optimistic projections for future
338performance³. Two major contributors to GHG emissions for the iHG-Current scenario are
339chemicals & fertilizers, and electricity (demand for upstream processes), contributing about 37%
340and 40%, respectively. Together, both these categories contribute around 74% of the total
341emissions, after subtracting 3% for the small electricity export credit. Major contributors in
342chemicals & fertilizers category include HCl required for pH adjustment during hydrolysis,
343nitrogen and ammonia required for fertilizer and lysine production, and ethylene and TMA
344required in choline hydroxide production. Overall, this route must achieve additional emissions
345reductions to qualify for the *cellulosic biofuel* category of RFS2, which requires at least 60%
346reduction compared to gasoline. Improving IL recovery efficiency (beyond 85%) can reduce the

347GHG contribution of chemicals & fertilizers. However, reducing electricity use for the IL
348regeneration process (electrodialysis), which is responsible for the bulk of the on-site electricity
349demand, would provide a much more dramatic impact. To eliminate this step, [Ch][Lys] would
350need to be replaced by a protic IL (eliminating the need for pH adjustment), as explored in the
351case of iHG-Projected scenario.

352

353***Integrated High Gravity-Projected configuration:***

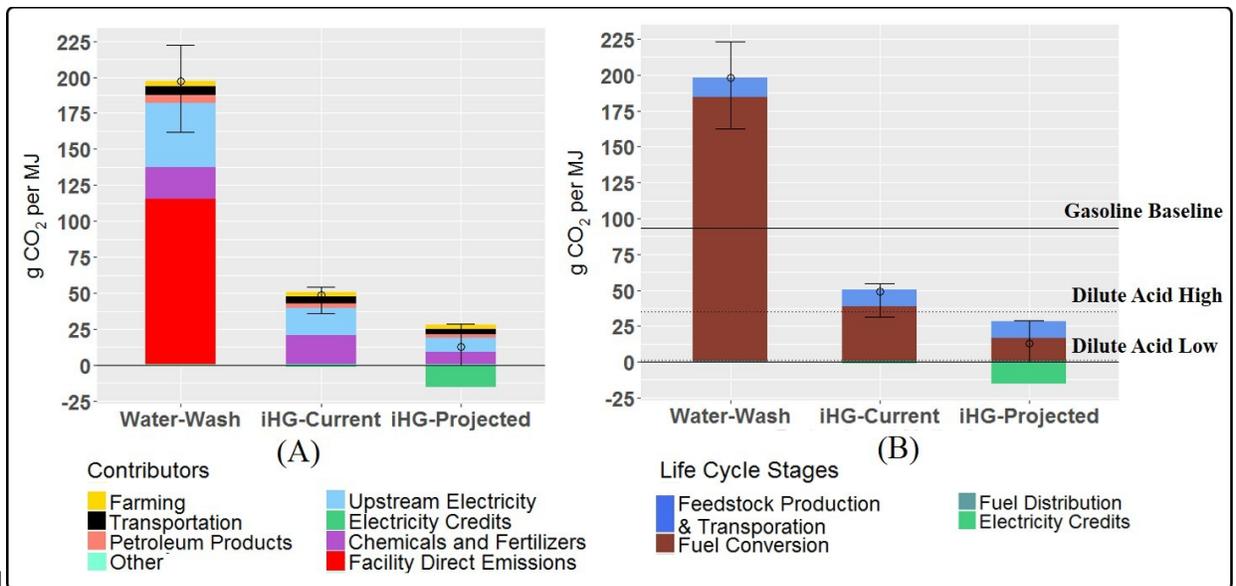
354 Eliminating the need for IL regeneration results in a GHG emissions reduction of ~70%
355for the ethanol output relative to gasoline on a per-MJ basis, before accounting for electricity
356export credits. Depending on the amount of surplus electricity available (assuming that the
357excess electricity is exported to the grid), the emissions reduction can reach as high as ~85%
358compared to gasoline if export credits are applied. The estimated quantity of electricity exported
359from the biorefinery to the grid (0.85 kWh/kg fuel) in the iHG-Projected scenario surpasses the
360supply chain-wide electricity requirement, thus the electricity credit alone reduced total GHG
361emissions by 19 g CO₂e/MJ ethanol. Studies of the GHG emissions for other, more conventional,
362biorefinery configurations also hinge on electricity credits⁶⁴. For instance, in the case of NREL
3632002⁶⁵ design for dilute acid process, Hsu et al (2010)⁶⁶ estimated the GHG emissions to be 34.8
364and 55 g CO₂e/MJ of ethanol, with and without credit, respectively. Similarly, in the case of
365cellulosic ethanol produced by biochemical conversion, Murphy et al (2015)⁴¹ estimated GHG
366emissions to be at 20-30 and 45-60 g CO₂e/MJ, with and without electricity credits, respectively.
367Our study reinforces the importance of the biorefinery's on-site energy balance and resulting
368electricity credits in improving the GHG footprint of cellulosic biofuels.

369

370 Compared to the iHG-Current scenario, the emissions corresponding to the chemicals &
371fertilizers category would be reduced by around 60% for the iHG-Projected scenario (from 20.5
372g/MJ to 8 g/MJ), although this category remains a major contributor to the total emissions
373(~37%). Enzyme loading impacts two categories: chemicals & fertilizers and electricity.
374Generally, higher enzyme loading improves sugar yields but enzyme production itself is carbon-
375intensive (~9.5 kg CO₂e/kg of enzyme produced). With enzyme loading of 20 mg/g of glucan,
376the contributions from enzyme production alone were about 9 g CO₂e/MJ in all scenarios. Given
377the emissions-intensity of enzymes and the impact of enzyme loading on yield, we have explored
378this parameter in our sensitivity analysis (Figure 6).

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383 **Figure 4:** Life-cycle GHG emissions-intensity of corn stover –based ethanol production with
 384 [Ch][Lys] pretreatment. (A) results based on the contribution of major inputs; (B) results based
 385 on the contribution of supply chain stages. For reference, baseline GHG emissions for
 386 conventional gasoline is represented by solid line (at 93 g CO₂e/MJ⁵¹), for dilute acid high and
 387 low ranges are represented by dotted lines (at 35 g CO₂e/MJ⁶⁶ and 1.5 g CO₂e/MJ⁴², respectively)
 388 . Uncertainty bars capture variation on all inputs by ± 10%.

389

390 **Life-Cycle Water Intensity of IL-Based Biofuel Production:** We calculated water-
 391intensity using two metrics: 1) consumption, and 2) withdrawals, as discussed in the Methods
 392section (Figure 5). Depending on the scenario, the water consumption is found to be in the range
 393of 0.2 to 0.4 liter/MJ (i.e., 7 to 14 liter/liter). Water withdrawals are in the range of 0.4 to 1.2
 394liter/MJ (i.e., 14 to 42 liter/liter) of fuel. These water-intensity estimates are comparable to the
 395estimates from other biochemical conversion processes with different pretreatment technologies.
 396For instance, in the case of biochemical conversion of switchgrass to ethanol using dilute acid
 397pretreatment, water consumption was estimated to be in the range of 5.3 to 9.8 liter/liter⁵⁶. Scown
 398et al (2014)³⁶ reported similar results for dilute acid pretreatment of corn stover to produce
 399biofuel -- they found an average consumption between 0.25 to 0.43 liter/MJ (i.e., 5.3 to 10
 400liter/liter) and withdrawal between -9.7 to 2.8 liter/MJ (i.e., -206 to 59 liter/liter; the large
 401variation is mainly due to differences in assumption with regards to co-product lignin handling).

402

403 The life-cycle water consumption for the WW, iHG-Current, and iHG-Projected scenarios
 404are 0.35, 0.4, and 0.2 liter/MJ, respectively. Despite requiring a water-intensive washing step, the
 405WW route performed slightly better than the iHG-Current scenario. Although initially
 406counterintuitive, this is because all the water used in the water-washing step eventually is
 407recovered in the multi-effect evaporative dehydration step and is recycled. Additionally, the

408water washing step happens to occur between two operations where a significant temperature
409drop is required (i.e., a temperature drop of 90° C between pretreatment, at 140° C and
410enzymatic hydrolysis, at 50° C). The water used in the washing step serves to cool the pretreated
411biomass, avoiding the need for cooling water that is otherwise required to drop the temperature
412to 50° C for optimal enzyme performance during hydrolysis. Since the make-up cooling water
413needed in the cooling towers is essentially proportional to the total cooling water demand, the
414make-up cooling water in the WW route is lower compared to that of iHG-Current route. More
415than 90% of the direct water consumption at the biorefinery is used for make-up cooling water,
416so even a small difference yields noticeable variation. The absence of turbo-generator and
417condenser in the WW route (as there is no surplus steam) also reduces the on-site cooling water
418demand, although the result is greater upstream water consumption because the facility must
419import power from the grid. For both iHG scenarios, the direct water use at the biorefinery is the
420most important component of total water consumption (around 60%). The water consumed in the
421iHG route is improved significantly in the iHG-Projected scenario, bringing total water
422consumption to 0.2 liter/MJ (i.e., around 50% reduction compared to iHG-Current scenario). As
423in the case of GHG emissions, this reduction is largely owed to the excess electricity production,
424which is assumed to displace the U.S. grid mix (with a water consumption of around 2
425liter/kWh).

426

427 In terms of withdrawals, the water-intensity of the WW, iHG-Current, and iHG-Projected
428scenarios is 1.2, 1.0, and 0.4 liter/MJ, respectively. Indirect (upstream) water use drives these
429results. Because the U.S. grid mix still relies on many power plants with open-loop cooling
430systems, the water withdrawals in the WW route (which imports electricity) are slightly higher.
431As in the water consumption results, the iHG-Projected scenario benefits from offset credits
432associated with the export of significant quantities of electricity to the grid. Other indirect water
433withdrawals can be attributed to chemicals, petroleum and products. In the iHG scenarios,
434chemicals & fertilizers alone contribute 60% of total withdrawals, in part because the water
435recycling rate in the chemical manufacturing industry is low (28% on average)⁶⁷.

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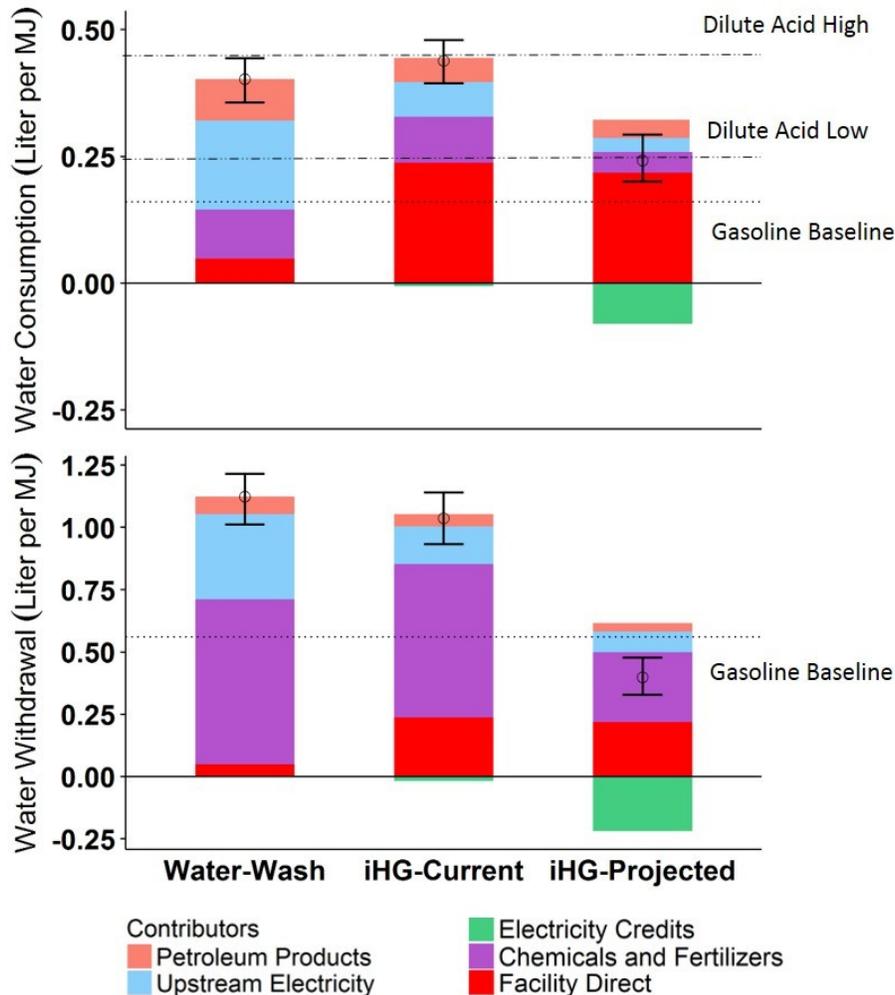
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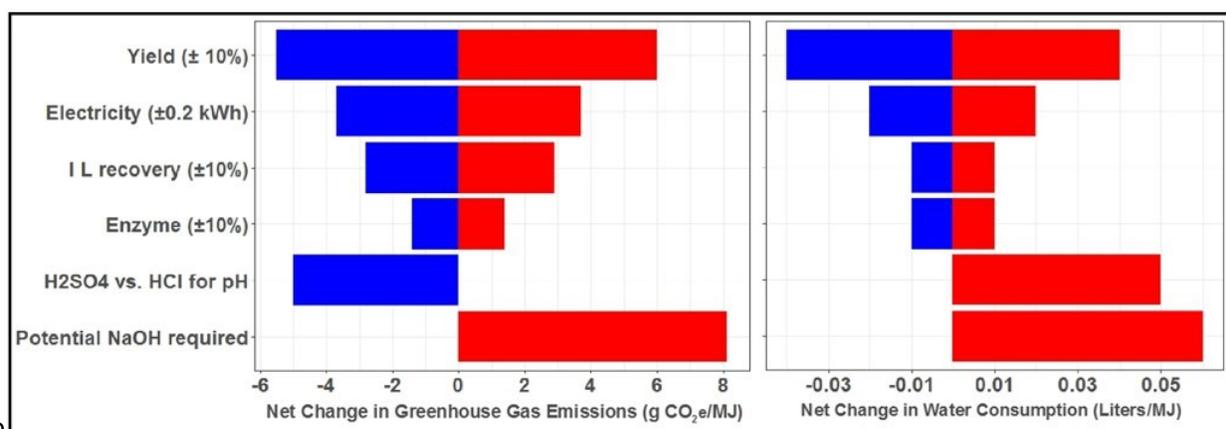


445
 446 **Figure 5.** Life-cycle water consumption (top) and withdrawal (bottom) results of corn stover –
 447 based ethanol production with [Ch][Lys] pretreatment. For reference, baseline water
 448 consumption and withdrawal for conventional gasoline is represented by dotted line (at 0.16
 449 liter/MJ³⁷ and 0.56 liter/MJ³⁴, respectively), for dilute acid, high and low water consumption
 450 ranges are at 0.43 liter/MJ³⁶ and 0.25 liter/MJ³⁶, respectively . Uncertainty bars capture variation
 451 on all inputs by $\pm 10\%$.

452
 453 **Sensitivity Analysis:** We performed a sensitivity analysis to evaluate the influence of key
 454 parameters and assumptions on the GHG-intensity and water consumption of ethanol production
 455 with IL pretreatment (Figure 6). As suggested by the previous studies^{64, 68}, key inputs that are
 456 uncertain and will potentially impact the emission intensity of biofuel production include: 1)
 457 biofuel yield, 2) IL recovery efficiency, 3) electricity import/export, 4) enzyme loading, and 5)
 458 the usage of chemicals such as acid (e.g., HCl) or base (e.g., NaOH). Given the early-stage
 459 nature of these processes, we do not have adequate information to establish true ranges for the
 460 input parameters. Thus, we performed this sensitivity analysis with +/- 10% variation in most of
 461 the key parameters (compared to the base case values presented in Table 2). We find that a 10%
 462 variation in fuel yield has changed base GHG emissions and water consumption by around 10%

463(because most water loss and emissions occur before the fuel leaves the biorefinery). A 10%
 464variation in enzyme loading results in 2% change in total GHG emissions and water
 465consumption. We found that IL recycle is particularly important in reducing GHG emissions. For
 466instance, when IL recovery was decreased by 10%, the GHG footprint increased by 6%. On the
 467other hand, water consumption results were changed by around 2% with 10% change in IL
 468recovery. Because ILs are costly, high IL recovery efficiency is important both from an economic
 469and environmental perspective. Furthermore, just by replacing HCl with H₂SO₄, the total
 470emissions can be reduced by 10%. This improvement is possible as HCl is more emissions-
 471intensive compared to H₂SO₄ (1.14 kg CO₂e/kg HCl vs. 0.15 kg CO₂e/kg H₂SO₄). This highlights
 472the need to select acids carefully to minimize the GHG footprint. Our sensitivity analysis shows
 473that replacing HCl with H₂SO₄ results higher water consumption footprint. This is because both
 474of these chemicals have nearly the same water consumption footprint while the amount of H₂SO₄
 475required is greater on per kg fuel basis (0.18 vs 0.54 kg/kg of ethanol). Likewise, if additional
 476NaOH were to be used, GHG emissions and water consumption footprint would be increased by
 477as much as 15% and 5%, respectively.

478



479

480 **Figure 6:** Sensitivity analysis of GHG emissions and water consumption with respect to the
 481 baseline iHG-Current scenario (51 g CO₂e/MJ and 0.4 liter/MJ, respectively). The +/- variation
 482 in the key process parameters refers to the change from the baseline values presented in Table 2.
 483

484

485 In conclusion, given the high GHG footprint of IL production, high IL recovery (>99%)
 486becomes an environmental necessity whenever such ILs are used for biomass pretreatment.
 487Considering the GHG footprint of ethanol produced using the most widely used WW route
 488revealed a GHG-intensity more than twice that of the gasoline (~198 vs 93 g CO₂e/MJ,
 489respectively), due to the energy intensity of the IL dehydration. The novel iHG process however
 490has the potential to reduce GHG emissions, compared to gasoline, by ~45% (iHG-Current) to 70-
 491185% (iHG-Projected). The life-cycle water consumption is less sensitive to the specific scenarios
 492and ranges from 0.2 to 0.4 liter/MJ of fuel. Water withdrawals range from 0.4 to 1.2 liter/MJ of
 493fuel. These estimates are comparable to the water-intensity of cellulosic biofuel production using

494other pretreatment technologies, indicating that the water use will be neither a major advantage
495nor impediment to the success of IL pretreatment technologies. The comparison between the
496WW and iHG processes also underscores the need for more research using biocompatible ILs,
497which are key to eliminating water-wash steps and subsequent emissions-intensive recovery. The
498development of protic ILs that are effective biomass pretreatment solvents is the natural next step
499in improving the environmental footprint of biorefineries using IL pretreatment. Recent progress
500has been made on the use of protic ILs⁴⁹, and further process optimization (e.g., improving yield
501and solids loading) will help IL-based biorefineries achieve their promise of competitive costs
502and substantial reductions in emissions.

503

504

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506

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513

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