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4 1 **Techno-economic analysis and life-cycle analysis of two light-duty bio-**  
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6 2 **blendstocks: isobutanol and aromatic rich hydrocarbons**

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45 19 **Abstract**

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47 20 Isobutanol and aromatic-rich hydrocarbons (ARHC) are two biomass-derived high octane  
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49 21 blendstocks that could be blended with petroleum gasoline for use in optimized spark-ignition  
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51 22 engines in light-duty vehicles, potentially increasing engine efficiency. To evaluate technology  
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53 23 readiness, economic viability, and environmental impacts of these technologies, we use detailed  
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3 24 techno-economic analysis (TEA) and life-cycle analysis (LCA). We assumed isobutanol is  
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5 25 produced via biochemical conversion of an herbaceous feedstock blend while ARHC is produced  
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7 26 via thermochemical conversion of a woody feedstock blend. The minimum estimated fuel selling  
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9 27 price (MFSP) of isobutanol ranged from \$5.57/gasoline gallon equivalent (GGE) (\$0.045/MJ)  
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11 28 based on today's technology to \$4.22/GGE (\$0.034/MJ) with technology advancements. The  
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13 29 MFSP of ARHC could decline from \$5.20/GGE (\$0.042/MJ) based on today's technology to  
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15 30 \$4.20/GGE (\$0.034/MJ) as technology improves. Both isobutanol and ARHC offer about 73%  
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17 31 GHG emission reduction relative to petroleum gasoline per LCA of these two bio-blendstocks.  
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19 32 On the other hand, water consumption in the production of both bio-blendstocks exceeds that of  
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21 33 conventional gasoline although process engineering offers routes to cutting water consumption.  
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23 34 Over their life cycles, both isobutanol and ARHC emit more NO<sub>x</sub> and PM<sub>2.5</sub> than petroleum  
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25 35 gasoline. Improving the energy efficiency and lowering air emissions from agricultural  
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27 36 equipment will reduce the life-cycle air pollutant emissions of these bio-blendstocks.  
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35 38 **Keywords:** techno-economic analysis, life-cycle analysis, bio-blendstock; isobutanol, aromatic-  
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37 39 rich hydrocarbons  
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## 41 **Introduction**

42 Nine U.S. Department of Energy (DOE) national laboratories are collaborating to determine fuel  
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44 43 properties that improve the engine efficiency of light- and heavy-duty vehicles through the Co-  
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46 44 Optima program.<sup>1</sup> Producing blendstocks, a compound or mixture that when blended into fuels  
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48 45 can improve spark ignition engine fuel economy, from biomass is a particularly interesting  
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50 46 approach to obtain fuels given that, in the case of fuels for light-duty vehicles, many of these  
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3 47 blendstocks have high octane and other desirable properties that are known to improve engine  
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5 48 efficiency.<sup>2</sup> Recently, 24 bio-blendstocks for light-duty vehicles were screened for their  
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7 49 environmental, scalability, and economic potential.<sup>3</sup> This type of screening improves  
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10 50 understanding of the factors that contribute to viability but does not lend detailed insight into  
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12 51 strategies to improve bio-blendstocks' economic and environmental performance. Detailed  
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14 52 techno-economic assessments (TEA) and life-cycle analysis (LCA) are tools that lead to these  
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16 53 insights.

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20 54 Following the bio-blendstock screening, two bio-blendstocks, isobutanol and aromatic rich  
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22 55 hydrocarbons (ARHC), were selected for detailed TEA and LCA. The intent was to assess their  
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24 56 current and potential economic viability, their environmental effects, and the research needed to  
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26 57 reach that potential performance levels. Bio-blendstocks are biomass-derived fuel components  
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28 58 that can be blended into conventional gasoline to produce a finished fuel. The two bio-  
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30 59 blendstocks were chosen because they can be produced via diverse conversion techniques and  
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32 60 offer high octane levels, a key driver of improved engine efficiency, among other favorable fuel  
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34 61 properties.<sup>4</sup> Isobutanol can be derived biochemically from herbaceous, cellulosic biomass, which  
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36 62 when pretreated with acids and enzymes releases monomeric sugars that can be utilized by  
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38 63 microorganisms.<sup>5</sup> ARHC can be derived thermochemically from woody, lignocellulosic biomass  
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40 64 which has a higher content of lignin material than cellulosic biomass. We assume that these bio-  
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42 65 blendstocks would be produced from herbaceous (isobutanol) and woody (ARHC) cellulosic  
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44 66 feedstock blends respectively.<sup>6,7</sup> In the isobutanol biochemical conversion pathway, herbaceous  
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46 67 feedstock is chosen for its availability from agricultural residues in the United States<sup>8</sup>. In the  
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48 68 ARHC thermochemical conversion pathway, woody feedstock is chosen for its availability and  
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50 69 capability to supply a mature biorefining industry at the scale envisioned by Co-Optima.<sup>9</sup>

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3 70 While there is some activity towards commercialization of isobutanol, activity towards  
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5 71 commercializing blendstocks with properties akin to ARHC is limited. Gevo, for instance, is  
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7 72 developing routes to isobutanol from corn starch and grain sorghum-derived sugars,<sup>10</sup> and plans  
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9 73 to tap sugars from cellulosic feedstocks.<sup>11</sup> Butamax is also developing routes from corn starch to  
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11 74 isobutanol.<sup>12</sup> Production of isobutanol from cellulosic feedstocks, which is under consideration  
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13 75 globally, could make use of additional U.S. biomass resources and avoid use of feedstocks that  
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15 76 are also food sources.<sup>8,12</sup>  
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20 77 Isobutanol is made biochemically. In contrast, ARHC, is produced thermochemically, starting  
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22 78 with gasification of the feedstock to syngas which is then converted to ethanol. Ethanol is then  
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24 79 catalytically converted to hydrocarbons. Furthermore, with the properties of a hydrocarbon,  
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26 80 ARHC is expected to be compatible with existing fuel infrastructure and, aside from limits on  
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28 81 aromatics and benzene in blended fuels (see Supporting Information), is not expected to face  
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30 82 blending limitations.  
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35 83 Cellulosic biomass-derived isobutanol has been the subject of past TEA and LCA studies with  
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37 84 varying results.<sup>13-23</sup> In general, previous studies indicate that both system variations and  
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39 85 methodology discrepancies can lead to variation in environmental performance of biofuel  
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41 86 production. Specifically, biomass feedstock choices, feedstock supply chain and logistics  
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43 87 operations, biomass conversion efficiency, conversion process energy and material requirements,  
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45 88 as well as types, quantities, and market dynamics of co-products, if any, have been found to be  
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47 89 important factors in literature that largely determine the environmental performance of biofuels.  
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49 90 In one previous study, isobutanol derived from corn stover was evaluated in terms of process  
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51 91 economics and energy and environmental performance with identification of technical,  
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53 92 economic, and environmental barriers on the route to technical maturity.<sup>5</sup> The present study goes  
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3 93 into significantly more depth regarding environmental impacts beyond GHG emissions, such as  
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5 94 emissions of nitrogen oxides (NO<sub>x</sub>) and particulate matter with an aerodynamic diameter below  
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8 95 2.5 micrometers (PM<sub>2.5</sub>), and routes to mitigation of those impacts. An LCA of corn-stover  
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10 96 derived isobutanol indicated it could exhibit 47% less GHG emissions compared to fossil-  
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12 97 derived isobutanol.<sup>24</sup> Bauer and Hultenberg conducted a TEA of producing isobutanol  
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14 98 thermochemically from glycerine, a major biodiesel co-product<sup>25</sup> and estimated isobutanol  
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16 99 produced in this manner would be 53% less GHG-intensive than petroleum gasoline. Recently,  
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19 100 under the Renewable Fuel Standard, the U.S. Environmental Protection Agency (EPA) approved  
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21 101 Gevo, Inc's butanol production pathway from corn starch or grain sorghum, determining this  
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23 102 isobutanol exhibits a GHG reduction potential compared to petroleum gasoline exceeding 50%  
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26 103 .<sup>10</sup> Notably, this process uses biogas in the conversion processes and produces excess electricity  
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28 104 that is sold to the grid. The ARHC system is based on ethanol conversion over zeolites to  
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30 105 aromatics. This process has been studied over the years<sup>26-31</sup>, and is analogous to the methanol-to-  
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32 106 gasoline process which has reached commercial status<sup>32</sup>. High-octane renewable gasoline with  
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34 107 high aromatic concentrations derived from an indirect biomass gasification route known as  
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36 108 indirect liquefaction could offer up to 67% reduction in life-cycle GHG emissions.<sup>33</sup>  
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41 109 In this paper, we describe detailed biochemical and thermochemical process engineering models  
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43 110 for isobutanol and ARHC that enable quantification of production costs and process energy and  
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45 111 material balances, which are critical inputs for the detailed LCA. We report minimum fuel  
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47 112 selling price (MFSP), life-cycle greenhouse gas (GHG) emissions, NO<sub>x</sub> and PM<sub>2.5</sub> emissions, and  
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49 113 water consumption. TEA and LCA results offer insights into how these bio-blendstocks  
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51 114 compare with conventional fuels on a cost and environmental basis and inform estimates of the  
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54 115 benefits they may bring if introduced to the transportation sector in large volumes. In addition to  
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3 116 reporting base case results, we investigate results under sensitivity cases and identify cost and  
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5 117 environmental impact drivers that can be addressed in future research and development targeting  
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7 118 these two bio-blendstocks. Information and research gaps of associated with various steps of the  
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9 119 technology development could be identified through these TEA and LCA efforts, guiding further  
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11 120 research priorities.  
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## 15 121 **Methodology and data**

### 16 122 **Techno-economic analysis**

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18 123 We created detailed process models for production of isobutanol in Aspen Plus (V 7.2).<sup>34</sup> For the  
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20 124 ARHC process, the process models were developed in CHEMCAD (V 6.5.5).<sup>35</sup> Both Aspen Plus  
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22 125 and CHEMCAD can be used to perform rigorous mass and energy balance calculations that  
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24 126 inform the TEA and LCA.<sup>36,37</sup> Using the resulting mass and energy balances, we then estimated  
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26 127 the capital and operating cost of the facility. A discounted cash flow rate of return (DCFROR)  
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28 128 determines the MFSP needed to have a 30-year plant reach a net present value (NPV) of zero  
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30 129 while simultaneously achieving an internal rate of return (IRR) of 10%.<sup>36,37</sup> All cost values are  
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32 130 provided in US currency (\$) inflated or deflated to a cost year of 2014 using the Plant Cost Index  
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34 131 from *Chemical Engineering Magazine* and chemical costs using the Producer Price Index from  
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36 132 IHS Consulting as documented in the U.S. DOE Bioenergy Technologies Office Multi-Year  
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38 133 Program Plan.<sup>38</sup> Additionally, for the isobutanol cases, isobutanol is considered the final fuel.  
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40 134 Process descriptions are provided in the Supporting Information (Figures S1 and S2).  
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49 135 We considered two commercial-scale production cases for each potential blendstock: a target  
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51 136 case that reflects technology advancements and a state of technology (SOT) case reflecting  
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53 137 current technology. Although not yet demonstrated in state-of-technology or commercial  
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55 138 application, several near-term process targets are assumed for the target case to understand the  
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3 139 potential of the technology if said targets can be met. The SOT case, on the other hand, only  
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5 140 uses values that have been demonstrated in the laboratory or in a pilot/demonstration plant. Both  
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7 141 cases use  $n^{\text{th}}$  plant economics which assumes several plants of the same technology have already  
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9 142 been built and are operating, which avoids artificial inflation of project costs associated with risk  
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11 143 financing, longer start-ups, and equipment overdesign.<sup>38</sup> Table 1 lists the SOT assumptions that  
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13 144 are different from the isobutanol target case. For example, from the SOT case to the target case,  
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15 145 fermentation time drops from 65 to 36 hours and the yield increases from 0.30 to 0.34 g  
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17 146 isobutanol/g sugar. Correspondingly, the target case requires fewer fermenters and less capital.  
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19 147 Electricity is co-generated in the isobutanol process (55,600 kW for the SOT and 43,121 kW for  
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21 148 the target case), and enough electricity is produced to meet the facility's needs, and any  
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23 149 additional electricity is fed to the grid (27,000 kW for the SOT to the grid and 16,900 kW for the  
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25 150 target case to the grid) (See Table S10 in Supporting Information). Excess electricity sent to the  
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27 151 grid is sold as a co-product. The ARHC SOT case differs from the target case in two main ways.  
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29 152 First, the yield is lower because an excess of light paraffins are produced that are routed to fuel  
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31 153 gas. Second, benzene content is higher, so, because of a U.S. Environmental Protection Agency  
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33 154 1.3 vol% limit for benzene in gasoline,<sup>39</sup> the amount of ARHC that could be blended is more  
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35 155 limited in the SOT case than in the target case.  
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43 156 Table 1: Comparison of SOT to target case process model inputs for isobutanol and ARHC  
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<b>Isobutanol</b>	<b>SOT</b>	<b>Target</b>
Hemicellulose Conversion	76%	90%
Cellulose Conversion	74%	90%
Enzyme Loading	12 mg/g cellulose	10 mg/g cellulose
Saccharification Time	5 days	3.5 days
Glucose Conversion to Isobutanol	95%	95%
Xylose Conversion to Isobutanol	72%	85%

Arabinose Conversion to Isobutanol	0%	85%
Fermentation Time	65 hours	36 hours
Number of 1,000,000 gallon Fermentors	14	9
Electricity Production (kW)	16,900	26,980
	ARHC	SOT
Overall C <sub>5+</sub> yield on alcohols	54 wt%	58 wt%
Benzene content in second reactor product	30 wt%	<10 wt%

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159 In this analysis, we focus on the target cases, aiming for deployment of the bio-blendstocks for  
160 use in engines tailored to exploit their fuel properties towards increased efficiency in the 2025  
161 timeframe, several years after the target case technology would be achieved.

### 162 **Life-cycle analysis**

163 The material and energy flows from the process models inform the LCA of isobutanol and  
164 ARHC in addition to energy and material intensity of biomass feedstock production and logistics  
165 and biomass conversion.<sup>6,7</sup> The LCA system boundary includes the biomass feedstock supply  
166 chain, biorefinery operations, and bio-blendstock transportation and combustion in a vehicle  
167 (Figure S3). GHG (CO<sub>2</sub>, CH<sub>4</sub>, and N<sub>2</sub>O) emissions calculated on the basis of the 100-year Global  
168 Warming Potentials for CO<sub>2</sub>, CH<sub>4</sub>, and N<sub>2</sub>O emissions, which are 1, 25, and 265, respectively,<sup>40</sup>  
169 water consumption, and emissions of two criteria air pollutants, NO<sub>x</sub> and PM<sub>2.5</sub> are the three  
170 environmental metrics assessed in this analysis. Given the target use of the bio-blendstocks as  
171 transportation fuels, we use per mega-joules (MJ) as the functional unit for both bio-blendstocks.  
172 For this analysis we used the Greenhouse gases, Regulated Emissions, and Energy use in  
173 Transportation (GREET<sup>®</sup>) model as released in 2017.<sup>41</sup> The GREET model, publicly available  
174 and developed with the support of the DOE, is a tool for the LCA of fuels and vehicle  
175 technologies, and permits users to investigate energy and environmental impacts such as fossil

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3 176 energy, petroleum, and total energy use (including renewable energy in biomass), GHG  
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5 177 emissions, and water consumption of various fuel production pathways.  
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9 178 Within the system boundaries illustrated in Figure S3, biomass production and conversion are the  
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11 179 key life-cycle steps to model for both bio-blendstocks. Techno-economic data for production of  
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13 180 conversion-ready biomass (feedstock) was taken from Idaho National Laboratory (INL)  
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15 181 Feedstock SOT reports.<sup>6,7</sup> The 2017 herbaceous feedstock blend meeting cost and quality  
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17 182 specification requirements for biochemical conversion technologies established by DOE's  
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19 183 Bioenergy Technologies Office (BETO) is derived from corn stover, switchgrass, and grass  
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21 184 clippings.<sup>6</sup> The 2017 woody feedstock blend meeting BETO cost and quality requirements is  
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23 185 entirely derived from pre-processed forest residues collected as part of regular forest  
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25 186 management and logging operations for higher value markets such as saw timber and/or pulp and  
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27 187 paper.<sup>7</sup> Costs for both feedstock blends include grower payments. Supporting Information  
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29 188 Tables S1-S7 detail the energy consumption, material requirements, and logistics associated with  
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31 189 the underlying supply chains of the two blends, which served as input variables to GREET.  
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37 190 For the conversion portion of the bio-blendstocks' life-cycle, GREET modeling used material  
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39 191 and energy flows from the above-described process models (Tables S10-S11). The isobutanol  
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41 192 pathway co-produces electricity that is sold to the grid. Energy-based allocation is used as the co-  
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43 193 product handling method. The ARHC pathway has no co-products.  
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#### 47 194 **Sensitivity analysis**

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49 195 To identify key cost drivers, financial and cost value parameters such as the return on  
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51 196 investment, total capital costs, feedstock cost, and interest rate were varied. In particular for the  
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53 197 isobutanol case, the influence of enzyme loading, glucose yields from enzymatic hydrolysis, and  
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3 198 xylose fermentation yields were investigated. For ARHC case, the impact of the fuel yield was  
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5 199 assessed. Altering these parameters changes the overall material and energy balances of the  
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7 200 conversion processes. Summary results are given below. The details may be found in the SI  
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10 201 (Tables S9, S10 and S11).  
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## 16 203 **RESULTS AND DISCUSSION**

### 17 204 **Techno-economic analysis results**

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21 205 Figure 1 illustrates the contributors to total cost of isobutanol production in the SOT and target  
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23 206 cases. The SOT case has a total installed capital investment of \$282 million, \$16 million higher  
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25 207 than the total installed capital investment for the target case. The boiler is the most capital-  
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27 208 intensive equipment in both cases, followed by capital costs for wastewater treatment, feedstock  
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29 209 pretreatment within gate, enzymatic hydrolysis and fermentation, and isobutanol recovery  
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32 210 process areas. The process areas with the smallest installed capital costs included enzyme  
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35 211 production, utilities (including the boiler), neutralization, and storage.  
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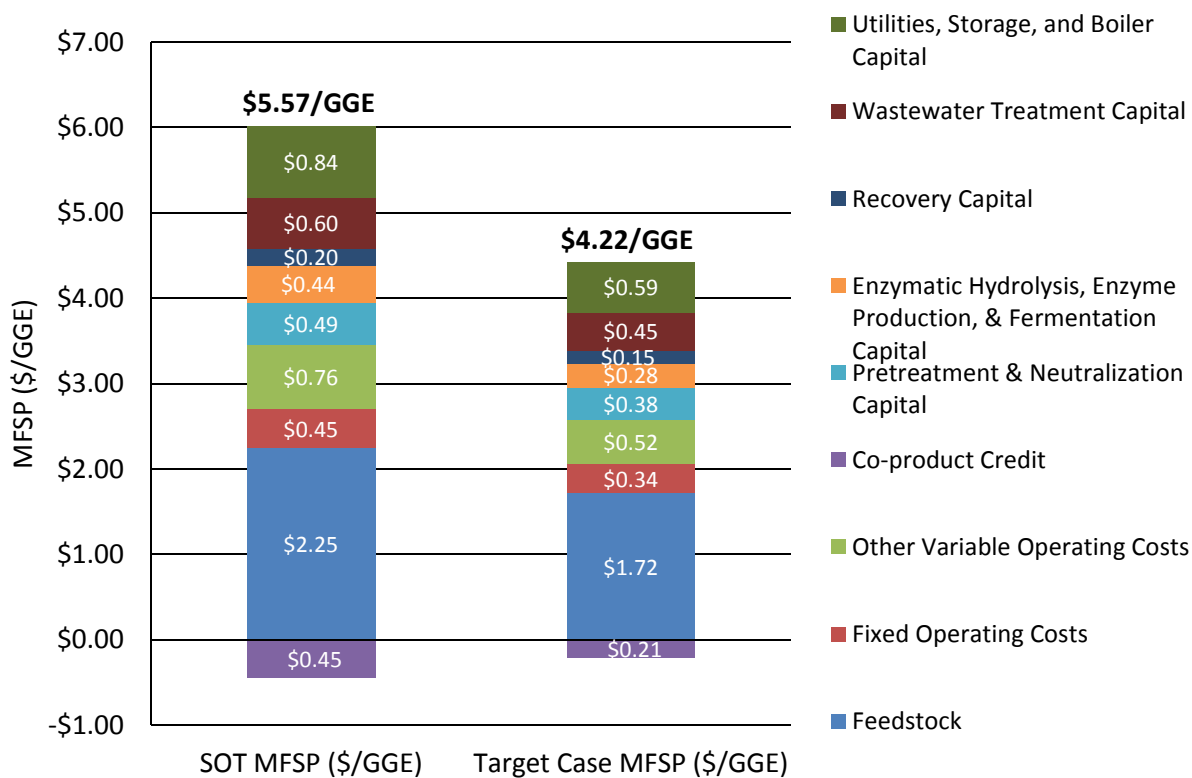


Figure 1: Cost Breakouts for the MFSP of Isobutanol SOT and Target Cases

In addition, the variable operating costs for the target case total \$2.03/GGE (\$0.017/MJ); fixed operating costs total \$0.34/GGE (\$0.003/MJ). Comparatively, in the SOT case, variable operating costs total \$2.56/GGE (\$0.021/MJ) and fixed costs equal \$0.45/GGE (\$0.004/MJ). In line with previous analyses,<sup>36,37</sup> the feedstock is the largest operating cost totaling \$61.7 million per year and \$1.72/GGE (\$0.014/MJ) for the target case or \$61.7 million per year and \$2.25/GGE (\$0.018/MJ) for the SOT case. Fixed operating costs, which include labor, maintenance, property issuance, and taxes, is the second largest operating cost for both cases. Factors influencing the variable operating costs include enzyme loading levels that dictate the amount of fed glucose used in the enzyme production train, other enzyme raw materials, purchase of caustic, sulfuric acid, ammonia, other fermentation raw materials, and other wastewater treatment raw materials, and, finally, ash disposal. Enough electricity is produced

227 through lignin combustion in the boiler to meet energy demand and provides a \$0.21/GGE  
 228 (\$0.002/MJ) co-product credit to the system for the target case or a \$0.45/GGE (0.004/MJ) credit  
 229 for the SOT case.

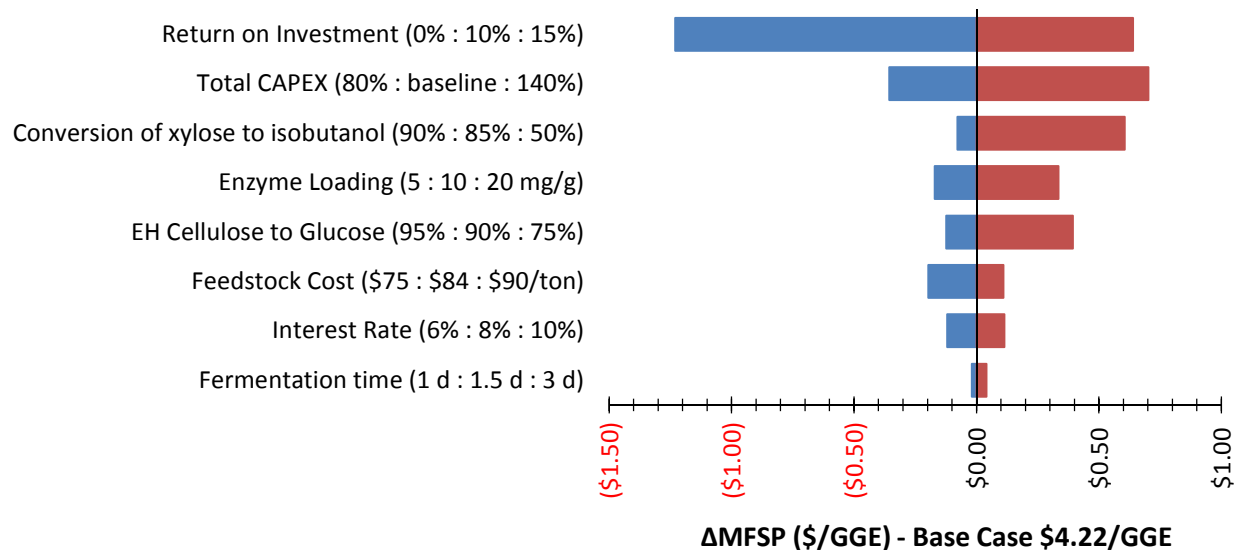
230 For the target case, the MFSP is \$4.22/GGE (\$0.034/MJ) as shown in Table 2. Comparatively,  
 231 the SOT for the isobutanol case has a MFSP of \$5.57/GGE (\$0.045/MJ). Between the SOT and  
 232 target cases, the lower yield, higher enzyme loading, and hydrolysis/fermentation time drive this  
 233 \$1.34/GGE (\$0.011/MJ) increase in MFSP. For example, the fuel yield is 22.1% for the SOT and  
 234 28.8% for the target case on a carbon basis.

235 Table 2 Costs, carbon efficiencies, and fuel yields for the SOT and target isobutanol cases

	Isobutanol	SOT	Target
Minimum Fuel Selling Price (\$/GGE or \$/MJ)		\$5.57/GGE (\$0.045/MJ)	\$4.22/GGE (\$0.034/MJ)
Percent Carbon from Biomass in Fuels (%)		22.1%	28.8%
Fuel Yields (MJ/metric ton feedstock) [L/metric ton]		5,083 [191.5]	6,614 [249.1]

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 237 Figure 2 shows the results of the single point sensitivity analysis in a tornado diagram with  
 238 sensitivity variables that have the largest affect sorted from the top. The largest cost driver is the  
 239 return on investment for the process. When the return on investment is 0% the MFSP drops to  
 240 \$2.99/GGE (\$0.024/MJ). Following the return on investment, when increasing the total capital  
 241 investment by 140% the MFSP increases to \$4.33/GGE (\$0.035/MJ). The conversion of xylose  
 242 to isobutanol is the third largest cost driver when the xylose conversion is only 50%. Enzyme  
 243 loading and cellulose conversion to glucose also can cause more than a \$0.25/GGE (\$0.002/MJ)  
 244 change in the MFSP. Parameters that have a smaller effect include the biomass cost, interest rate,  
 245 and fermentation time.

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Figure 2: Cost Sensitivity Analysis in the Isobutanol Target Case

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250 The cost breakouts for the ARHC process are shown in Figure 3 for the SOT and target cases.

251 The SOT has a total installed capital investment of \$300 million, \$15 million below the total

252 installed capital investment for the target case. The higher target case capital cost results from

253 greater off-gas recycle which increases the size of alcohol and hydrocarbon production.

254 Gasification, syngas cleanup, and compression and alcohol production account for 70% of the

255 total installed capital in both cases. Also in both cases, ARHC capital is less than 10% of the

256 total, allowing little room for further capital cost reduction. The operating costs are dominated by

257 feedstock and labor cost (shown as fixed operating costs). Catalyst costs associated with alcohol

258 conversion to mostly aromatic hydrocarbons are relatively lower-cost, regenerable zeolite-types

259 and have small impact on the overall cost.

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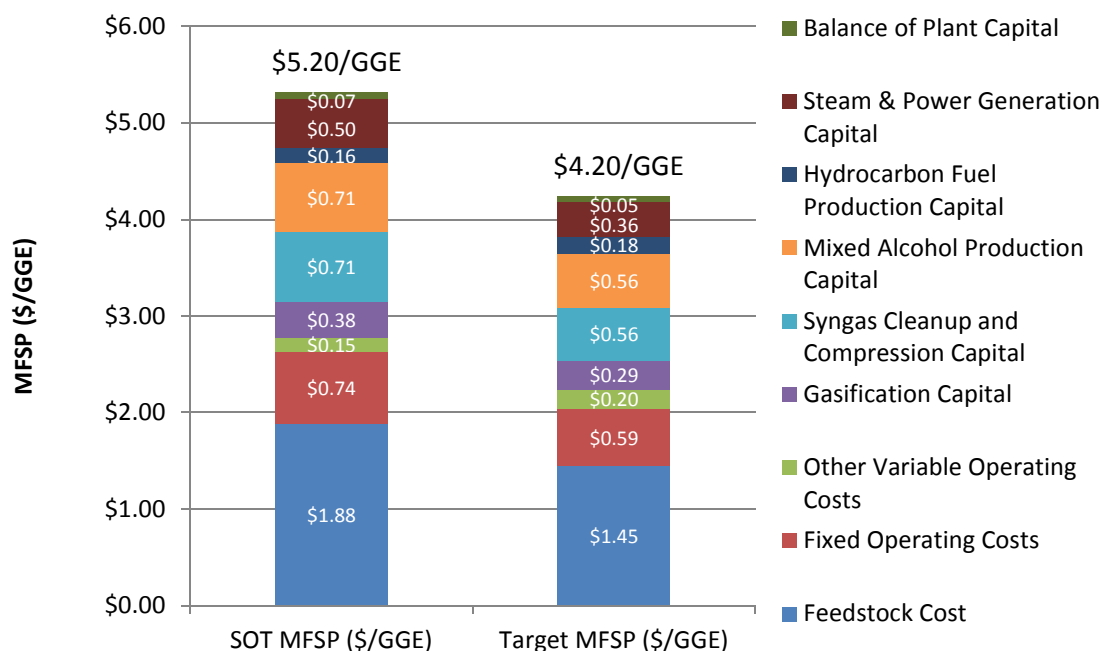


Figure 3: Cost Breakouts for the MFSP of ARHC SOT and Target Cases

As shown in Table 3, the target case MFSP is \$4.20/GGE (\$0.034/MJ) and the SOT is \$5.20/GGE (\$0.042/MJ). While the yield improvements could decrease the MFSP by \$1/GGE (\$0.008/MJ), further cost reductions through this specific thermochemical route are unlikely.

Table 3 Costs, carbon efficiencies, and fuel yields for the SOT and target ARHC cases

ARHC	SOT	Target
Minimum Fuel Selling Price (\$/GGE or \$/MJ)	\$5.20/GGE (\$0.042/MJ)	\$4.20/GGE (\$0.034/MJ)
Percent Carbon from Biomass in Fuels (%)	30%	33%
Fuel Yields (MJ /metric ton feedstock) [L/metric ton]	6,054 [203]	7,890 [227]

Sensitivities for the target ARHC case are shown in Figure 4. Return on investment has the largest effects on MFSP. A pioneer plant would likely need a return greater than 15%. Fuel yield

271 is also significant. A fuel yield at 90% of the base target adds more than \$0.30/GGE (\$0.002/MJ)  
 272 to the production costs. Reduced yield increases off-gas used for internal power generation,  
 273 which in turn increases power generation capital-related costs, but also eliminates purchased  
 274 electricity. A yield increase of 110% requires introducing natural gas to balance the plant heat  
 275 load and additional purchased electricity. However, these additional costs are more than offset by  
 276 the increased ARHC blendstock production, thus this sensitivity reduces the MFSP by  
 277 approximately \$0.24/GGE (\$0.002/MJ). Lastly, capital costs have varying impact, but a  
 278 combined increase of 40% brings the MFSP to nearly \$5/GGE (\$0.041/MJ). The gasification and  
 279 syngas compression section each have the largest single processing area effects.

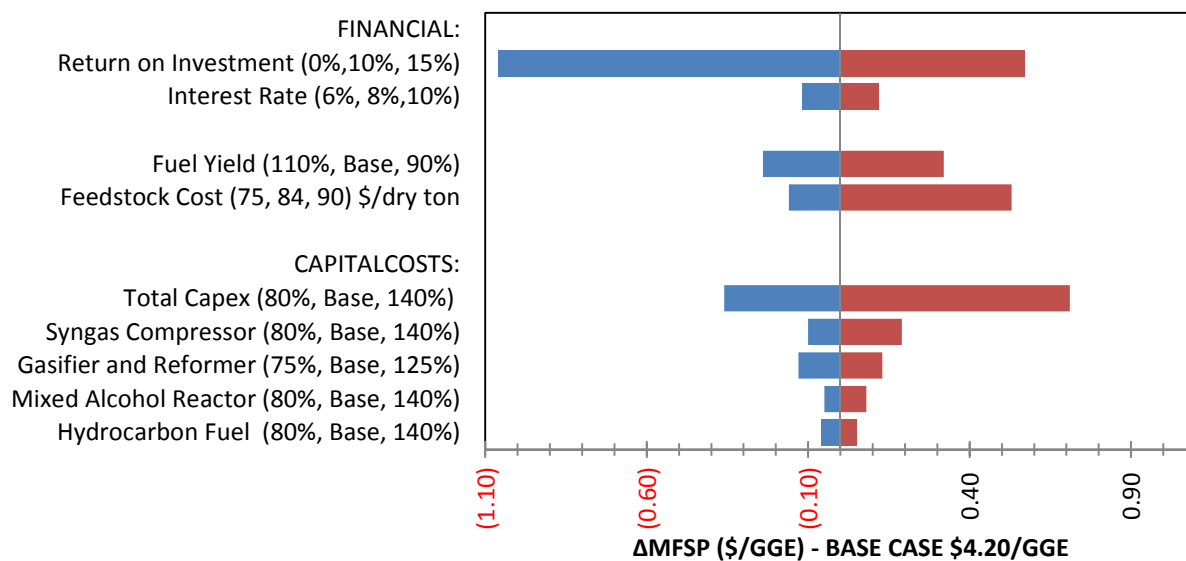


Figure 4: Cost Sensitivity Analysis in the Isobutanol Target Case

## 283 **Life-cycle analysis results**

### 284 ***GHG emissions***

285 LCA considered the target case for both bio-blendstocks. Life-cycle GHG emissions of target  
286 case isobutanol and ARHC were each approximately 26 g CO<sub>2</sub>e/MJ (3,185 g CO<sub>2</sub>e/GGE),  
287 compared to approximately 95 g CO<sub>2</sub>e/MJ (11,636 g CO<sub>2</sub>e/GGE) for petroleum gasoline, as  
288 shown in Figure 5. This translates to a GHG emission reduction of about 73% for both bio-  
289 blendstocks.

290 Sensitivity case isobutanol life-cycle GHG emissions results ranged from 25 to 28 g CO<sub>2</sub>e/MJ.

291 The case with reduced enzyme loading exhibited the lowest emissions whereas the low  
292 isobutanol from xylose case exhibited the highest life-cycle GHG emissions. When the  
293 isobutanol yield from xylose and glucose yield from enzymatic hydrolysis are increased, fuel  
294 yield increases mildly, cutting chemical consumption intensity and GHG emissions compared to  
295 the base target case (See Table S11 in Supporting Information). Among the base target and  
296 sensitivity cases, the conversion step contributes the most to GHG emissions (48% in the target  
297 case, 46%-52% in sensitivity cases varying enzyme loading). Most conversion process emissions  
298 are from consumption of chemicals in dilute acid pretreatment and nutrients for enzyme  
299 production. Lower process chemical requirements, higher isobutanol yield, and more co-  
300 produced electricity contribute to lower conversion GHG emissions in the target case conversion  
301 step, compared to Tao et al.<sup>5</sup> Energy-intensive feedstock preprocessing (pelletizing, fractional  
302 milling, grinding, and comminution) at the depot is another major contributor to isobutanol GHG  
303 emissions, accounting for 23% of GHG emissions in the target case, and ranging from 22% to  
304 25% in cases varying enzyme loading. Biomass and feedstock transportation (including biomass  
305 transportation from the field to the depot and subsequent feedstock transportation from the depot

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3 306 to the biorefinery) accounts for about 11–13% of the life-cycle GHG emissions among all the  
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5 307 cases, followed by fertilizer use during feedstock growth (3%, see Supporting Information for  
6  
7 308 details), biomass harvest and collection (6%), fuel transportation (3%) and fuel consumption  
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9  
10 309 (2%). CO<sub>2</sub> emissions from isobutanol combustion in vehicles are entirely compensated by  
11  
12 310 carbon uptake during biomass growth therefore neither of these are explicitly shown in Figure  
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14 311 5(a). In contrast, there is no such biogenic carbon offset for CO<sub>2</sub> emissions from petroleum  
15  
16 312 gasoline combustion, the dominant source of life-cycle GHG emissions for this fuel. Although  
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18  
19 313 CO<sub>2</sub> uptake during feedstock growth is treated as offsetting CO<sub>2</sub> emissions from biofuel  
20  
21 314 combustion, this combustion emits small amounts of CH<sub>4</sub> and N<sub>2</sub>O. As a result, blendstock  
22  
23 315 combustion emissions are non-zero. Compared to the Tao et al. study,<sup>5</sup> differences in the  
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26 316 maturity and performance (e.g., yield) of isobutanol production, feedstock identity and logistics,  
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28 317 and life-cycle data sources resulted in varied life-cycle GHG emission results.  
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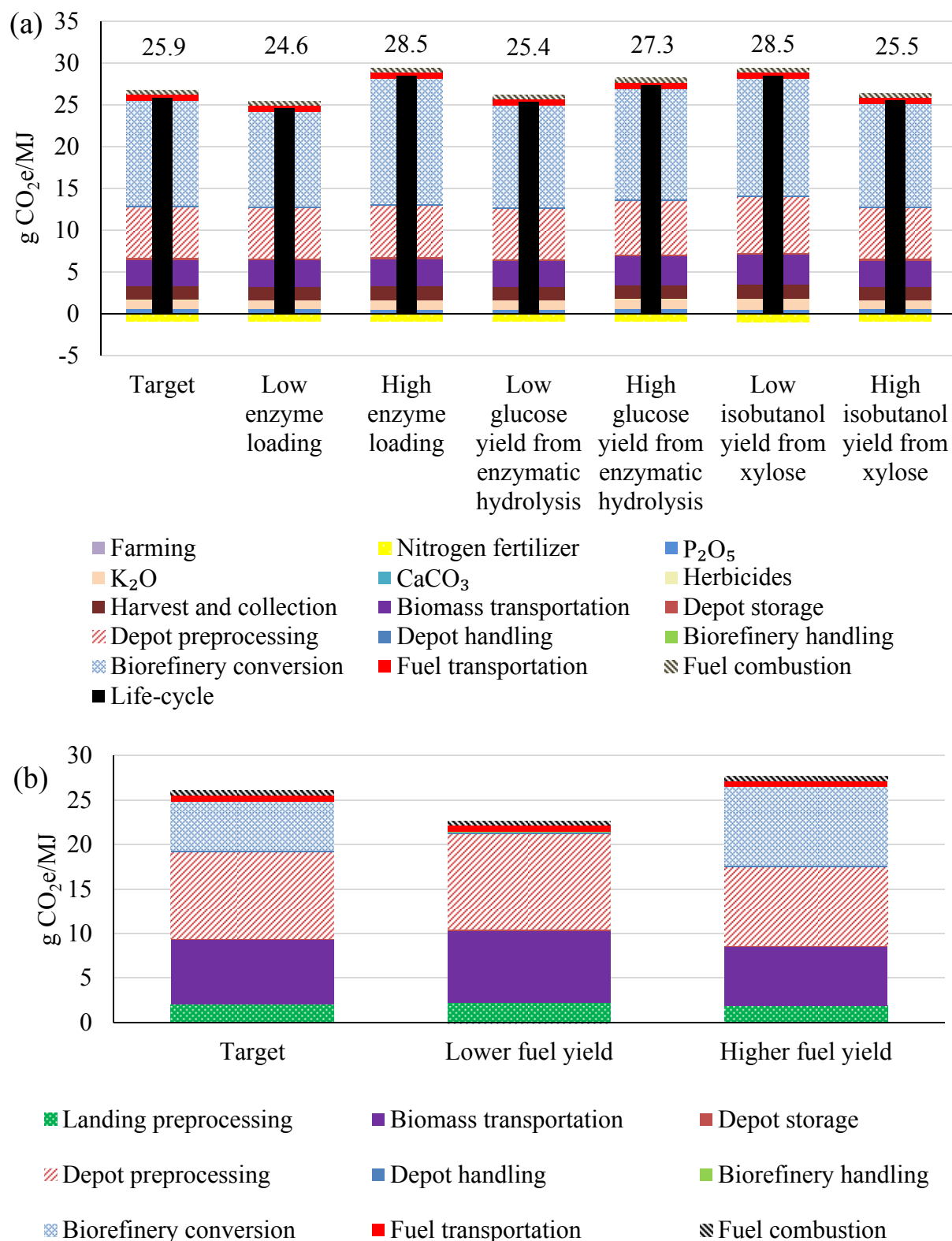


Figure 5: Life-Cycle GHG Emissions (g CO<sub>2</sub>e/MJ) of (a) Isobutanol and (b) ARHC in the Target and Sensitivity Cases. Petroleum Gasoline has Life-Cycle GHG Emissions of 95 g CO<sub>2</sub>e/MJ.

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3 324 For ARHC, as shown in Figure 5(b), energy-intensive preprocessing of woody biomass at the  
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5 325 depot is the primary contributor to the life-cycle GHG emissions in the target case, accounting  
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7 326 for 37% of the emissions. Transportation by truck for over 70 miles (see Table S4) to the  
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10 327 biorefinery with a 2,000 dry metric ton per day capacity design contributes 28%. Biorefinery  
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12 328 conversion that consumes grid electricity and catalysts is responsible for 21%. Biomass  
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14 329 preprocessing at the landing for size reduction and sorting at the fieldside where the woody  
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16 330 biomass is harvested<sup>7</sup> accounts for another 8% of the emissions. When fuel yield increases 10%,  
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19 331 GHG emissions intensity of ARHC slightly increases compared to the target case (28 vs. 26 g  
20  
21 332 CO<sub>2</sub>e/MJ) and when it decreases by 10%, the GHG emissions intensity of ARHC decreases  
22  
23 333 compared to the target case (22 vs. 26 g CO<sub>2</sub>e/MJ). These results are in contrast to the TEA  
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26 334 results, which exhibited a cost decrease when fuel yield increased. In the LCA, the emissions  
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28 335 stemming from increased consumption of natural gas and electricity to achieve the increased  
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30 336 yield outweighed the emission benefit of the increased yield, whereas in the TEA case, the  
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33 337 increased yield offset the increased costs associated with achieving it. Process energy  
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35 338 requirement differs significantly between the lower and higher fuel yield cases: the lower fuel  
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37 339 yield case requires no grid electricity and little natural gas for fired heaters during the  
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40 340 thermochemical conversion, which lead to few GHG emissions in this step, whereas the higher  
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42 341 fuel yield case requires a significant amount of natural gas and grid electricity to sustain the  
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44 342 conversion process, resulting in about 9 g CO<sub>2</sub>e/MJ during this step. Table S8 illustrates that,  
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47 343 although the carbon intensity (on a per GGE basis) of the fuel in the high yield scenario is  
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49 344 greater, the increased biorefinery output of the fuel offers more GHG emission reduction at the  
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51 345 biorefinery level. Overall, biomass preprocessing at the depot and transportation to the  
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54 346 biorefinery present the biggest opportunities to further reduce emissions, for instance through  
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3 347 technology advancements such as wet densification that could reduce energy consumption while  
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5 348 simultaneously ensuring feedstock meets cost, quality, and quantity requirements of a  
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7 349 commercial-scale biorefinery.  
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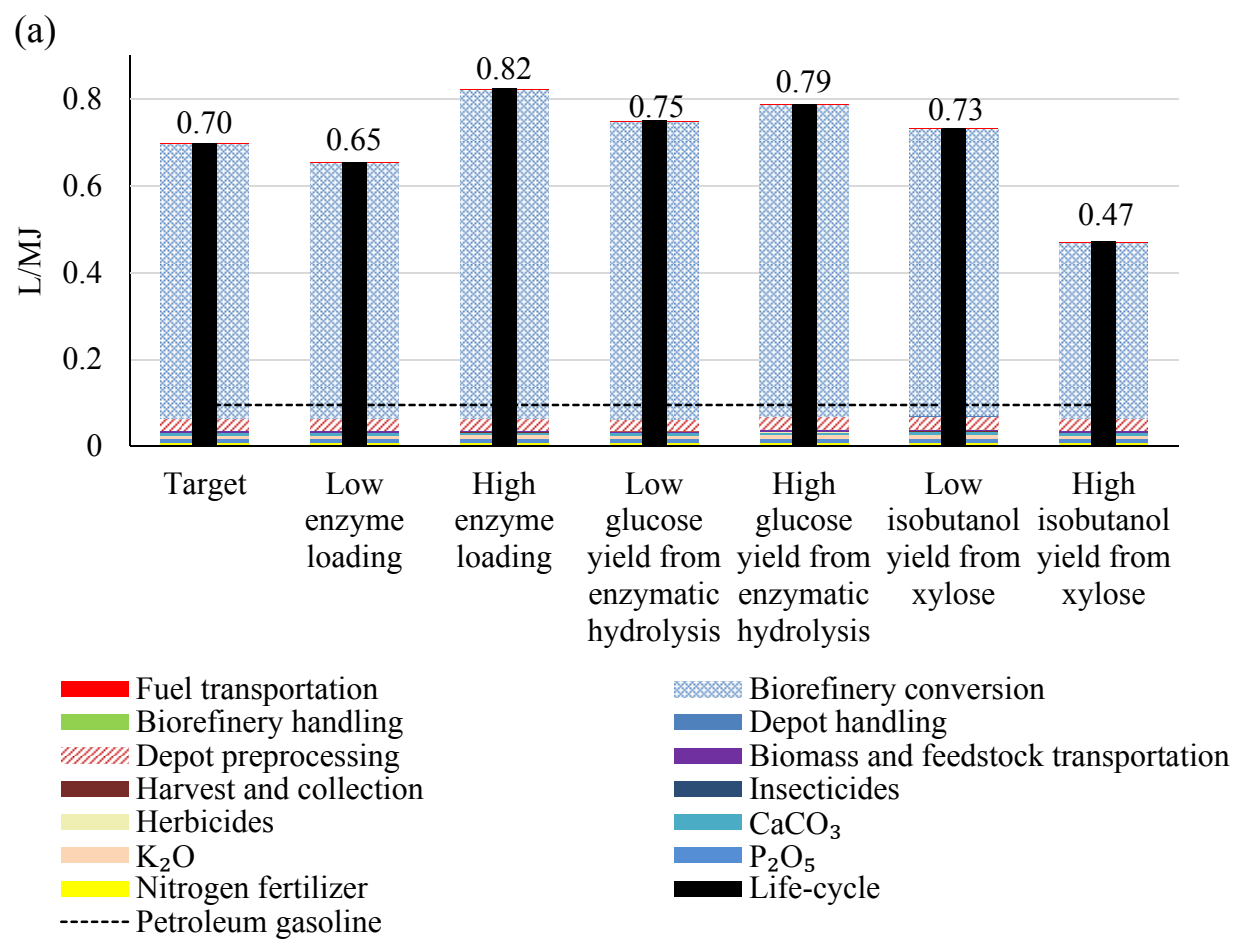
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11 350 For isobutanol in the target case, electricity is about 11% (9-16% in sensitivity cases) by energy  
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13 351 content in the biorefinery product slate. This electricity can be exported to the grid. The life-  
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15 352 cycle GHG emissions of isobutanol are different depending on how this co-produced electricity  
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17 353 is treated. The 26 g CO<sub>2</sub>e/MJ carbon intensity discussed above is the result when an energy-  
18  
19 354 based allocation method is used to allocate the emission burdens associated with supply chain  
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21 355 operations between isobutanol and electricity. This method is chosen because both products are  
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23 356 energy products, despite their differences in value and application. Alternatively, the analysis  
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25 357 could employ the displacement method which gives a displacement credit to isobutanol for  
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27 358 displacing conventional electricity generation through exporting co-produced electricity to the  
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29 359 grid. Using this method, isobutanol in the target case has life-cycle GHG emissions of about 13  
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31 360 g CO<sub>2</sub>e/MJ, 87% less than petroleum gasoline. Depending on the sensitivity case, isobutanol life-  
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33 361 cycle GHG emissions when the displacement method is employed range from 8-17 g CO<sub>2</sub>e/MJ.  
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35 362 The share of electricity between the two products based on energy content ranges from 8-14%.  
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### 42 363 ***Water consumption***

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44 364 Isobutanol and ARHC have a life-cycle water consumption of 0.7 and 0.3 L/MJ, respectively,  
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46 365 both of which are significantly higher than that of petroleum gasoline (0.1 L/MJ) (Figure 6). On  
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48 366 the other hand, life-cycle water consumption of corn ethanol and corn stover ethanol are about  
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50 367 1.7 and 0.8 L/MJ, respectively.<sup>42</sup> Higher water consumption of ethanol is largely attributable to  
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52 368 high irrigation water use for corn farming and to embedded high water consumption intensities  
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54 369 of chemicals used for stover pretreatment.<sup>42</sup>  
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3 370 The most significant contributor (59% total in the target case) to isobutanol's life-cycle water  
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5 371 consumption is consumption of process chemicals (sodium hydroxide, sulfuric acid, and  
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7 372 ammonia), the production of which consumes water. Water consumption associated with  
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10 373 providing make-up water during feedstock conversion (32% contribution to life-cycle water  
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12 374 consumption) alone is about double the life-cycle water consumption of petroleum gasoline.  
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14 375 Water consumption associated with the production of diesel, natural gas, and electricity  
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16 376 consumed in the feedstock supply chain accounts for the remaining 9% of the life-cycle water  
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19 377 consumption. This metric ranges from 0.47 to 0.82 L/MJ among the sensitivity cases, mostly  
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21 378 driven by variation in water consumption during the conversion step.  
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25 379 For ARHC in the target case, 79% of the life-cycle water consumption stems from use of process  
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27 380 make-up water during feedstock conversion. 17% is embedded water consumption associated  
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29 381 with energy production for use at the depot. When the yield increases, both the total water  
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31 382 consumption of the conversion step and the water consumption per MJ of fuel output at this step  
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33 383 decline and, overall, life-cycle water consumption is 24% less than in the target case. In the  
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35 384 lower fuel yield sensitivity case, less water is consumed indirectly via electricity consumption,  
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38 385 but process materials and make-up water use rises on a unit fuel produced basis. Overall, life-  
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41 386 cycle water consumption in this case is about on par with the target case.  
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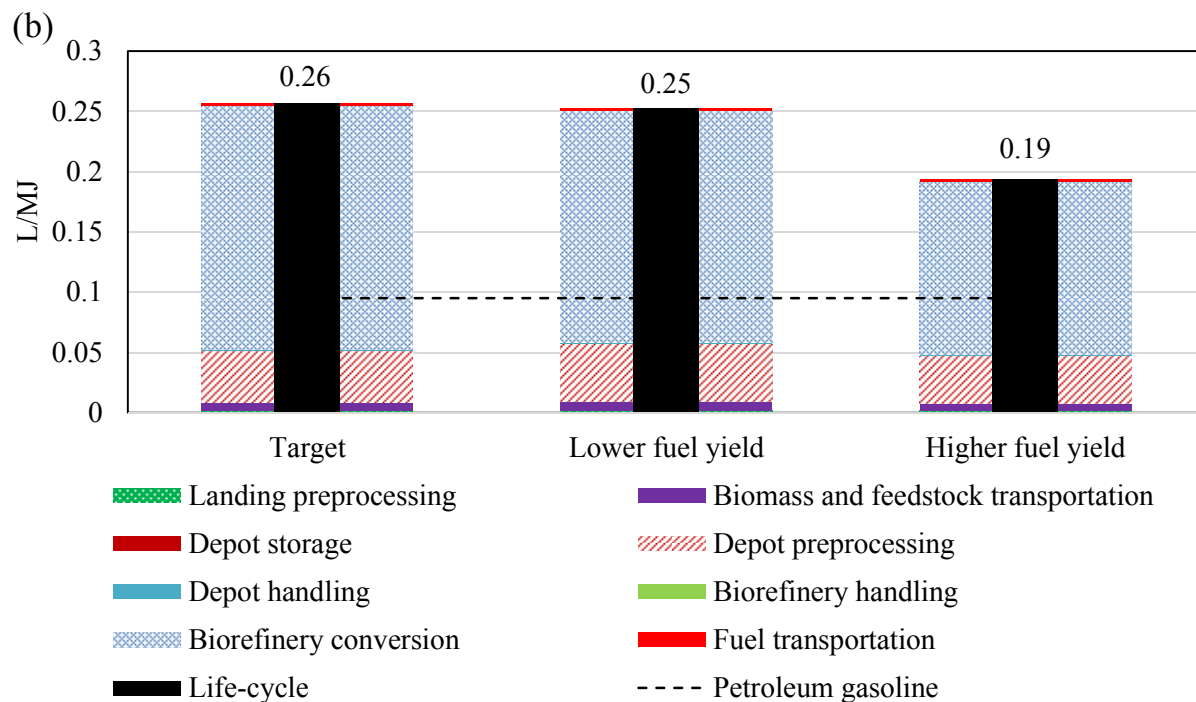


Figure 6: Life-Cycle Water Consumption, in L/MJ, of (a) Isobutanol and (b) ARHC, in Comparison to Petroleum Gasoline (Dashed Black Line)

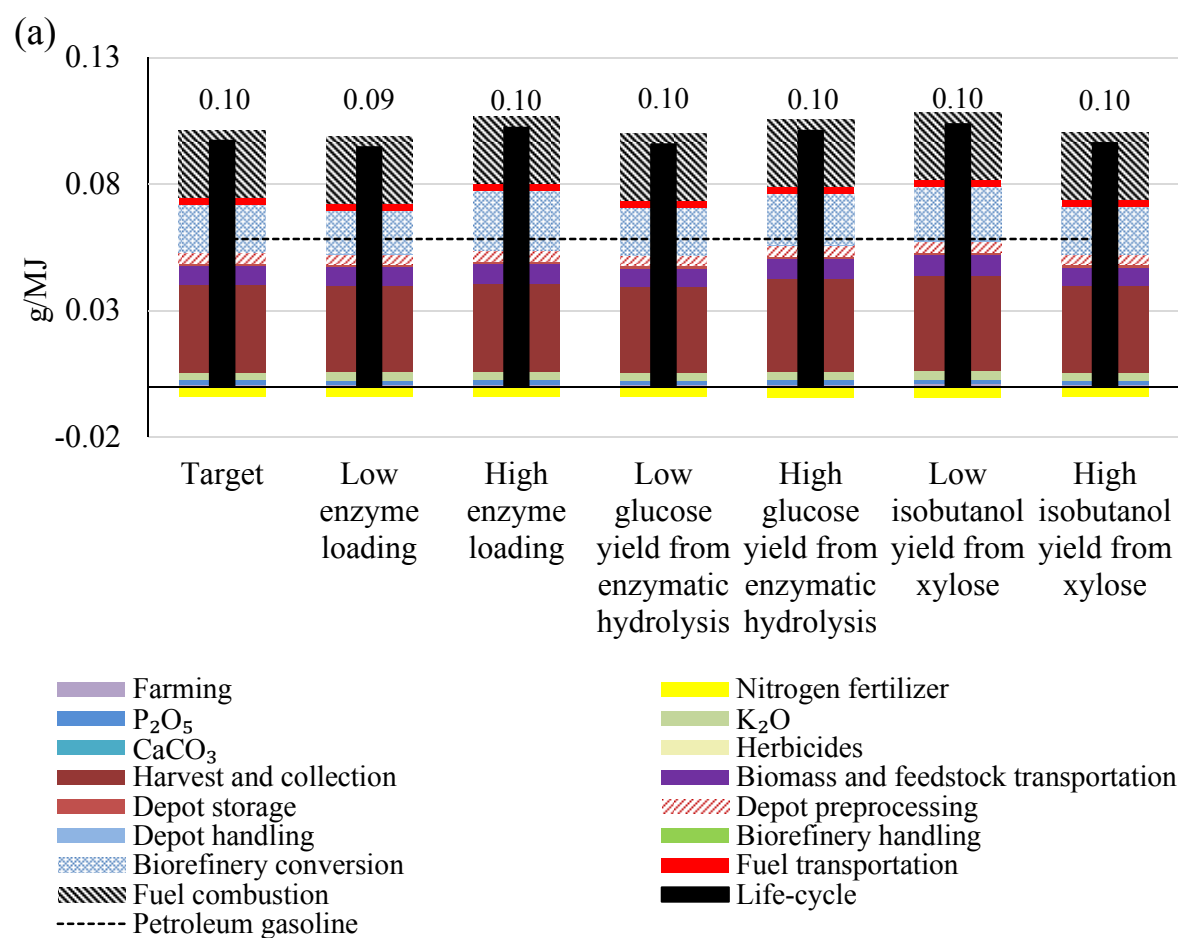
### *NO<sub>x</sub> emissions*

Isobutanol and ARHC bio-blendstocks have life-cycle NO<sub>x</sub> emissions of 0.1 and 0.07 g/MJ, respectively, in the target cases. These levels are about 66% and 25%, respectively, higher than that of petroleum gasoline. As shown in Figure 7, various unit processes contribute to the NO<sub>x</sub> emissions differently between isobutanol and ARHC.

For isobutanol, harvest and collection of herbaceous biomass by diesel-powered equipment accounts for about 35% of the total emissions, followed by tailpipe emissions from fuel combustion (27%), biorefinery conversion (20%) owing to the embedded emissions associated with the production and transportation of process chemicals, biomass and feedstock transportation by diesel-powered truck (8%), and emissions associated with electricity generation for depot preprocessing steps (4%). Life-cycle NO<sub>x</sub> emissions in the sensitivity cases vary

406 slightly because of relatively small variations in the emissions during the conversion step. As a  
 407 result, all these cases have higher life-cycle  $\text{NO}_x$  emissions than those of petroleum gasoline.

408 For ARHC in the target case, emissions from the ARHC fuel combustion accounts for 36% of  
 409 the total, followed by emissions from fuel consumed during biomass and feedstock  
 410 transportation (23%), preprocessing at landing (19%) and the depot (9%), and biorefinery  
 411 conversion (6%). The higher and lower fuel yield sensitivity cases show a similar level of life-  
 412 cycle  $\text{NO}_x$  emissions as a result of tradeoffs between emissions from feedstock conversion and  
 413 biomass logistics that are impacted by the fuel yields.



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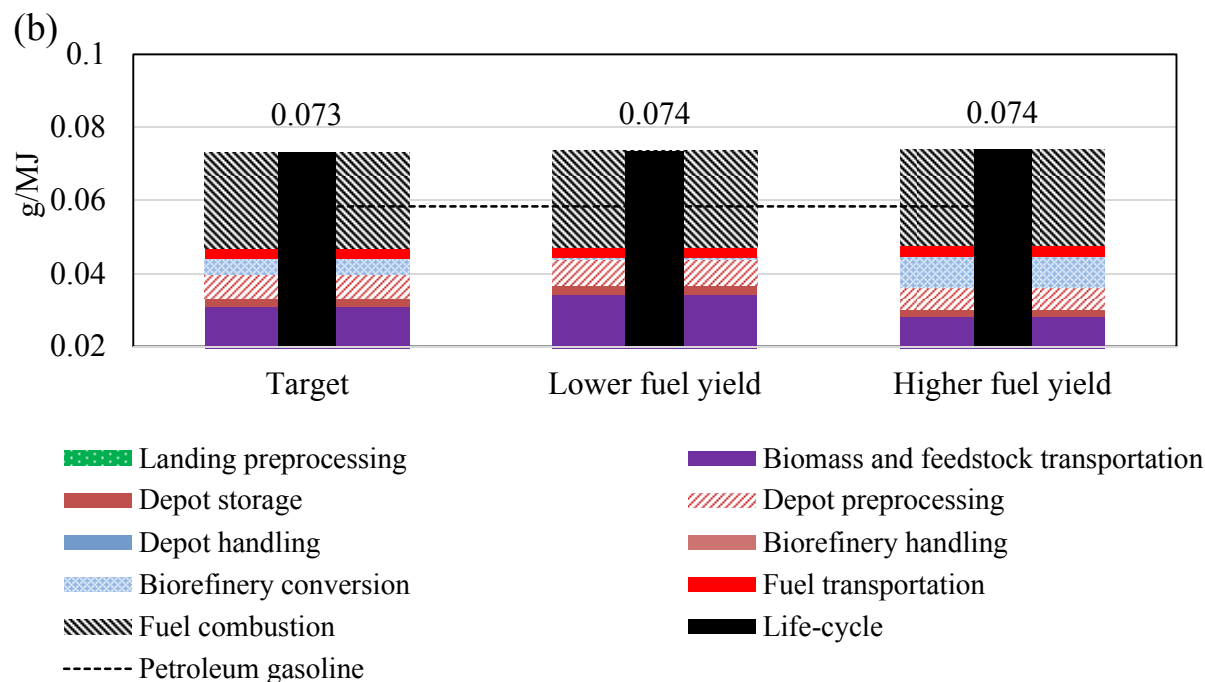


Figure 7: Life-Cycle NO<sub>x</sub> Emissions of Biomass-Derived (a) Isobutanol and (b) ARHC, in Comparison to Those of Petroleum Gasoline (Dashed Black Line)

It is worth noting that, given the lack of data about combustion emissions from isobutanol and ARHC in spark-ignition engines, we have assumed that these two bio-blendstocks have the same tailpipe NO<sub>x</sub> emission factors as that of petroleum gasoline. Previous studies suggested that oxygenated butanol fuels produced lower NO<sub>x</sub> emissions for all fuel-air mixture configurations of the engine compared to their non-oxygenated hydrocarbon analog, butane, which falls in the range of petroleum gasoline.<sup>43</sup> Therefore, it is possible that our current assumption overestimates the tailpipe NO<sub>x</sub> emissions for isobutanol. Recently, a study<sup>44</sup> focused on air permitting issues associated with biorefineries that convert sugars to hydrocarbons estimated NO<sub>x</sub> emissions from such a biorefinery at 0.024 g/MJ. Herein, we produce a comparable estimate of 0.020 g/MJ. Although the conversion route is not identical, there are many similar unit operations including acid pretreatment and lignin combustion in a boiler, which lends confidence to this approximation. Overall, biorefinery air pollutant emissions and NO<sub>x</sub> emissions from combustion

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3 432 of isobutanol-gasoline and ARHC-gasoline blends merit further investigation. New data should  
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5 433 be incorporated into LCAs for enhanced insights into NO<sub>x</sub> emissions drivers.  
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#### 8 9 434 ***PM<sub>2.5</sub> emissions***

10 435 Another air pollutant of concern to air quality and public health is PM<sub>2.5</sub>. Isobutanol and ARHC  
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12 436 bio-blendstocks have life-cycle PM<sub>2.5</sub> emissions of 0.006 and 0.005 g/MJ, respectively, which  
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14 437 are about 42% and 13%, respectively, higher than that of petroleum gasoline. Various unit  
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16 438 processes contribute to the PM<sub>2.5</sub> emissions differently between isobutanol and ARHC. Again,  
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18 439 further research is needed to better characterize PM<sub>2.5</sub> emissions from biorefineries and from  
19  
20 440 isobutanol- and ARHC-gasoline blends. See Supporting Information for details on the major  
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22 441 drivers of PM<sub>2.5</sub> emissions for isobutanol and ARHC.  
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#### 28 442 ***TEA and LCA results synthesis***

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31 443 Whereas TEA results are driven both by costs associated with physical systems (e.g., capital  
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33 444 equipment and process inputs) and financial instruments (e.g., return on investment), LCA  
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35 445 results depend solely on physical systems and therefore routes to energy and environmental  
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37 446 impact reduction are possible to achieve through changing that system. MFSP's dependence on  
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39 447 return on investment implies that this key factor for bio-blendstock commercialization can't be  
40  
41 448 fully improved through engineering and science advancements. The ARHC TEA and LCA  
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43 449 illustrate the trade-offs and synergies between the two types of analysis. The target base case and  
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45 450 high yield sensitivity do not internally generate sufficient power to meet plant demands, and thus  
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47 451 require some purchased power. The CO<sub>2e</sub>/MJ for both cases are similar because of the trade-off  
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49 452 between fossil-based power input (numerator) and yield (denominator). However, the increased  
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51 453 yield more than offsets the cost to purchase additional power. The low yield sensitivity allows  
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3 454 more offgas to go to power generation resulting in excess production over plant needs that can  
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5 455 then be sold to the grid. The CO<sub>2</sub>e/MJ drops, but the MFSP rises because the value of the  
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7 456 electricity sales is insufficient to offset the yield loss. The implication is that it may be possible  
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9 457 to optimize the balance of fossil inputs and yields to meet both TEA and LCA targets.  
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## 13 458 **Conclusions and future work**

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15 459 Detailed TEA and LCA were conducted to evaluate the economic viability and environmental  
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17 460 impacts, and opportunities for improvement in these areas, of biomass-derived isobutanol and  
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19 461 ARHC as octane-enhancing bio-blendstocks that can be blended with petroleum gasoline to  
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21 462 increase engine efficiency in co-optimized light-duty SI engines. Both SOT and target cases were  
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23 463 analyzed in the TEA, only the target case was considered in LCA.  
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28 464 Further reduction of MFSP for the isobutanol fermentation beyond \$5.57/GGE (\$0.045/MJ) is  
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30 465 possible. Within the fermentation, if the yield of isobutanol from sugar can be increased with  
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32 466 modifications to the microbial pathway, then the MFSP will decrease. Additionally, increasing  
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34 467 isobutanol productivity will reduce the amount of capital required for the fermentation reactors.  
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36 468 Finally, reducing the enzyme loading while maintain high conversion of sugar oligomers to  
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38 469 monomers will reduce operating costs. These changes can reduce the MFSP to \$4.22/GGE  
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40 470 (\$0.034/MJ), but further reduction in the MFSP may require co-products or additional utilization  
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42 471 of the lignin feedstock beyond combustion, which could alter LCA results considerably.<sup>23</sup>  
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46

47 472 There are opportunities to reduce the MFSP of ARHC below the \$5.20/GGE (\$0.042/MJ) cost  
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49 473 estimated here. For example, ethanol sources less expensive than syngas catalysis to mixed  
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51 474 alcohols would trim the 90% of the capital devoted to ethanol production. Refining some or all  
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53 475 of the aromatics for chemical sales could offset the blendstock production costs somewhat, but  
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3 476 will not likely be sufficient to substantially reduce the fuel blendstock cost to below the target  
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5 477 case estimate under the current assumptions. In any case, new or improved catalysts are needed  
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8 478 that convert more of the carbon to fuel-range molecules, in particular limiting light paraffin  
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10 479 production. Catalysts development is also required to reduce the benzene content without adding  
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12 480 an additional step. All of these process changes could have implications for life-cycle energy  
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15 481 and environmental metrics.

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18 482 Both isobutanol and ARHC offer about 73% GHG emission reduction relative to petroleum  
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20 483 gasoline. Conversion process emissions of both isobutanol (12.5 g CO<sub>2e</sub>/MJ) and ARHC (5.4 g  
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22 484 CO<sub>2e</sub>/MJ) were somewhat similar to refinery emissions in the gasoline supply chain (7.8 g  
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24 485 CO<sub>2e</sub>/MJ).<sup>45</sup> For isobutanol, improving fuel yield without significantly increasing process  
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27 486 chemical and energy consumption presents the biggest opportunity to mitigate the GHG emission  
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29 487 impacts. On the other hand, routes to cutting water consumption in conversion processes through  
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32 488 optimized process designs need to be explored because water consumption of both bio-  
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34 489 blendstocks are significantly higher than their petroleum gasoline counterpart. Improving  
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36 490 conversion yields while possibly reducing process chemical use is key to reducing water  
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39 491 consumption for isobutanol. For ARHC, cooling tower and boiler feedwater makeup could be  
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41 492 reduced through optimized heat integration. Air pollutant emissions were also higher and  
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43 493 improvements upstream of the biorefinery will be important to lowering them. Feedstock  
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45 494 preprocessing is the primary NO<sub>x</sub> emission driver for isobutanol and ARHC, and thus represents  
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48 495 a good opportunity to mitigate the emission impact. Research is needed to quantify tailpipe NO<sub>x</sub>  
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50 496 and PM<sub>2.5</sub> emissions for isobutanol and ARHC as bio-blendstocks with petroleum gasoline to  
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52 497 allow a better understanding of their air pollutant emission impacts. Environmental implications  
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55 498 on a per kilometer vehicle driven basis as a result of potential fuel economy enhancing benefits  
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3 499 of optimized downsized and boosted spark-ignition vehicles running on these high-octane bio-  
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5 500 blendstocks are beyond the scope of this study, and warrant further investigation when engine  
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7 501 dynamometer testing of both fuel consumption and air pollutant emission performances become  
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9 502 available.

### 13 503 **Abbreviations**

16 504 **ARHC**, Aromatic-Rich Hydrocarbons; **BETO**, Bioenergy Technologies Office; **DOE**, U.S.  
18 505 Department of Energy; **EPA**, U.S. Environmental Protection Agency; **GGE**, Gasoline Gallon  
20 506 Equivalent; **GHG**, Greenhouse Gas; **GREET**, Greenhouse Gases, Regulated Emissions, and  
22 507 Energy use in Transportation; **LCA**, Life-Cycle Analysis; **MFSP**, Minimal Fuel Selling Price;  
24 508 **DCFROR**, Discounted Cash Flow Rate of Return; **NPV**, Net Present Value; **IRR**, Internal Rate  
26 509 of Return; **SOT**, State-of Technology; **TCI**, Total Capital Investment; **TEA**, Techno-Economic  
28 510 Analysis; **VTO**, Vehicle Technologies Office.

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5 522 opinions of the authors expressed herein do not necessarily state or reflect those of the United  
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7 523 States Government or any agency thereof. Neither the United States Government nor any agency  
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9 524 thereof, nor any of their employees, makes any warranty, expressed or implied, or assumes any  
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11 525 legal liability or responsibility for the accuracy, completeness, or usefulness of any information,  
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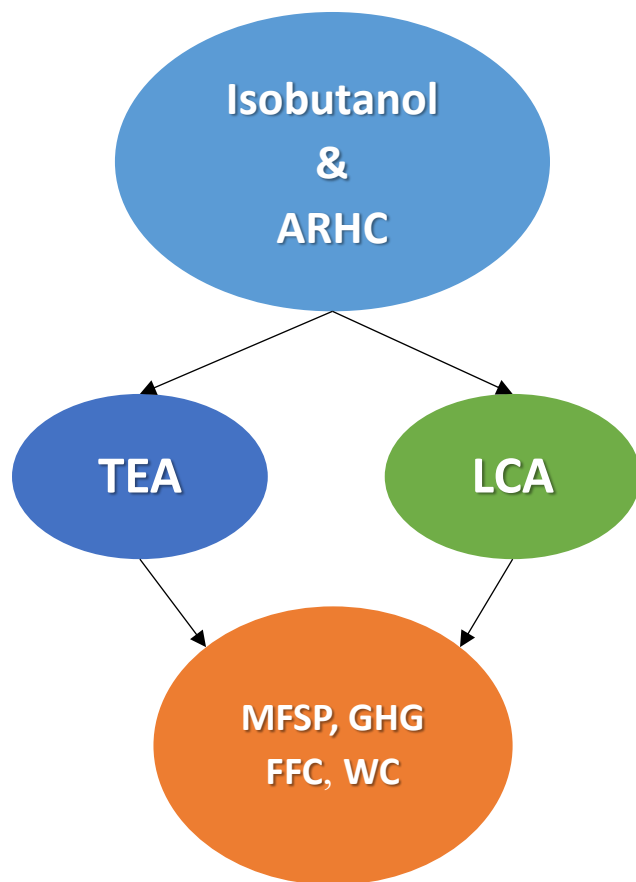
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3 680 **Supporting Information.** The contents of the material supplied as Supporting  
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5 681 Information include: Aromatics and benzene blending limits; Process flow diagram and  
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7 682 process description of isobutanol; Process flow diagram and process description of  
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9 683 aromatic-rich hydrocarbons (ARHC); System boundary of life-cycle analysis; Key data  
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11 684 and assumptions about herbaceous feedstock blend and woody forest residues; Life-cycle  
12  
13 685 analysis: Methodology to calculate NO<sub>x</sub> and PM<sub>2.5</sub> emissions; Life-cycle analysis:  
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15 686 Biorefinery-level results; Key assumptions of sensitivity cases for TEA; Key assumptions  
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17 687 of sensitivity cases for LCA; PM<sub>2.5</sub> emissions.  
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**TOC/Abstract Graphic and Synopsis.** Two potential bioblendstocks are analyzed to determine economic, energy, and environmental impacts such as minimum fuel selling price (MFSP), fossil fuel consumption (FFC), Greenhouse gas (GHG) emissions, water consumption (WC), and air pollutants (NO<sub>x</sub> and PM<sub>2.5</sub>).