ABSTRACT: Tungstate-catalyzed hydrogenolysis of sugars in untreated woody biomass to ethylene glycol (EG) has so far been unsuccessful. This work shows that production of EG is predominantly hampered by the presence of inorganic impurities in the biomass, which can be selectively removed by an acid leaching step at room temperature. Catalytic hydrogenolysis of untreated and acid-leached samples of woody biomass was run at 245 °C using sodium polytungstate and Raney Ni catalysts at low loadings, which make them sensitive to deactivation by biomass impurities. Acid-leached pine and poplar samples gave a combined glycol yield (ethylene glycol + propylene glycol) of ∼44 wt %, similar to microcrystalline cellulose, whereas their untreated counterpart only delivered a yield of 22 wt %. Measurement of the dissolved fraction of the homogeneous tungstate catalyst, i.e., active, after the experiment was found to be a key predictor of the EG yield: inorganic contaminants, such as calcium, are indeed shown to precipitate the tungstate catalyst.

1. INTRODUCTION

Ethylene glycol (EG) is among the bulk chemicals that are of great interest to be produced from sugar with very high atom efficiency. In 2008, Zhang et al.1 discovered a selective route to convert saccharides to ethylene glycol via a bifunctional tungsten−Ni catalyst. Tungstate was found to be active for the cleavage reaction of monosaccharide to glycolaldehyde, which was subsequently hydrogenated over a metal catalyst, e.g., Raney Ni, to ethylene glycol, see Figure 1. Initially, heterogeneous catalysts were developed,2−6 but they appeared to suffer from leaching of W to the reaction medium.3−5,7 On the contrary, a binary catalytic system of Raney Ni or Ru/C and tungstic acid could be recycled at least 20 times without a significant loss of EG yield.8,9 We therefore selected similar catalysts, homogenous sodium polytungstate and heterogenous Raney Ni.

Cellulose is an attractive feedstock for this chemistry as it is the most abundant polysaccharide available. Moreover, this chemistry is typically run in acidified hot-compressed water (~245 °C), which facilitates in situ depolymerization of cellulose. However, native cellulose is entangled by lignin and hemicellulose that could inhibit the catalyst(s). When run in excess of catalysts, still similar yields for untreated biomass and microcrystalline cellulose were obtained, but when operating under catalyst lean conditions, untreated biomass delivered substantially lower EG yield than microcrystalline cellulose.10 This means that one or some components present in biomass deactivate the catalyst(s), and we have already shown in a previous study that lignin is not the key inhibitor.10

Studies on catalyst deactivation for this specific chemistry and conditions are limited, but Pang et al.11 previously showed that divalent ions (Mg, Ca, and Fe) present in biomass, such as calcium, form insoluble tungstate precipitates (e.g., CaWO4), which are not catalytically active. However, they performed hydrogenolysis of microcrystalline cellulose mixed with well-
soluble chloride salts, which undermines the complexity of native biomass. Moreover, they applied a not representative and unrealistically high cation-to-WO$_3$ molar ratio during their experiment (e.g., 1.4 for calcium to WO$_3$). Thus, in their experiments, the presence of divalent ions in biomass does not readily explain low EG yields obtained after hydrogenolysis of untreated biomasses.

In our previous work, we developed a hydrogenolysis protocol that is highly sensitive to catalyst poisons. We demonstrated that lignin was not the main inhibitor responsible for the low EG yield observed with untreated biomass and concluded that it did not significantly affect the hydrogenation of glycolaldehyde to EG. Moreover, the previously discussed study by Pang et al. provides a hint that inorganics present in biomass harm the WO$_3$ catalyst. Therefore, we hypothesized that the WO$_3$ catalyst, which catalyzes the cleavage of glucose to glycolaldehyde, was deactivated by inorganic components present in biomass. We have applied a novel low-severity pretreatment to selectively remove the majority of the inorganics from woody biomass while leaving the cellulose, hemicellulose, and lignin fractions untouched. These samples have been subjected to a poison-sensitive hydrogenolysis protocol to study catalyst deactivation phenomena. Moreover, we have confirmed and quantified these effects by the addition of corresponding model compounds to a cellulose reference experiment. To bolster the yield observations, we have developed an HPLC-based analytical method to measure the quantity of dissolved tungstate, i.e., active tungstate catalyst, in the reactor effluent.

### Table 1. Biomass Composition of Untreated and Acid-Leached (AL) Feedstocks on Dry Basis

<table>
<thead>
<tr>
<th>components</th>
<th>cellulose</th>
<th>poplar</th>
<th>AL poplar$^a$</th>
<th>pine</th>
<th>AL pine$^a$</th>
</tr>
</thead>
<tbody>
<tr>
<td>H$_2$O extractive (wt %)</td>
<td>7.2 ± 0.3$^b$</td>
<td>9.2 ± 0.4$^b$</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>EtOH extractive (wt %)</td>
<td>1.8 ± 0.2$^b$</td>
<td>0.7 ± 0.5$^b$</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>lignin (wt %)</td>
<td>21.4 ± 0.1$^b$</td>
<td>23.1$^c$</td>
<td>24.8 ± 0.2$^b$</td>
<td>27.4$^c$</td>
<td></td>
</tr>
<tr>
<td>α-acetyl groups (wt %)</td>
<td>3.1 ± 0.1$^b$</td>
<td>3.3$^c$</td>
<td>1.4 ± 0.1$^b$</td>
<td>1.6$^c$</td>
<td></td>
</tr>
</tbody>
</table>

$^a$Quantification was performed at least in duplicate. $^b$Data previously published in refs. 10,12. $^c$Recalculated from untreated feedstocks.

2. EXPERIMENTAL METHODS

2.1. Materials. The catalysts, Raney Ni (W.R. Grace and Co. Raney 2800) and sodium polytungstate (≥85% WO$_3$ basis) were purchased from Sigma-Aldrich. Other relevant chemicals, glacial acetic acid (≥99%), ethanol (≥99%), sodium hydroxide (≥99%), and barium carbonate (≥99%), were acquired from Sigma-Aldrich as well.

Poplar wood was kindly provided by a local wooden shoe company, pine wood (Lignocel 9) was bought from Rettenmaier & Söhne GmbH, and hay was purchased from a local garden and animal store. The desired sieved fraction was obtained by grinding with a hammer mill followed by sieving to <53 μm. Microcrystalline cellulose (Avicel PH-101, particle size ≈ 50 μm) was purchased from Sigma-Aldrich. The composition of these feedstocks is reported in Table 1. A large batch of ash was prepared according to the procedure described later in section 2.4.1 and used as an additive in experiments. The AAEM composition of this ash was 2.4 wt % Na, 13.4 wt % K, 0.6 wt % Mg, and 2.9 wt % Ca.

2.2. Acid Leaching. Acid leaching of poplar and pine was executed at room temperature in a stirred vessel for at least 24 h, where the biomass loading was typically ≤1 wt %. The leaching medium was composed of 10 wt % acetic acid in water. The compositions of untreated and acid-leached feedstocks are displayed in Table 1. The ash and AAEM content of the acid-leached (AL) feedstocks were significantly decreased compared to the untreated feedstocks, which is in line with previous studies. Acetic-acid leaching at mild temperatures (≤90 °C) is also known to remove the extractives from biomass but conserves the cellulose, hemicellulose, and lignin fractions. We therefore assumed that the extractives were completely removed after acid leaching and recalculated the remaining biomass composition for the acid-leached (AL) feedstock based on the untreated feedstocks.

2.3. Catalytic Hydrogenolysis. We developed a poison-sensitive hydrogenolysis protocol in a previous work. In a typical experiment, 14.25 g of HAc/Na-acetate buffer, 0.75 g of biomass, 0.04 g of retro-aldo catalyst (sodium polytungstate), and 0.1 g of hydrogenation catalyst (Raney Ni, dry basis) were added to a 45 mL autoclave. Optionally, an additive (e.g., CaCl$_2$) was added. The mixture was thoroughly mixed at the start of the experiment. The pH was set around 3.3 at the start of the experiment, and the hydrogen pressure was set at 60 bar. The autoclave was mounted on the pneumatic arm, which allowed for submersion of the autoclave in a fluidized bed for heating and a water bath for cooling. Typically, the reactor was kept at the reaction temperature, 245 °C, for 1 h while stirring at ~1300 rpm.

The yield was conservatively defined on the presumed holocellulose (cellulose + hemicellulose) content; see eq 1 in which $m_{\text{product}}$ is the mass of the product (e.g., EG), $m_{\text{feed}}$ is the mass of the biomass feed, and $f_{\text{lig}}$, $f_{\text{HAc-extr}}$, $f_{\text{EtOH-extr}}$, and $f_{\text{Ash}}$ are the lignin, water extractives, ethanol extractives, ash, and acetyl weight fractions of the dry feedstock.
2.4. Analytical Methods. 2.4.1. Biomass Characterization. The biomass composition, i.e., sugar, lignin, acetyl, water/EtOH extractives, and total ash, was extensively characterized, following NREL protocols: 1517 (1) a two-step sulfuric-acid-based hydrolysis protocol15 was used to quantify the lignin and acetyl contents and sugar composition, (2) Soxhlet extraction16 was performed for 24 h with water followed by ethanol for 24 h to quantify the extractives content, and (3) dry oxidation was performed at 575 °C for 24 h 17 to obtain the ash content. The ash was subsequently dissolved in 0.01 M nitric acid followed by ion chromatography (IC) for AAEM quantification.

2.4.2. Analytical Techniques. All relevant organic molecules, ethylene glycol (EG), propylene glycol (PG), and sugar alcohols (SA), were identified and quantified by high-pressure liquid chromatography (HPLC). HPLC (Agilent 1200 series) was operated on a HiPlex H+ column at 65 °C, running with 5 mM H2SO4 as eluent (0.6 mL min−1) and equipped with a refractive index detector (RID) and variable wavelength detector (VWD) that were operated at 285 nm. Organic moieties were quantified based on the RID signal and sodium-polytungstate was quantified based on the VWD signal, see the Supporting Information S1 for detailed information. Ion chromatography for the identification and quantification of sodium, potassium, calcium, and magnesium was performed on a Metrohm 850 Professional IC operated on a Metrosep C6-150/4.0 column at 20 °C, with a running 0.1 M HNO3 + 0.02 M dipicolinic acid mobile phase. For both techniques, HPLC and IC, samples were filtered (Whatman 0.2 μm filter) prior to analysis and calibration curves for the relevant components were established.

3. RESULTS & DISCUSSION

3.1. Selective Ash Removal. In this work, we have developed a method to measure the concentration of soluble sodium polytungstate after the experiment and reanalyzed the effluent obtained after hydrogenolysis of (pretreated) biomass and physical mixtures of cellulose and lignin of our previous work with varying lignin contents (0–44 wt %).10 The pretreated samples were prepared by solvent-based (water/ethanol/acetic acid) pretreatments at 180–200 °C for 0.5–5 h. The EG + PG yields appeared to drop with the decreasing concentration of soluble W-species after the experiment, while all experiments started with the same catalyst and biomass loadings, see Figure 2. This means that components present in native biomass poison the tungstate catalyst but can be removed by pretreatment.

To test whether the removal of tungstate poisons from biomass by pretreatment is related to the inorganics content of the feed, poplar and pine wood were acidi-leached with a solvent composed of 10 wt % acetic acid in water for 24 h at room temperature, which selectively removes the majority of the ash and alkali and alkali earth metals (AAEM). Acid-leaching removed some 80 wt % of the total ash and >90 wt % of the AAEM, see Table 1. We then subjected untreated and acid-leached feedstock to hydrogenolysis. The EG + PG yield of 45 wt % observed for acid-leached poplar and acid-leached pine was identical to that of cellulose, our reference case, whereas untreated pine and poplar (n = 2) gave a poor EG + PG yield of only ~22 wt % under our poison-sensitive conditions at a W input of 120 mole/kg biomass see Figure 3. Upon increasing the tungstate loading, however, the combined glycol output of untreated poplar also started to approach that of cellulose.

In fact, the EG + PG yields for (un)treated poplar, pine, and cellulose are superimposed when plotted versus the output W concentration, see the Supporting Information Figure S6, and was in line with the trend seen in Figure 2. Moreover, the EG + PG yields reported in Figures 2 and 3 are superimposed when displayed against the output W concentration, see the Supporting Information Figure S3. Thus, acid leaching clearly removes catalyst inhibitors that precipitate the tungstate catalyst.

Note that we report here EG + PG yield because the saccharide fractions of poplar and poplar are partly composed of pentose (C5), which delivers EG (C2) and PG (C3), while cellulose is entirely composed of hexose (C6), which theoretically could deliver solely EG (C2). Due to the

$$\text{yield (wt wt)} = \frac{m_{\text{Product}}}{m_{\text{Feed}}(1-f_{\text{Lig}}-f_{\text{H2O-ext}}-f_{\text{EtOH-ext}}-f_{\text{Ash}}-f_{\text{Ac}})} \times 100$$

Figure 2. EG + PG yield expressed on holocellulose content for untreated biomass, pretreated biomass, and physical mixtures of cellulose and lignin as a function of the W-catalyst output measured after the experiment per kg of biomass feed. EG + PG yield data from our previous work,18 but the data from the X-axis (W-catalyst output) is new. Reaction conditions: 5 wt % biomass loading, T = 245 °C, t = 1 h, P_{\text{H2}} (initial) = 60 bar, pH_{\text{initial}} ≈ 3.3, Ni-catalyst to biomass mass ratio = 0.12, and W-catalyst to biomass mass ratio = 0.03. Line drawn is for clarity.

Figure 3. EG + PG yield expressed on holocellulose content for cellulose, poplar, pine, acid-leached poplar, and acid-leached pine as a function of the W-catalyst input at the start of the experiment per kg of biomass feed. Reaction conditions: 5 wt % biomass loading, T = 245 °C, t = 1 h, P_{\text{H2}} (initial) = 60 bar, pH_{\text{initial}} ≈ 3.3, Ni-catalyst/biomass mass ratio = 0.13. Experiments were performed in duplicate: poplar and cellulose at ~120 and cellulose at ~225 moleWO$_4$/kgBiomass; error bars were plotted but are typically too small to be observed. Lines were drawn for clarity.
compositional difference, the woody biomasses delivered substantially higher PG yields of 9–12 wt %, compared to ~5 wt % for cellulose, see the Supporting Information Figure S8. On the other hand, cellulose gave some 5–9 wt % more EG than acid-leached poplar and acid-leached pine, see the Supporting Information Figure S7.

3.2. Addition of Ash. To further investigate our hypothesis, we also added poplar ash to a cellulose reference experiment. The ash used as an additive for these experiments was obtained by calcination of poplar at 575 °C for 24 h. Obviously, the ash is oxidized during combustion, and therefore it is not fully representative of the ash present in native biomass. As can be observed in Figure 4, the EG yield plummeted from 45 to 28 wt % after the addition of just 1 wt % ash to cellulose, which is comparable to the ash content of untreated poplar (0.8 ± 0.1 wt %) and pine (0.6 ± 0.1 wt %). In fact, the EG yield obtained for untreated poplar was very similar, namely, 29 wt %. At the same time, the sugar alcohol (SA) yield increased slightly from 9 ± 2 to 14 wt %, see the Supporting Information Figure S12. This shows that the tungstate catalyst is deactivated by ash but that the hydrogenation catalyst is still active. In addition, the W-catalyst concentration in the reactor effluent correlates with the EG yield, see the Supporting Information Figure S14.

When raising the share of ash in the feed mixture to 20 wt %, however, the sugar alcohol yield drops to 3 wt %, showing that large quantities of ash also inhibit the hydrogenation catalyst, see the Supporting Information Figure S12. The increase in ash share in the feed mixture was accompanied by an increase in the pH of the reactor effluent. The pH was similar at 3.3–3.4 for the experiments performed with cellulose, untreated poplar, and cellulose + 1 wt % ash mixture but rose substantially to 3.8 and 4.5 for mixtures with 5 and 20 wt % ash, respectively, see the Supporting Information Figure S13. pH measurement of the liquid effluent after the experiment is thus an easy tool to identify a probable impact of basic ash.

3.3. Addition of Inorganic Model Compounds. It is now evident that inorganic components present in biomass (ash) precipitate the homogenous tungstate catalyst. To gain further understanding, we subjected mixtures of cellulose and different salts to hydrogenolysis. In addition to silica, alkali and alkaline earth metals are the most prominent inorganic constituents. Furthermore, trace amounts of iron, zinc, and manganese are present in biomass. We evaluated their effects by adding the respective chloride salt to the cellulose reference test at a 1:1 molar ratio of the cation to tungsten. We selected chloride salts for their relatively high solubility in water. We are well aware that halogens, such as chloride, are poisonous to metal catalysts, such as Raney Ni, and we therefore performed a reference test with sodium chloride in a 20:1 molar ratio. Sodium was not expected to spoil the hydrogenolysis outcome as sodium tungstates are highly soluble. Indeed, the addition of sodium chloride, even in a 20:1 molar ratio to the WO3 catalyst, did not reduce the ethylene glycol yield, 51 wt % compared to 46 ± 2 wt % (n = 2) for the reference test.

Once again, the EG yield appeared to correlate well with the tungstate concentration measured in the reaction mixture after the experiment, see closed dots in Figure 5. At the same time, the product selectivity changed from EG to SA with the decrease in the W-catalyst output, as such that the sum of hydrogenated products (EG + PG + SA) remained at 50–60 wt %, see the Supporting Information Figure S15. This test suggests that additives, which reduce the tungstate concentration compared to the benchmark, form insoluble precipitates that are not catalytically active while the hydrogenation catalyst remained sufficiently active. Indeed, only 20% of the added calcium remained dissolved (YEG = 6 wt %), whereas all the supplemented sodium (YEG = 51 wt %) and potassium (YEG ≈ 48 wt %) remained dissolved. These observations are in line with past reports on the solubility of various tungstates, i.e., poor solubility of calcium tungstate and high solubility of sodium and potassium tungstates. These results are in agreement with the work by Pang et al., who made the same observations after hydrogenolysis of microcrystalline cellulose and chloride salts. Moreover, Pang et al. showed that CaWO4 is inactive for aldol cleavage.

Magnesium appears to deviate from the cluster seen around 160 mmol/kg biomass as it shows a low EG yield of 35 wt % but a typical EG + PG + SA yield of ~60 wt %. The change in selectivity towards SA suggests that magnesium is depressing the W activity without precipitating it out of the solution, but this assumption requires further studies. A mildly negative
effect of magnesium on the EG yield (46 C %) has been reported before (60 C% for the benchmark).11

We have noted a significantly lower pH (2.7) for the addition of aluminum chloride compared to the benchmark experiments (3.2–3.3). The observed precipitation of tungstate by H+ can, therefore, not be ruled out.

As the vast majority of cations in biomass are not present in the form of chlorides, we evaluated alternative and more representative calcium salts, namely, calcium carbonate, calcium oxalate, calcium phosphate, and calcium silicate. These calcium salts are typically poorly soluble at neutral pH but may show significant solubility at the acidic conditions under hydrogenolysis (pH ≈ 3.3). The EG yield was also low (<8 wt %) under the addition of these alternative calcium species. Again, the output tungstate concentration was low (<2 mmol/kgbiomass), see crosses in Figure 5, and most of the calcium (>70 wt %) was consumed, indicating that tungstate was titrated by calcium. Thus, a wide variety of calcium species deactivate the tungstate catalyst and are thereby detrimental for the EG yield. This suggests that their specific composition, i.e., cation–anion pair, can be ignored and that measurement of the feedstock divalent cation content would suffice to estimate the W-catalyst consumption.

Albeit the poisoning effect of divalent ions, such as calcium, on tungstate species is evident; their presence in biomass does not readily explain the low EG output after hydrogenolysis of untreated biomass compared to cellulose, as the tungstate to calcium + magnesium molar ratio in a typical WOxlean experiment is at least 3.6 for poplar and 1.5 for pine (see the supplementary information S5.1). A potential explanation lies in the possible formation of tungstate salts (XWO4) with non-reactive calcium species. Again, the output tungstate concentration was low (<2 mmol/kgbiomass), see crosses in Figure 5, and most of the calcium (>70 wt %) was consumed, indicating that tungstate was titrated by calcium. Thus, a wide variety of calcium species deactivate the tungstate catalyst and are thereby detrimental for the EG yield. This suggests that their specific composition, i.e., cation–anion pair, can be ignored and that measurement of the feedstock divalent cation content would suffice to estimate the W-catalyst consumption.

We then ran several experiments with varied Ca2+ to WOx molar ratios from 1 to 3 to find the stoichiometry, n, of the resulting Ca(WOx)n. An increase in added calcium resulted in a decrease in the measured W-catalyst after the experiments, showing that calcium indeed precipitates the W-catalyst. Moreover, the EG yield versus the output W concentration roughly superimposed that of experiments with and without calcium, (Supporting Information, Figure S18). The stoichiometry of the formed calcium tungstate Ca(WOx)n appeared to be 1, as the amount of calcium that is consumed (Caacidal − Caacid) was directly proportional with the decrease in the W-catalyst, see Figure 6. This observation is in line with the observation of Pang et al.,11 who observed CaWO4 in the spent catalyst.

3.4. WOx Consumption—beyond Ca. It has become clear that the tungstate catalyst is deactivated by inorganic species present in biomass. With few exceptions, it appears that the combined glycol yield data obtained in our previous work10 and this work correlates well with the concentration of soluble tungstate species in the reactor effluent, see the Supporting Information Figure S4. In particular, divalent cations appear to form insoluble tungstates. For industrial operation, the catalyst consumption should be minimized and preferably stay below 1 kgcatalyst/tonproduct12. Under the assumption that 1 mol of cation titrates: 1 mol of WOx, we previously derived that the divalent cation content of the biomass feedstock can be 4 mmol of divalent ions per kg biomass at max. This assumption was validated in this work as we showed that calcium precipitates with tungstate in an equimolar ratio. Untreated poplar and pine do not meet this criterion as they contain 8.4 and 21.3 mmol Ca + Mg per kg biomass, respectively, but microcrystalline cellulose (Avicel) does with 0 mmol Ca + Mg per kg biomass, see Table 1.

Acid leaching of biomass effectively removes the water-soluble fraction, the majority of the alkali and alkaline earth metals14 and a major part of the overall ash, without deteriorating the cellulose, hemicellulose, and lignin fractions.13 Moreover, acid leaching also extracts heavier metals, such as manganese22 and iron,23 from the biomass. Our acid-leaching approach avoids the use of inorganic acids that can be poisonous to metal catalysts25 and relies on organic acid that can be produced in situ. This mild pretreatment avoids the hydrolysis of hemicellulose, which typically accounts for ~30% of the polysaccharide fraction in biomass and, as a result thereof, allows for achieving much higher glycol yields on overall biomass intake. Most importantly, acid-leached poplar and pine meet the specification of ≤4 mmol of Ca + Mg per kg biomass as they contain 2.1 and 1.1 mmol of calcium + magnesium per kg biomass, respectively, see Table 1. Note that water leaching is rather ineffective for the removal of divalent ions such as calcium as was previously shown.26 This mild pretreatment was more effective in removing calcium and magnesium than the high severity pretreatments PT-A (ethanol−water, 50/50, 200 °C, 3 h) and PT-B (70 wt % acetic acid in water, 180 °C, 1 h) reported in our previous work,12 whose solid residues had a combined calcium and magnesium content of 9 and 3.2 mmol per kg biomass, respectively. On the contrary, acid leaching only removes inorganics and water-soluble extractives, whereas lignin removal might be imperative for long-term operation. In that case, acid leaching could be a part of multistep pretreatment with the objective to remove inorganics from biomass.

In addition to measurement of the calcium and magnesium content of the feedstock, the actual measured W-catalyst consumption could provide a much better picture on whether the targeted maximum of 4 mmol of divalent ions per kg biomass can be achieved. However, we observed that part of the tungstate is also consumed during the cellulose benchmark experiments, see the Supporting Information S5.2. It turned out that this consumption was not related to the cellulose feed but to the presence of the Raney Ni catalyst, see the Supporting Information S1. We have therefore corrected the
W-catalyst consumption of (treated) feedstocks with the consumption found in their corresponding cellulose benchmark experiment, as it is our target to quantify the W-catalyst consumption by the (treated) biomass and not by the metal catalyst (Raney Ni), see Figure 7. Consequently, the W-
catalyst input and the maximum W-catalyst consumption do not follow a parity line. Acid-leached poplar (open circle) and acid-leached pine (open triangle) did not consume more W-catalyst than the cellulose reference experiment, i.e., ~0 mmol/kg_{biomass} whereas untreated poplar and pine titrated all tungstate for a W-catalyst input of 115 mmol/kg_{biomass} see Figure 7, namely 45 mmol/kg_{biomass} for poplar and 37 mmol/kg_{biomass} for pine. The trend was similar when the initial load of the W-catalyst was higher, 225 mmol/kg_{biomass} untreated poplar consumed 66 mmol/kg_{biomass} of tungstate, which was twice as high as its acid-leached counterpart. The catalyst consumption for a cellulose + 1\% ash mixture appeared nearly identical to untreated poplar that contains 0.8 ± 0.1 wt \% ash, see the top right of Figure 7.

Figure 7 reveals that acid leaching can reduce the concentration of tungstate precipitants down to the level seen for microcrystalline cellulose. The observed tungstate consumption was systematically at least 35 mmol per kg of biomass higher for untreated biomasses than for microcrystalline cellulose. However, the Ca + Mg contents of untreated poplar and pine are only 8 ± 2 and 21 ± 3 mmol/kg_{biomass} respectively, see gray areas in Figure 7 and Table 1. Although refinement of the experimental method to reduce error is desirable, the difference in the measured and expected W-catalyst consumption seems too large to be explained solely by the calcium and magnesium content of the feed. Moreover, the addition of poplar ash to cellulose was much more detrimental than what would be expected from its calcium + magnesium content in comparison with the addition of CaCl\textsubscript{2}, see Figure S22 in the Supporting Information. Also, the data on five (treated) substrates in the study by Pang et al., which we carefully analyzed, does not allow to explain poor glycol yields exclusively by divalent cation content of the respective feedstock, see the Supporting Information S2.2. It is therefore reasonable to expect that there are other catalyst inhibitors present in the ash beyond calcium and magnesium. The concentrations of other divalent cations in biomass are typically much lower than that of calcium and magnesium and therefore unlikely to provide an explanation. Silica typically accounts for the majority of inorganics in biomass, but it was previously shown to be inert when added in the form of SiO\textsubscript{2} to a cellulose reference experiment. Further studies are needed to explain the discrepancy.

We have experienced after running tungstate catalyzed hydrogenolysis experiments for several years that this system is heavily intertwined. Our approach, comparing the experimental outcome with a benchmark offsets, or at least dampens, errors that arise from the experimental procedure. For example, tungstate consumption by metals leached from the hydrogenation catalyst or experimental setup could be incorrectly attributed to the biomass feedstock, when not compared to a benchmark experiment. Leaching of metal, e.g., Ni, from the catalyst has been reported before and poses, besides contaminants that are present in biomass, an additional deactivation risk for the tungstate catalyst. Furthermore, precipitation of tungstate with species present in biomass, e.g., calcium, on the surface of the hydrogenation catalyst poses another potential deactivation risk.

4. CONCLUSIONS

In this work we have shown that inorganics present in biomass, in particular, divalent cations such as Ca\textsuperscript{2+}, are the primary inhibitor in the WO\textsubscript{4}– catalyzed hydrogenolysis of lignocellulosic biomass to ethylene glycol. The EG yield correlated well with the concentration of the soluble tungstate, i.e., active W-catalyst, in the reactor effluent. Divalent cations such as Ca\textsuperscript{2+}, form insoluble precipitates with the homogenous tungstate catalyst. These inorganic components can be selectively removed by acid leaching, which is a very mild pretreatment performed at room temperature with a solvent composed of 10 wt % acetic acid in water. Such simple treatment boosts the EG + PG yield of poplar and pine from ~22 to 44 wt %, equal to the yield obtained with pure cellulose when operating under sensitive, WO\textsubscript{4}–-lean conditions (Figure 8). This poisoning effect is masked by an operation with excessive WO\textsubscript{4}– loading, which also shows a high glycol yield, 48 wt %.

![Figure 8.

The claim that the inorganic fraction is the key inhibitor was further supported by the addition of ash to the cellulose reference experiment and seeing that the EG yield dropped under 10 wt % for the addition of 5 wt % ash. Moreover, the hydrogenation catalyst appeared to suffer as well since no sugar alcohol was produced for a mixture of cellulose and 20 wt % ash. By mixing cellulose with an additive, we have shown that divalent ions deactivate the tungstate catalyst, by the formation of insoluble tungstate precipitates. The insoluble salt, at least for calcium, is composed of an equimolar amount of calcium and tungstate.

https://doi.org/10.1021/acs.iecr.1c02353
The calcium and magnesium content of the untreated feedstocks, however, could not explain the measured tungstate consumption, which requires further studies. Nevertheless, we experimentally showed that acid leaching effectively removed (nearly) all tungstate poisons from the biomass. Importantly, the content of divalent cations was reduced below 4 mmol per kg of biomass, which is critical in the context of industrial operation.

### ASSOCIATED CONTENT

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acs.iecr.1c02353.

Detailed information on the analysis method for tungstate quantification, literature study, and supporting graphs on the results, specifically on the selective ash removal and reintroduction and on model ash compounds (PDF)

### AUTHOR INFORMATION

**Corresponding Author**

M. Pilar Ruiz — Sustainable Process Technology, Faculty of Science and Technology, University of Twente, Enschede 7522 NB, The Netherlands; orcid.org/0000-0003-1437-5578; Email: m.p.ruizramiro@utwente.nl

**Authors**

Thimo D.J. te Molder — Sustainable Process Technology, Faculty of Science and Technology, University of Twente, Enschede 7522 NB, The Netherlands

Sascha R.A. Kersten — Sustainable Process Technology, Faculty of Science and Technology, University of Twente, Enschede 7522 NB, The Netherlands; orcid.org/0000-0001-8333-2649

Jean-Paul Lange — Sustainable Process Technology, Faculty of Science and Technology, University of Twente, Enschede 7522 NB, The Netherlands; Shell Global Solutions International B.V.; Shell Technology Centre Amsterdam, Amsterdam, HW 1031, The Netherlands; orcid.org/0000-0001-6567-2957

Complete contact information is available at: https://pubs.acs.org/doi/10.1021/acs.iecr.1c02353

**Notes**

The authors declare no competing financial interest.

### ACKNOWLEDGMENTS

The authors thank Shell Global Solutions International B.V. for funding this research, S.S. Sunilkumar for performing part of the experiments, and Benno Knaken, Johan Agterhorst Ronald Borst, and Erna Fränzel-Luiten for the technical support.

### REFERENCES


