

High yield production of levulinic acid by catalytic partial oxidation of cellulose in aqueous media†

Hongfei Lin,^{*a} Jason Strull,^a Ying Liu,^a Zachary Karmiol,^a Kelsey Plank,^a Glenn Miller,^b Zhanhu Guo^c and Lisha Yang^a

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A high yield of levulinic acid was produced by directly converting cellulose over a ZrO₂ catalyst by a one-pot catalytic aqueous phase partial oxidation (APPO) process. Compared to conventional acid hydrolysis, APPO is a highly selective and environmentally benign process with merits of easy recovery and re-use of heterogeneous catalysts.

Conversion of cellulosic biomass is of vital importance in the biofuel/biochemical industry.¹ Recently, several groups have reported that combining hydrolysis and hydrogenolysis of cellulose over noble metal² or metal carbide³ catalysts produced sugar alcohols or polyols such as sorbitol, mannitol, or ethylene glycol, which are precursors in the production of fuels, polymers, and pharmaceuticals. However, these processes suffer from the high costs associated with mineral acids, cellulase enzymes, noble metals, external hydrogen, *etc.*

Moreover, sugars or sugar alcohols contain excess oxygen and thus are not good platform building block chemicals for fuel production.

In contrast, levulinic acid (LA) derived from cellulose is considered a suitable building block for synthesizing hydrocarbon liquid fuels⁴ or valeric esters⁵ as fuel additives, as well as a variety of chemicals.⁶ The conventional LA production is *via* an acid catalysed process using mineral acids as homogeneous catalysts.⁷ Such processes raised concerns related to the environment and high separation cost.⁸ As an alternative to the liquid acid catalyst, solid acid catalysts^{4b,9} have been pursued. Though solid acids have shown reasonably high activities for glucose¹⁰ and fructose,¹¹ they fail for water insoluble cellulose toward LA production.^{9d} The low yields of LA by reacting cellulose over solid acid catalysts are attributed to the poor solid–solid mass transfer between biomass and the solid catalysts. Therefore, it is still demanding to produce LA from cellulosic biomass cost-effectively over acid catalysts.

Our group has recently developed a non-traditional pathway for the deconstruction of lignocellulosic biomass: aqueous phase partial oxidation (APPO), a patent-pending technology¹² for converting lignocellulosic biomass into a platform organic acid product, which can be further upgraded to liquid transportation fuels, using environmentally benign water and air as the reaction media over inexpensive metal oxide catalysts (Scheme S1†). Herein we report that a high yield of LA, 50.0 ± 2.0% (molar carbon yield), has been produced directly from cellulose through the APPO process using zirconium oxide (ZrO₂) as the catalyst. This yield is approximately 60% of the theoretical value and is comparable to those obtained in

^aDepartment of Chemical and Materials Engineering, University of Nevada, 1664 N. Virginia St., Reno, NV 89557, USA. E-mail: hongfeil@unr.edu; Fax: +1 7753275059; Tel: +1 7757844697

^bDepartment of Natural Resources and Environmental Science, University of Nevada, 1664 N. Virginia St., Reno, NV 89557, USA

^cDepartment of Chemical Engineering, Lamar University, 4400 South MLK Junior Parkway Beaumont, Texas 77705, USA

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Broader context

Levulinic acid is a versatile biomass-derived renewable platform building block for the production of liquid transportation fuels and a variety of chemicals. Acid hydrolysis has been used for decades to produce levulinic acid from cellulose with mineral acid catalysts. However, this traditional process suffers from high cost of separation of mineral acids, high corrosivity, and low carbon efficiency due to the formation of humins. For the first time, we present an alternative pathway, aqueous phase partial oxidation (APPO), to produce levulinic acid directly from cellulose with lean air and water over inexpensive solid metal oxide catalysts. The maximum obtainable yield of levulinic acid in the APPO process is ~60% of the theoretical, comparable to yields of levulinic acid which have been achieved *via* acid hydrolysis. Our findings reveal that redox properties of the APPO catalyst play a key role and that superoxide radical anions are the possible active oxidant species in aqueous media, which distinguish APPO from acid hydrolysis. The APPO process has the inherent merits of environmental friendliness, low humin formation, and ease of separation of catalyst, and thus it has the potential to replace the current acid hydrolysis process for commercial production of levulinic acid.

processes using mineral acids as homogeneous catalysts.^{7b,13} For the first time, an alternative catalytic reaction pathway of converting cellulose to LA, other than acid hydrolysis, is proposed.

Table 1 compares the mass conversions, the total organic carbon (TOC) yields, and the carbon molar yields of major carboxylic acids by reacting cellulose with and without catalysts. Solid acid catalysts, including zeolite β , zeolite Y, and ZSM-5, increased the yields of LA and formic acid compared to the case without a catalyst. Hydroxalcite, a solid base, completely suppressed the production of LA but catalysed lactic acid formation. Amongst the solid catalysts, ZrO_2 gave the highest yields of both LA and lactic acid. By optimizing the process conditions and the loadings of biomass and catalyst, the maximum LA yield of 52% (Table 1 entry 6) was achieved from the APPO of cellulose over the ZrO_2 catalyst (surface area $108 \text{ m}^2 \text{ g}^{-1}$) at 240°C and 2.8% initial O_2 partial pressure. An average LA yield of $50.0 \pm 2.0\%$ was obtained by repeating six experiments under the same conditions as those in Table 1 (entry 7). The initial biomass loading obviously affects the product yield as a decrease of LA yield from 52% to 42% was observed with increasing the cellulose loading from 4.8 wt% to 9.1 wt%.

A study of the effects of temperature and O_2 partial pressure on the APPO of cellulose shows that a narrow operating range exists to maximize the LA yield. As shown in Fig. 1(a), the LA yield reached the maximum at 240°C , and either increasing or decreasing reaction temperatures substantially decreased the LA yield. Similarly, Fig. 1(b) shows that the LA yield is also sensitive to the oxygen partial pressure and the maximum yield of LA was obtained with 2.8% O_2 . Higher oxygen partial pressures resulted in lower LA yields as LA was further degraded to acetic acid and CO_2 by strong oxidation. The results also show that there is a decrease of 5% in LA yield when not feeding with O_2 compared to the case with 2.8% O_2 loading. Although purging with N_2 is used to remove dissolved O_2 from deionized water, the complete elimination of oxygen from solution is not possible. In terms of the redox state of the subcritical water, the residual oxygen is significant. We thus consider that the residual O_2 is still important in initiating and propagating the partial oxidation reactions. High product yields associated with a narrow operation range are not uncommon for a catalytic partial oxidation reaction.¹⁴ However, this observation is very different from the acid hydrolysis process in which the maximum LA yield varied little with changing the initial cellulose concentration, catalyst loading and temperature.¹⁵

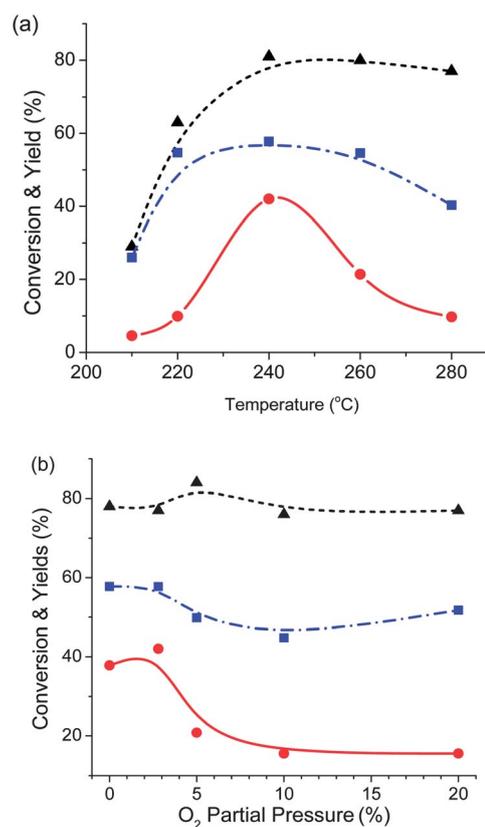


Fig. 1 The effects of temperature and O_2 partial pressure on the conversion and TOC and LA yields of the catalytic partial oxidation of cellulose in the aqueous phase: (a) temperature profiling; (b) O_2 partial pressure profiling. Reaction conditions: 240°C , 20 minutes, 2.8% O_2 , 540 psi initial pressure, 9.1 wt% cellulose loading, 1 : 2 catalyst to substrate mass ratio. Mass conversion (▲), TOC yield (■), levulinic acid yield (●).

It is also interesting to find that, under the APPO conditions, the molar ratio of formic acid to LA was only ~ 0.35 with a ZrO_2 catalyst. In contrast, if the LA production from cellulose is through acid catalysis, the formic acid/LA molar ratio should be close to 1 : 1 according to the stoichiometry. Our control experiment result showed that using 0.5 M H_2SO_4 a molar ratio of 1.06 : 1 formic acid to LA

Table 1 Comparison of the mass conversions, the TOC yields, and the carbon molar yields of major carboxylic acids of the APPO of cellulose with and without catalysts (100 mL Parr reactor; 2.0 g cellulose, 20.0 g water, and 1.0 g catalyst; initially charged with 350 psi 97.2% N_2 + 2.8% O_2 ; reaction time was 25 min). The mass balances were in the range of 98–101%

Entry	Catalyst	Temp. ($^\circ\text{C}$)	Mass conversion	TOC yield	Carbon yields of aqueous products					
					Formic	Acetic	Glycolic	Lactic	Levulinic	Others
1	No catalyst	240	72%	50%	1.7%	1.7%	2.4%	0.6%	7.8%	37.5%
2 ^a	0.5 M H_2SO_4	150	74%	66%	8.4%	0.1%	0.0%	0.0%	39.7%	27.2%
3	$\gamma\text{-Al}_2\text{O}_3$	240	75%	43%	2.1%	0.5%	1.5%	5.7%	15.5%	17.7%
4	TiO_2	240	43%	31%	1.7%	0.6%	2.4%	0.0%	5.5%	21.4%
5	ZrO_2	240	81%	61%	2.9%	1.5%	3.6%	8.3%	42.0%	2.6%
6 ^b	ZrO_2	240	87%	67%	3.2%	0.0%	3.6%	9.0%	51.9%	2.5%
7	Zeolite β	240	50%	33%	4.6%	0.8%	1.4%	0.7%	11.6%	13.9%
8	ZSM-5	240	50%	45%	4.1%	0.7%	1.1%	0.2%	13.5%	25.4%
9	Zeolite Y	240	41%	35%	1.8%	0.6%	1.9%	2.6%	10.1%	18.0%
10	Hydroxalcite	240	24%	29%	2.4%	0.8%	2.1%	3.6%	0.0%	20.1%

^a Reaction time was 6 hours. ^b Cellulose and catalyst loading were 1.0 g and 0.5 g, respectively.

was obtained (calculated from Table 1 entry 3). The $\sim 1 : 1$ ratio is in agreement with the literature reported values obtained from acid hydrolysis of cellulose using either mineral acids^{15,16} or solid acid catalysts.^{9c,d,17} With formic acid as a probe reactant, we found that it was fairly stable in the presence of 0.5 g ZrO_2 under the APPO conditions: $\sim 28\%$ formic acid was converted at 240 °C (Fig. S1†), indicating that the low yield of formic acid is not due to its rapid decomposition during the APPO reaction. The low formic/levulinic acid molar ratio implies that, unlike acid hydrolysis, APPO follows a pathway in which formic acid is no longer a major by-product.

The low formic acid yield also distinguishes the catalytic APPO process from other non-catalytic hydrothermal oxidation processes. Jin *et al.* found that the hydrothermal oxidation of carbohydrate biomass produced a significant amount of formic acid at 300 °C and with 70% H_2O_2 or O_2 supply.¹⁸ The reaction went through a consecutive rupture of the C1–C2 bond (α -scission) to release formic acid until the aldoses were degraded entirely. However, in the presence of the ZrO_2 catalyst, the oxidation of LA was inhibited to form shorter chain carboxylic acids such as succinic acid, acetic acid and formic acid, as shown in Fig. S1.† Without adding a catalyst, 82% LA was converted and a significant amount of acetic acid, 22%, was produced. Conversely, only 11% LA was degraded by adding 0.5 g ZrO_2 . However, further increasing the catalyst loading enhances the conversion of both LA and formic acid.

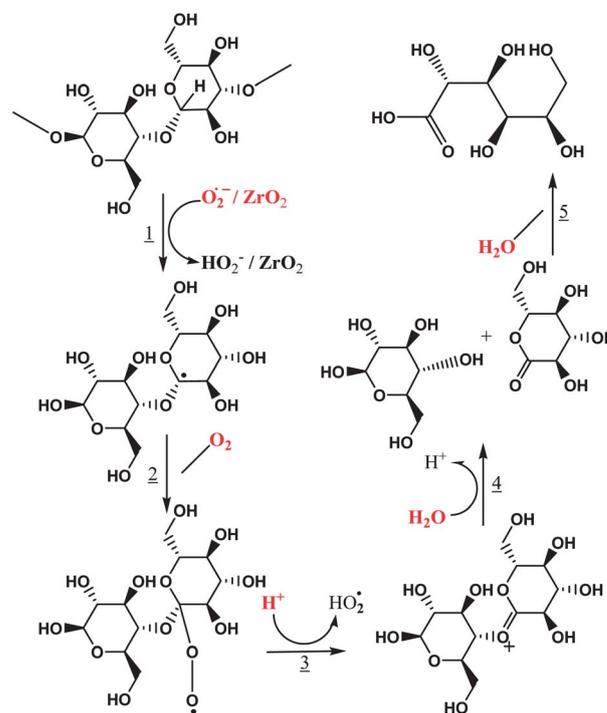
Another uniqueness of the APPO process is the low yield of water insoluble humins. The carbon distribution of the products in Table 1 (entry 6) is shown in Fig. S2.† X-ray diffraction (XRD) analysis (Fig. S3†) indicates the structure change from crystalline cellulose to an amorphous solid residue before and after the APPO reaction, respectively. Therefore, strictly speaking, cellulose was 100% converted into gas, liquid, and solid phase products by APPO. Approximately 12 mol% of carbon was in the form of solid residue by the APPO of cellulose over ZrO_2 , while water insoluble humins contained ~ 23 mol% of carbon during the sulfuric acid catalyzed process (Table 1 entry 2). It is well accepted that HMF is the precursor of humins during the acid hydrolysis of cellulose.^{7c} But we only observed 1–2% HMF yield after the APPO of cellulose over ZrO_2 . Due to enriched water dissociated protons in subcritical water,¹⁹ the probability cannot be excluded that a small portion of cellulose was hydrolysed and dehydrated to HMF catalysed by protons. However, the low yield of humins implies that HMF cannot be the dominant intermediate in the APPO of cellulose.

The role of zirconia as the catalyst is critical for the conversion of cellulose to LA in the APPO process. As shown in Table 1, the LA yield is only $\sim 8\%$ at 240 °C without adding a catalyst, which is far less than the maximum yield of 52% with the ZrO_2 catalyst. ZrO_2 is a multifunctional catalyst containing weak basicity and acidities, as well as redox properties.²⁰ Watanabe *et al.* claimed that ZrO_2 was a base catalyst in that ZrO_2 promoted isomerization between glucose and fructose but suppressed the formation of HMF.²¹ Charonlimkun *et al.* also found that ZrO_2 was active for isomerization reaction in the hydrolysis of cellulose and fructose was the major product.²² Both studies were conducted in an inert atmosphere but did not report a high LA yield. However, the APPO of cellulose over the ZrO_2 catalyst leads to an exceptional high yield of LA which cannot be simply stemmed from the catalyst surface acidity/basicity. A decrease of the LA yield was observed on $\text{SO}_4^{2-}/\text{ZrO}_2$ or Na^+/ZrO_2 , which has a stronger Brønsted acidity or basicity than unmodified ZrO_2 , respectively (Table S1†). Instead, in the APPO

process, cellulose is presumed to undergo partial oxidation by *in situ* generated radicals to form water soluble oligomer and monomer compounds that will be subsequently transformed into LA. It has been demonstrated that superoxide is a form of activated oxygen on ZrO_2 surfaces.²³ Moreover, the formation of superoxide species from molecular oxygen was found to have a lower energy barrier when the surface is in a hydrated state.^{23b}

We therefore propose a reaction pathway (Scheme 1) showing that the superoxide radical anion breaks the glycosidic bond of a cellobiose unit in cellulose and forms one glucose molecule and a gluconic acid (GA) molecule. ZrO_2 first interacts with dissolved oxygen in water to form superoxide radical anions O_2^- on the surface. Radical reactions are initiated by abstracting H atoms and then through a series of transformation described in Scheme 1, the cellobiose unit in cellulose is finally converted into glucose and glucono δ -lactone. The latter is hydrated to form GA and the former can be oxidized to produce GA.²⁴ The GC/MS analysis of silylated aqueous phase products confirmed the presence of GA derived lactone compounds including glucono δ -lactone, as shown in Fig. S4.† On the other hand, only trace amounts of HMF and glucose were observed by HPLC and GC/MS analysis.

To investigate the effects of superoxide radical anions on the APPO of cellulose, radical scavengers including 2-propanol, guaiacol, ascorbic acid, and quercetin were deliberately added at the beginning of the reaction. The scavengers were employed in 2 : 1 molar ratios



Scheme 1 Reaction pathway of converting a cellobiose unit in cellulose to glucose and gluconic acid by superoxide radical anions. (1) Hydrogen at the C1 position is abstracted by a superoxide radical; (2) molecular oxygen is inserted into the C1 position and formed a new organic radical; (3) the organic radical is combined with a proton to form a hydroperoxy radical and leaves the carbonyl bond on the C1 carbon; (4) the carbonyl bond is hydrated and the glycosidic bond connecting the two sugar units is cleaved; (5) the 3,4,5-trihydroxy-6-hydroxymethyl-tetrahydro-pyran-2-one is further hydrated to form gluconic acid.

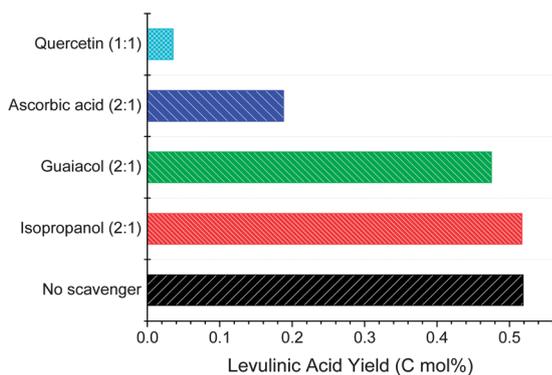
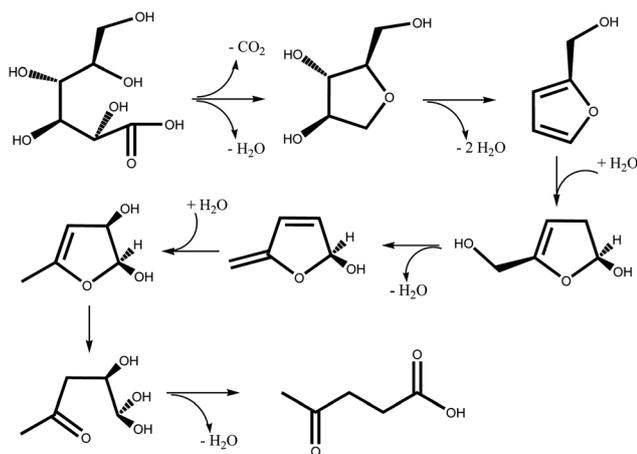


Fig. 2 The effects of radical scavengers on levulinic acid yields in catalytic partial oxidation of cellulose in the aqueous phase. *Reaction conditions:* 240 °C, 20 minutes, 2.8% O₂, 330 psi initial pressure, 4.8 wt% cellulose loading, 1 : 2 mass ratio of catalyst to cellulose. The values in the parentheses are the molar ratios of radical scavengers to cellulose.

with cellulose except quercetin which was added in a 1 : 1 ratio. Short-chain alcohols are known to be efficient hydroxyl radical scavengers.²⁵ Fig. 2 shows that 2-propanol has no effect on the APPO of cellulose, indicating no OH in the system. In contrast, flavonoids (e.g. quercetin), ascorbic acid, and phenolic compounds such as guaiacol are known for their antioxidant activity and thus the reactive O₂⁻ scavengers.²⁶ The LA yields decreased with addition of various O₂⁻ scavengers and the corresponding inhibitory effect on LA production occurred in the order of quercetin > ascorbic acid > guaiacol. Interestingly, such an order is the same as the literature reported order of the inhibitory strength of the three scavengers on O₂⁻ generation in both aprotic and aqueous media.^{26a,b} Therefore, it is suggested that O₂⁻, instead of OH, was attributed to the high selectivity toward LA production in the APPO of cellulose.

Scheme 2 shows a possible reaction mechanism of converting GA to LA: GA is deoxygenated through an initial Hofer–Moest-type decarboxylation²⁷ followed by a series of consecutive dehydration/rehydration reactions. A significant amount of LA was produced over the ZrO₂ catalyst through APPO using GA as the probe reactant (Table S2[†]). In contrast, the ZrO₂ catalyst appears to suppress



Scheme 2 Proposed reaction pathway of converting gluconic acid to levulinic acid by a Hofer–Moest-type decarboxylation reaction followed by consecutive dehydration/rehydration reactions.

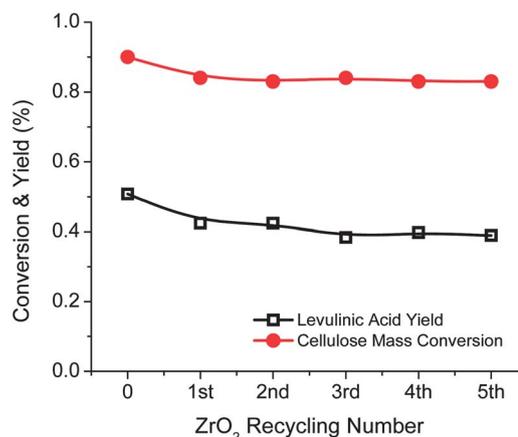


Fig. 3 Zirconia catalyst recycling performances. The spent catalyst was regenerated by calcination and then reused. *Reaction conditions:* 240 °C, 20 minutes, 2.8% O₂, 330 psi initial pressure, 4.8 wt% cellulose loading, 1 : 2 mass ratio of catalyst to cellulose.

the LA production when using HMF as the reactant. The LA yield increased with decrease in the initial GA concentration. Unlike HMF, GA is more stable against forming humins through self-condensation or polymerization. As GA is the dominant intermediate to produce LA from the APPO of cellulose, the formation of HMF is bypassed and higher carbon efficiency is realized.

Catalyst stability is essential for a heterogeneously catalyzed reaction system. Fig. 3 shows that the LA yield decreased from ~50% to ~44% after the first cycle of reaction/regeneration of the ZrO₂ catalyst and then stabilized at ~40% thereafter till the fifth cycle. The corresponding BET surface area of ZrO₂ decreased from 108 m² g⁻¹ of the fresh sample to 72 m² g⁻¹ of the catalyst regenerated and reused 3 times and then was stabilized thereafter. The ZrO₂ catalyst maintains the high stability against leaching under the APPO conditions, confirmed by the inductively coupled plasma (ICP) analysis of the post-reaction aqueous product which showed undetectable Zr⁴⁺ ions. The crystalline structure of the spent ZrO₂ catalyst was confirmed to be unchanged by XRD analysis, as shown in Fig. S5.[†] Therefore, the APPO process is a promising alternative to replace the acid hydrolysis processes for cost-effective production of LA from cellulosic biomass.

Conclusions

In summary, we report a new approach to convert cellulose to LA through the aqueous phase partial oxidation (APPO) over heterogeneous catalysts. The yield of LA was highly dependent on the catalyst properties, biomass loading, reaction temperature, as well as oxygen partial pressure. Under the optimum reaction conditions, a maximum yield of LA, 50.0 ± 2.0 mol%, was achieved by converting cellulose over the ZrO₂ catalyst in the presence of lean air with 2.8% O₂. It is concluded that the APPO reaction pathway is distinguishable from that of the conventional acid hydrolysis. Redox, rather than acid–base, properties of the ZrO₂ catalyst play the central role in the oxidative deconstruction of cellulose in the APPO reactions. The proposed APPO reaction mechanism indicates that gluconic acid, other than HMF, is the key intermediate to produce LA. The catalytic APPO system described in this communication report provides an efficient, environmentally friendly, and cost-competitive one-pot

processing strategy for producing LA from cellulose. Further research will be carried out toward in-depth investigations of the APPO reaction mechanism and the applications of APPO to process hemicellulose and lignin. Eventually the APPO process will be integrated into a biorefinery of the complete manufacturing of advanced biofuels and/or bio-based commodity chemicals from raw lignocellulosic biomass.

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