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Ketonization of levulinic acid and γ-valerolactone to hydrocarbon fuel precursors

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ABSTRACT

A new process for direct conversion of either levulinic acid (LA) or γ-valerolactone (GVL) to hydrocarbon fuel precursors was studied. The process involves passing an aqueous solution of LA or GVL containing a reducing agent, such as ethylene glycol or formic acid, over a ketonization catalyst at 380–400 °C and atmospheric pressure to form a biphasic liquid product. The organic phase is significantly oligomerized and deoxygenated and comprises a complex mixture of open-chain alkanes and olefins, aromatics, and low concentrations of ketones, alcohols, ethers, and carboxylates or lactones. Carbon content in the aqueous phase decreases with decreasing feed rate; the aqueous phase can be reprocessed through the same catalyst to form additional organic oils to improve carbon yield. Catalysts are readily regenerated to restore initial activity. The process might be valuable in converting cellulosics to biorenewable gasoline, jet, and diesel fuels as a means to decrease petroleum use and decrease greenhouse gas emissions.

1. Introduction

Open-chain compounds are necessary fuel blend stock components, in particular, for diesel and jet fuel. For example, JP-8 jet fuel contains on average about 60% *n*- and *iso*-paraffins [1]. In addition, refiners are gasoline rich but diesel poor. Future growth and increasing market demand is for diesel fuel, even in North America [2]. However, current thermal methods to biorenewable hydrocarbon fuels such as fast pyrolysis (FP) and hydrothermal liquefaction (HTL) of terrestrial biomass form hydrocarbon products that are primarily aromatic with little open-chain fuel components [3]. Feedstocks (lipids, fatty acids) that can give open-chain components in HTL or catalytic processing suffer from poor availability. A need exists for new routes to paraffinic fuel blend stocks using abundant biomass resources.

Catalytic processing potentially offers advantages over high-temperature pathways (FP, HTL, gasification) by allowing lower temperature and pressure processing of sugar, sugar oligomer, and sugar-derived intermediates [4,5]. The challenges of using sugar-based feeds for fuel production are that they have a high oxygen content, which must be reduced, and they have a low molecular weight (carbon number), which must be increased. Deoxygenation presents trade-offs that must be considered; removal of oxygen as water, such as through hydrodeoxygenation (HDO) [3], incurs the costs of high pressure hydrogen production, while deoxygenation as CO_2, such as by ketonization of sugar-derived acids, incurs costs associated with loss of valuable and expensive biomass carbon.

Ketonization is the process of combining two carboxylic acids over a catalyst to eliminate CO_2 and water and form a ketone product [6], thereby increasing carbon number and removing oxygen in the same process. This reaction is thought to proceed via metal carboxylate intermediates, although mechanistic details remain to be described [7] and the process varies with metal type. Basic alkali and alkaline earth oxides form bulk carboxylates which decompose to the ketone products, whereas for high lattice energy oxides such as CeO_2, TiO_2, ZrO_2, and others, the reaction occurs via surface carboxylate intermediates [8]. Ketonization can occur in both the condensed and vapor phases [7].

A potential advantage of ketonization in the gas phase is that the conversion can be conducted at atmospheric pressure, which can help to simplify reactor designs and reduce capital expenses [9]. In addition, the ketones formed can be further oligomerized, such as by aldol condensations, and converted to olefins by dehydration of alcohol intermediates with further deoxygenation. Olefins are reduced under conditions milder than HDO using non-precious metal catalysts, again potentially leading to less capital intensive processing.

Levulinic acid (LA), a biomass-derived carboxylic acid, is a potential fuel precursor [10–12] available from both pentose and hexose sugars, but not by the same chemistry [13]. Hexose sugars are dehydrated by acid catalysts to hydroxymethylfurfural (HMF), which is further

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converted by acid-catalyzed rehydration to LA with concurrent formation of 1 equivalent of formic acid. At the biorefinery scale, LA yields of 70–80% of theoretical have been obtained [14] and development of an industrial process for LA production is underway with a 10,000 MT/a plant scheduled to reach full capacity by 2017 [15]. The conversion of glucose to HMF is not easy, however, and is facilitated by prior isomerization to fructose, such as with Lewis acids [16], enzymes [17], or bases [18]. Pentose sugars are readily converted to furfural by acid catalysis [19]. Furfural can be hydrogenated to furfural alcohol, which can then be converted by acid to LA [20]. Formation of humins is a side reaction that reduces yield, although biphasic systems can help minimize their formation [21,22].

LA and its hydrogenation product γ-valerolactone (GVL) have been investigated as sugar-derived intermediates for the production of liquid hydrocarbon fuels [23]. Wheeler et al. [9,24–26] report the batch ketonization of LA promoted by strong base ($Ca(OH)_2$) in the presence of formate to produce an organic phase product consisting of predominately cyclic ketones. The initial ketonization product 2,5,8-nonanetrione was proposed to undergo internal aldol condensation and fragmentation to the observed cyclopentenone products. 2,5,8-Nonanetrione was observed by Schlaf et al. [27] to be a transient intermediate in the red-mud catalyzed ketonization of LA. The nonanetrione, if it could be prepared, may be a useful precursor to open-chain hydrocarbons in the fuel range.

The work described here studied the ketonization of LA and GVL over Ce- and La-doped zirconias as an approach to open-chain hydrocarbon liquids in the distillate fuel range. Both LA and GVL were found to ketonize in the presence of reducing agents (ethylene glycol (EG) or formic acid (FA)) to a complex mixture of mostly open-chain unsaturated hydrocarbons that have been largely de-oxygenated. Process development of this catalytic conversion to liquid hydrocarbon fuel precursors is presented.

2. Materials and methods

2.1. Catalyst preparation and characterization

Catalyst powders were obtained from MEL Chemicals, Inc., Flemington, NJ. Powders were pressed, calcined at 450 °C, and sieved to 60–100 mesh size for reactor studies. The work described was conducted with MEL XZO 802/03 (17% CeO_2 doped $Zr(OH)_4$). Other catalysts tested under conditions of high conversion gave identical results. These catalysts were MEL XZO 1289/01 (17% CeO_2 doped $Zr(OH)_4$), XZO 1289/01 (17% CeO_2 doped $Zr(OH)_4$), XZO 1290/01 (25% CeO_2 doped $Zr(OH)_4$), XZO 892/02 (17% CeO_2 + 5% La_2O_3 doped $Zr(OH)_4$), XZO 1291/01 (17% CeO_2 + 5% La_2O_3 doped $Zr(OH)_4$), and XZO 945/03 (10% La doped $Zr(OH)_4$).

Fresh catalyst, recovered catalysts after flow reactor runs, and catalysts regenerated at 450 °C in air were characterized by surface area, pore volume, and X-ray diffraction analyses. Surface area and pore size measurements of spent catalysts were performed on samples degassed at 25 °C under vacuum. Calcined and regenerated catalysts were degassed at 150 °C. The data from nitrogen adsorption/desorption at 77.4 K were collected with a Quantachrome Autosorb 6-B gas sorption system (Quantachrome Instruments, Boynton Beach, FL). The surface area was determined from the isotherm with the five-point Brunauer-Emmett-Teller (BET) method [28]. The Barrett–Joyner–Halenda (BJH) method [29] was used to calculate the total pore volume and pore size distribution including average pore diameter.

X-ray powder diffraction (XRD) patterns of all samples were recorded on a Phillips X-Pert (50 kV and 40 mA) diffractometer using Cu Kα radiation (λ 1.54059 Å). Each sample was scanned in the range between 10° and 80°. The scan time was 4 s per step with a step size of 0.04 ° per step.

2.2. Flow reactor studies

Catalytic conversions were conducted in simple flow reactors consisting of either 3/8” or ½” diameter stainless steel tubes packed with 3.5–5.5 g catalyst. Gases were introduced to the top of the reactor at atmospheric pressure with flow rates controlled by a Brooks mass flow controller. Nitrogen was used during conversion experiments at a flow rate of 10 cm^3/min. Air at a flow rate of 10 cm^3/min was used during in situ coke burning to regenerate the catalyst (450 °C, 4 h). Liquid feeds were aqueous solutions containing various concentrations of LA or GVL (approximately ranging from 6 wt% to 34 wt%) and FA or EG (approximately ranging from 3 wt% to 16 wt%, except for a control containing no reductant). The mole ratio of reductant to LA or GVL was 1:1. Feeds were introduced to the top of the reactor using a Chrom Tech Series III HPLC pump (Apple Valley, MN). Feed rates corresponding to weight hourly space velocities (with respect to LA or GVL) between 0.042 and 0.123 h^{-1} were used. Products exiting the reactor were cooled by flowing through a chilled condenser, then collected in a chilled sample vial. Exit gases were sampled for gas chromatography analysis. The reactor tube was heated with a band heater controlled by a Digi-Sense temperature controller using an external thermocouple. Internal reactor temperatures were monitored by a thermocouple inserted into the bottom of the catalyst bed. Bed temperatures between 330 °C and 400 °C were typically used.

2.3. Product characterization

Aqueous and organic products were analyzed by gas chromatography/mass spectroscopy (GC/MS) for product identification with use of a 6890N Agilent GC with a 5875C MSD attached. Gas chromatography used a HP-5MS 5% phenyl methyl siloxane column with 0.25 µm film thickness (Agilant). Total ion chromatograms are presented. GC/flame ionization detection (GC/FID) was used for quantification of analytes. Elemental analyses (CHN, ASTM D5291/D5373; O, ASTM D5373 mod) were conducted by ALS Environmental (Tucson, AZ) in duplicate. Simulated distillation of organic phases was run according to ASTM D 2887.

Solution NMR studies were conducted in deuterated chloroform using an Agilent DD2 console with a 5 mm OneNMR probe, and 11.75 T Oxford magnet (13C − 125.79 MHz, 1H − 500.22 MHz). The ^{13}C pulse sequence used inverse gated H decoupling during 1 s of acquisition time after a 45 ° carbon rf pulse. The recycle delay was 10 s and 4000 transients were collected for each sample. The data were processed using MestReNova with 20 Hz line broadening and the carbon chemical shift scale was referenced by setting the solvent peak to 77.36 ppm. Integrations should be considered semi-quantitative.

Two-dimensional ^{1}H-^{13}C heteronuclear single quantum coherence (HSQC) spectra of samples dissolved in $CDCl_3$ were acquired at 20 °C on a 600 MHz Varian Inova equipped with an HCNP triple resonance z-axis pulsed-field gradient probe (Varian pentaprobe) using the BioPack gChsqc pulse sequence. For this data, the decoupler offset was centered either in the aliphatic (52 ppm) or aromatic (122 ppm) region of the ^{13}C chemical shift range. Delay times tCH and lambda for 1/4*JCH were 1.8 ms and 1.6 ms for aliphatic spectra and 1.45 ms and 1.3 ms for aromatic spectra. The ^{1}H spectral width was 17 ppm and ^{13}C spectral width was 120 ppm or 60 ppm for aliphatic and aromatic spectra, respectively, with either 96 or 192 complex points in the indirect dimension and 1024 complex points collected in the direct dimension. Spectra were processed with cosine bell apodization followed by 2 x zero filling in both dimensions, and linear prediction of 30% more points in the indirect dimension. Spectra were referenced to TMS or residual $CHCl_3$.

Carbon mole balance was estimated for runs with 13.7 wt% GVL and 6.3 wt% FA at 400 °C with use of elemental analyses of aqueous and organic phase products and estimation of moles carbon in CO_2 formed based on GVL conversion. Aqueous and organic products were collected over at least three campaigns of about 2 days each with catalyst regeneration conducted between campaigns to ensure high conversions throughout sample collection. Composited samples were analyzed as is without drying or other processing. CO_2 was identified in the gas phase, but was not quantified. Mole balance was determined when GVL and FA were 100% converted and assuming one mole of CO_2 for every two moles of GVL and one mole of CO_2 for every mole FA fed. ^{13}C NMR analyses estimated that carboxyl groups in the organic phase comprised about 0.5 mol% of the carbon present for these samples indicating the high degree of ketonization in these experiments. In addition, carboxylic acid number (CAN) determinations verified the absence of carboxylic acid groups in both the organic and aqueous phases.

3. Results and discussion

Ketonization of levulinic acid (without a reducing agent) over MEL 802/03 at 360 °C produced α- and β-angelica lactones and 3-methyl-2-cyclopenten-1-one. The lactones are well-known thermal ring-closure products and the cyclopentenone was observed by Wheeler [24], presumably by ring-closing internal aldol condensation and fragmentation. Thus, the weakly acidic Ce-doped zirconia was not found to be effective at preventing the follow-on reactions also seen with the strong base catalysts.

An attempt was made to prevent ring-closure by protecting the ketone group of levulinic acid as the ethylene glycol (EG) ketal [30]. Ketals of LA are well known [31]. Strong acid-catalyzed reaction of EG with LA gave the desired cyclic ketal, which was isolated. An aqueous solution of the ketal fed to the ketonization reactor gave surprising results, discussed below, but it was subsequently discovered after the run that the carboxylic acid of the LA ketal was a strong enough acid in the aqueous solution to hydrolyze the ketal. Thus, the actual feed to the reactor was a 1:1 mol ratio solution of LA and EG. When a 1:1 LA:EG solution was fed to the reactor, identical results were obtained.

The product of the reaction of LA and EG in a 1:1 mol ratio at 330 °C (under N_2) was a single-phase aqueous solution containing GVL, acetaldehyde, acetone, and ethanol (Fig. 1a). LA was hydrogenated by EG to GVL. A possible mechanism of this hydrogenation and the origin of the by-products are discussed below. At a higher temperature of 380 °C, the 1:1 LA:EG feed was converted to a 2-phase product consisting of an aqueous phase and a dark organic phase. GC/MS analysis (Fig. 1b) of the organic phase shows a complex mixture of higher molecular weight compounds comprising alkanes, olefins, polyolefins, and aromatics. Functional group analyses determined by NMR of oil products are presented below.

These results suggested the possibility that GVL was an intermediate to the formation of the organic phase. Indeed, when an aqueous solution of GVL and EG in a 1:1 mol ratio was converted over MEL 802/03 at 380 °C, the oil phase was again formed (Fig. 1c). When GVL was fed without EG present, the oil phase forms, but a series of light ketones was also produced. These ketones are consistent with ketonization of acids formed when GVL is ring-opened over an acid catalyst, as discussed further below. Presumably, when EG is present, these ketones are hydrogenated to alcohols, which are then dehydrated to the olefins observed in the GC/MS chromatograms and NMR spectra.

Formic acid as a reductant in place of EG is also effective. Formic acid as a reductant in LA conversions was first reported by Wheeler et al. [24]. Both LA and GVL fed with one molar equivalent of formic acid in the feed solution gave complex organic oil products. This is a significant result because when six-carbon sugars are converted to LA, one equivalent of formic acid is also produced. Thus, the possibility exists that cellulosics could be converted to LA and formic acid and fed to the ketonization reactor to make hydrocarbon oils.

The oils produced are significantly oligomerized. Simulated distillation curves for three representative organic oil products are shown in Fig. 2. The LA- and GVL-derived products have distillation profiles similar to diesel and kerosene fuels. These products still contain oxygen so they cannot be considered distillate fuels, but with half of the material boiling in the range 210–500 °C for GVL and 250–500 °C for LA it is clear that molecular weights have increased in the process. For reference, GVL boils at 207 °C and LA boils at 245 °C. GC/MS identification of high boiling compounds is not sufficiently reliable to determine the carbon number range (or individual compound identities) of products and further work is needed to better characterize the molecular weight range (and speciation) of these materials. Furthermore, the yield in the distillate range following hydrotreating has yet to be determined and is the subject of continuing research.

The organic oils are deoxygenated. Elemental analyses show that the LA products contain less oxygen (about 18%) than LA (41%). Similarly, the GVL products contain less oxygen (7–11%) than the GVL feed (32%) and about half the amount of oxygen as in the LA-derived products. ^{13}C NMR spectra indicate that of the carbon atoms detected, on average, about 4% are associated with carbonyl functionalities, 2% with alcohol or ether groups, and about 1% with carboxyl groups (Fig. 3). 2-D NMR was used to deconvolute the aromatic and olefin resonances, allowing estimation of carbon contained in these groups. Most of the carbon is present in alkane groups (69%), aromatics (13%), and olefins (12%). Over several runs at different temperatures, alkane and olefin carbon content trends downward and aromatic content trends upwards with increasing temperature.

The 2-D NMR spectra of oils from the reaction of GVL and FA at 380 °C show a predominance of terminal olefins in the product oil phase (Fig. 4). Terminal olefins could be formed by ketonization of pent-4-enoic acid from GVL ring opening which we believe is an important step in the mechanism of hydrocarbon oligomerization, discussed below.

Experiments were conducted with feeds consisting of 1:1 GVL:FA mole ratio fed at a WHSV (with respect to GVL) of $0.12\,h^{-1}$ to determine catalyst lifetime and regeneration. In one experiment, 34.3 wt % GVL and 15.7 wt% FA was fed at a reactor temperature of 360 °C. The MEL XZO 802/03 catalyst was found to deactivate rapidly as shown in Fig. 5. Activity was returned to about 80% of the original by calcining the catalyst in situ with air at 450 °C for 4 h. In a second experiment (Run 72) using a feed of 13.7 wt% GVL and 6.3 wt% FA, 100% conversion was maintained for about two days before slowly dropping. Regeneration with air at 450 °C completely restored catalyst activity to the original level. Three regeneration cycles for a total TOS of 220 h are shown in Fig. 5, but in other long-term runs the catalyst was regenerated at least a dozen times without loss of activity.

The spent and regenerated catalysts from the end of the 13.7% GVL, 6.3% FA experiment (Run 72) and another identical experiment run for only 8 h TOS (Run 76) were analyzed for pore properties, surface area, and phase change. Table 1 shows that regenerated catalysts lose surface area with TOS. Spent catalysts have very low surface areas and lower pore volumes, presumably because pores are filled with non-volatile organics (either high boiling products or soft coke). Regeneration in air removes carbon deposits and restores the original pore volume. Constant pore volume and decreasing surface area with TOS suggested that pores coalesced during catalysis and/or regeneration. This is consistent with pore size data shown in Fig. 6, which shows that pore sizes of regenerated catalysts increased with TOS. XRD data (Fig. 7) indicate that although pores may be coalescing, the bulk crystalline structure does not change noticeably over 220 h TOS.

A series of experiments was conducted to investigate the effect of GVL feed rate on organic oil yield and elemental composition and to determine mass balance and estimate carbon mole balance. The feed for these experiments conducted at 400 °C was 13.7 wt% GVL and 6.3 wt% FA. Mass balances were excellent (99%) at every feed rate tested (Table 2). Mole balances of 95–101% were measured at the fastest flow rates tested, but dropped to 83% at the lowest flow rate, possibly because material losses in reactor hold-up and sampling were relatively more significant at the smaller sample size. As GVL space velocity was decreased, less carbon was found in the aqueous phase, and (at least for the decrease from $0.123\,h^{-1}$ to $0.077\,h^{-1}$) a higher molar yield of

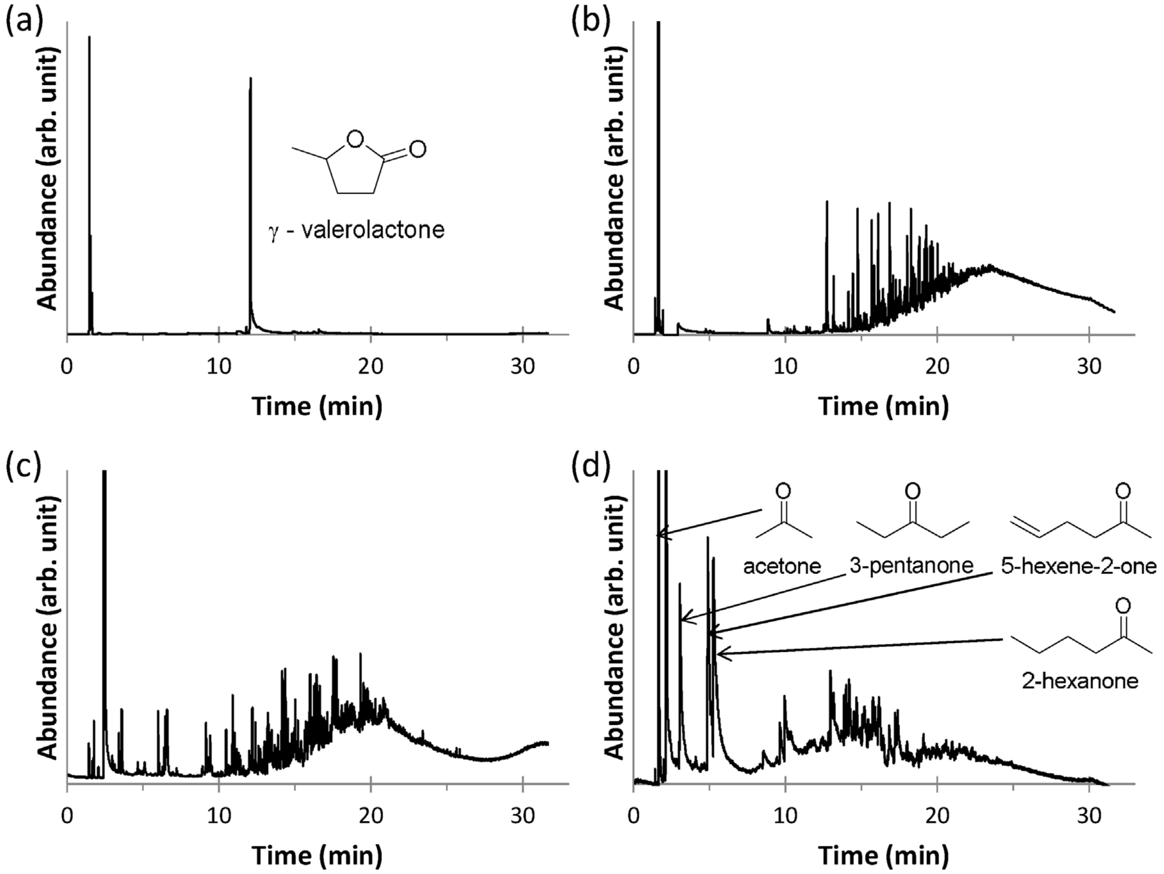


Fig. 1. GC/MS analyses of ketonization products formed on MEL 0802/03 with various feeds and reaction conditions. For (a), (b), and (c), aqueous solutions contained a 1:1 mol ratio of LA or GVL to EG and were fed at a WHSV of 0.08 h^{-1}. For (d), an aqueous solution of GVL without EG was fed with WHSV of 0.08 h^{-1}. (a) LA + EG (6.5 wt% LA, 3.5 wt% EG), 330 °C; (b) LA + EG (6.5 wt% LA, 3.5 wt% EG), 380 °C; (c) GVL + EG (5.9 wt% GVL, 3.9 wt% EG), 380 °C; (d) GVL (6.5 wt%) without reductant, 380 °C.

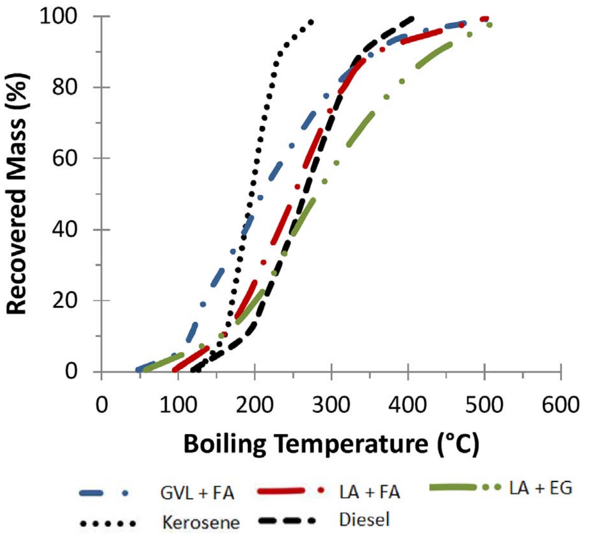


Fig. 2. Simulated distillation of organic oil products produced over MEL XZO 802/03 compared with standard kerosene and diesel. Mole ratio of LA or GVL to reductant is 1:1. GVL + FA: Run 105-1, 400 °C, 13.7 wt% GVL, 6.3 wt% FA, WHSV 0.08 h^{-1}; LA + FA: 400 °C, 6.2 wt% LA, 2.7 wt% FA, WHSV 0.08 h^{-1}; LA + EG: 380 °C, 11.3 wt% LA, 7.6 wt % EG, WHSV 0.16 h^{-1}.

carbon in the organic phase was obtained (43%). Consistent with this was that when the aqueous phase was re-fed over the same catalyst, additional organic oil was formed, indicating that light ketones in the aqueous phase continued to convert to organic products.

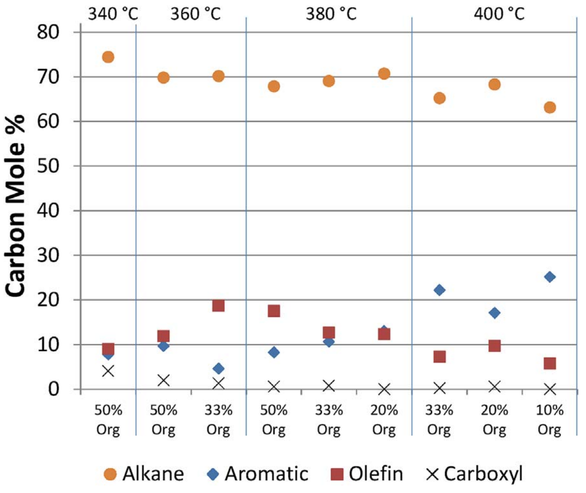


Fig. 3. Functional group analysis using solution ^{13}C NMR for 1:1 GVL:FA ketonization over MEL XZO 802/03 at various feed concentrations and temperatures. WHSV was 0.08 h^{-1} except for 50% Org which was 0.13 h^{-1}. 10% Org = 6.7% GVL, 3.3% FA; 20% Org = 13.6% GVL, 6.4% FA; 33% Org = 22.2% GVL, 10.6% FA; 50% Org = 34.3% GVL, 15.7% FA.

At a GVL WHSV of 0.123 h^{-1}, about half the carbon (other than CO_2 from ketonization) was found in the organic phase with the rest in the aqueous phase (Table 3). At 0.077 h^{-1}, about twice the amount of product carbon was in the organic phase compared to the aqueous phase. Elemental analyses showed that the oxygen content decreased

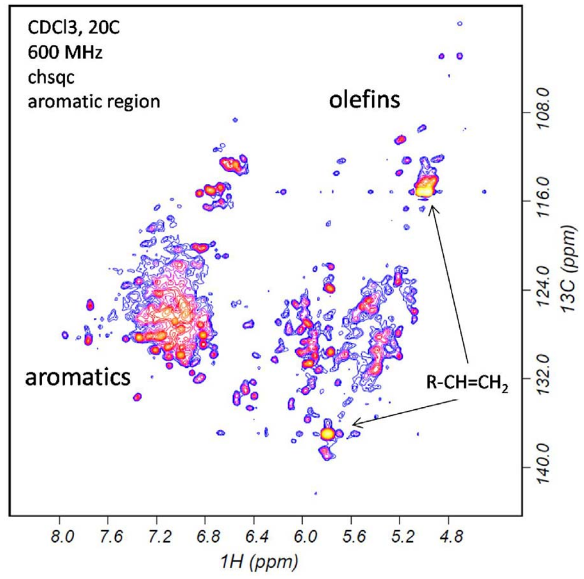


Fig. 4. 2D NMR of organic oils from GVL conversion over MEL XZO 802/03 at 380 °C. Feed solution is 1:1 mol ratio GVL:FA, 22.2 wt% GVL, 10.6 wt% FA fed at WHSV 0.08 h^{-1}.

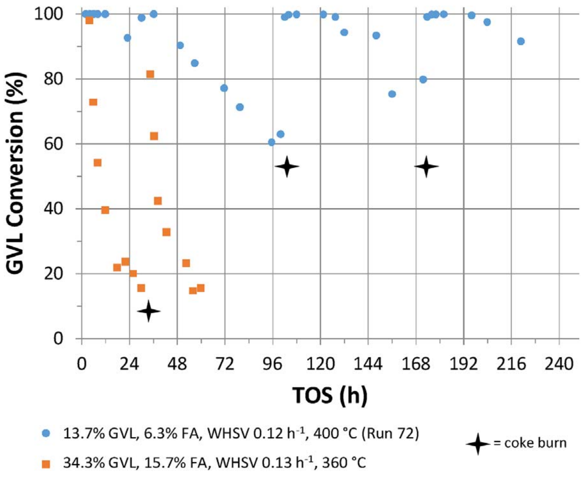


Fig. 5. Catalyst lifetime and regeneration. MEL XZO 802/03, 1:1 mol ratio of GVL:FA. (●) 13.7 wt% GVL, 6.3 wt% FA, WHSV 0.12 h^{-1}, 400 °C (Run 72); (■) 34.3 wt% GVL, 15.7 wt % FA, WHSV 0.13 h^{-1}, 360 °C.

Table 1
Surface area and pore volume analyses for fresh, spent, and regenerated MEL 802/03 catalyst.

Sample[a]	TOS, h	BET SA (m^2/g)	Pore Vol, cm^3/g
Fresh 802/03, Calcined	0	108.3	0.22
Run 76 Spent	8	47.7	0.18
Run 76 Regenerated	–	88.4	0.22
Run 72 Spent	220	26.9	0.15
Run 72 Regenerated	–	73.7	0.22

[a] Calcined and regenerated samples prepared by calcination in air at atmospheric pressure at 450 °C; Runs 72 and 76: aqueous feed containing 13.7 wt% GVL and 6.3 wt% FA, WHSV 0.12 h^{-1}, 400 °C.

from 31.96% in the GVL feed to 10.54% at the highest WHSV tested and 7.26% at the slowest. Carbon content increased with decreasing WHSV and increased residence time led to more highly deoxygenated organic oils. Simulated distillation curves were nearly identical for these three samples and nearly identical to the GVL + FA curve in Fig. 2.

Mechanistic pathways are suggested by the results of these studies.

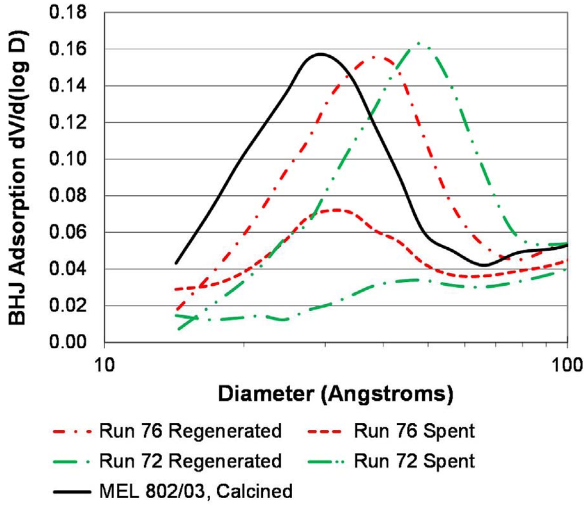


Fig. 6. Pore diameter analyses of fresh, spent, and regenerated MEL XZO 802/03 catalysts. See footnote for Table 1.

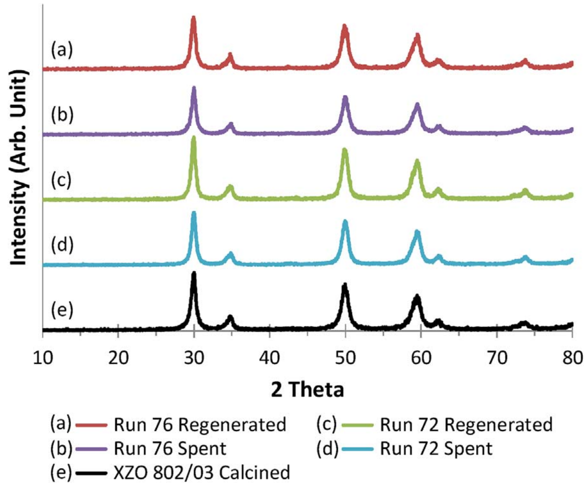


Fig. 7. XRD spectra of fresh, spent, and regenerated catalysts. See footnote for Table 1.

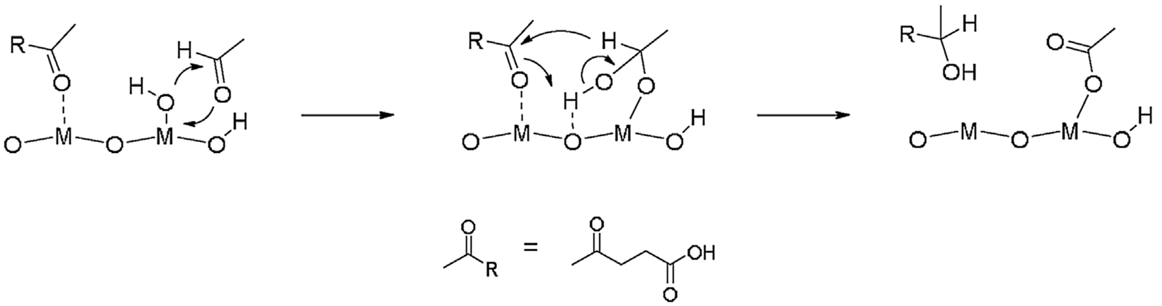
Table 2
Mole and Mass Balance and Molar Yield as a Function of Aqueous GVL Feed Rate (13.7 wt % GVL, 6.3 wt% FA; 400 °C).

Run	Feed Rate, cm^3/min	GVL WHSV, h^{-1}	Collected Oil Product, g	Oil Molar Yield, % C	Aqueous Molar Yield, % C	Mole Balance, % C [a]	Mass Balance, wt% [a]
105 – 1	0.08	0.123	28.09	37	35	101	99
105 – 2	0.05	0.077	26.87	43	22	95	99
105 – 3	0.03	0.042	10.11	37	17	83	99

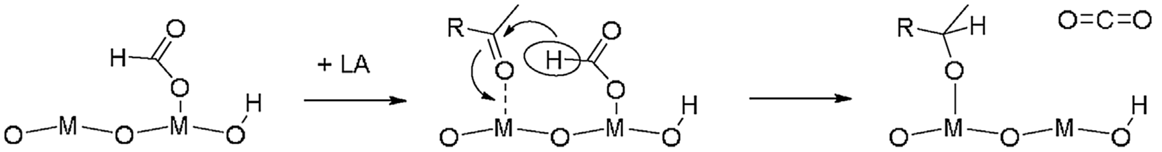
[a] using theoretical values for CO_2.

Table 3
Distribution of Carbon in Products and Elemental Analyses of Organic Products (13.7 wt% GVL, 6.3 wt% FA; 400 °C).

Run	Moles C				Oil Elemental Analysis, wt%		
	Feed	Oil	Aqueous	CO_2	C	H	O
105 – 1	5.04	1.84	1.74	1.51	78.88	10.43	10.54
105 – 2	4.16	1.79	0.89	1.25	80.13	10.42	7.83
105 – 3	1.87	0.69	0.31	0.56	81.79	10.46	7.26
GVL (feed)	–	–	–	–	59.98	8.05	31.96



Scheme 1. Proposed levulinic acid reduction via a Cannizzaro-like surface reaction.



Scheme 2. Proposed formic acid reduction of levulinic acid.

Catalytic transfer hydrogenation (CTH) of ketones by alcohol reductants [32], especially of LA to GVL, by the Meerwein-Ponndorf-Verley (MPV) reduction is well known in both the liquid [33] and gas [34] phases. However, under our reaction conditions using isopropanol (IPA), a common transfer reducing agent, GVL was only a minor product at 325 °C. Perhaps this is because of the low IPA:LA mole ratio of 1 in our experiments in contrast to prior work conducted at ratios of 5–7 or in IPA as reaction solvent. If hydrogenation of LA to GVL by EG occurred by CTH, the expected product derived from EG would be glycolaldehyde (and its condensation products), which was not observed in the reaction solution. In addition, the presence of acetone in the solution when EG was used as reductant is difficult to explain by this hydrogenation mechanism.

More likely is operation of the Cannizzaro reaction. Dehydration of EG would form acetaldehyde (an observed product), which could react on the oxide surface with a second equivalent of acetaldehyde to form ethanol (an observed product) and acetic acid. Acetic acid will ketonize to acetone (an observed product). The Cannizzaro reaction has been observed over metal oxides in the conversion of benzaldehyde to benzoic acid and benzyl alcohol [35]. By analogy to Haffad, LA would be reduced by acetaldehyde to 4-hydroxypentanoic acid, such as by Scheme 1, which would then ring close to GVL. A mechanism involving initial ketone group reduction followed by ring closure, rather than ring closure to α-angelica lactone followed by hydrogenation, is supported by the observation that α-angelica lactone is not hydrogenated by this system. It is probable that FA can hydrogenate LA through similar adsorbed intermediates such as shown in Scheme 2.

Reactions of GVL on the Ce-doped zirconia differs from reported reactivity on silicoaluminates [36]. GVL ring-opens and decarboxylates to butenes on silicoaluminates, but does not give an organic oil phase. On the doped zirconias, while a small amount of 1-butene is observed in the gas phase, the decarboxylation route does not appear to be the dominant pathway. Experiments with GVL not containing EG or FA form light ketones, which suggests that ring-opened GVL undergoes ketonization and other reactions to form the observe products. The observed ketone products could be produced by ketonization of combinations of pentenoic acid, pentanoic acid, acetic acid, and propanoic acid. For example, one of the major products is a hexene-2-one (the position of the double bond is not confirmed by GC/MS data), which would be produced by ketonization of pentenoic acid (a GVL ring-opened intermediate) and acetic acid. The origin of acetic and propanoic acids is a matter of speculation, but one possibility could be that they are beta-scission products of the primary GVL ring-opened intermediate. The observed presence of small amounts of ethylene and propylene in the gas phase and ethanol and propanol in the liquid phase may be consistent with beta-scission, but further work would need to be conducted to demonstrate this pathway. In addition, the observation in 2D NMR analyses of terminal olefins in the organic phase indicates that kinetic products are formed, but factors that contribute to this, such as rates of ring opening and ketonization versus rates of olefin isomerization, are unknown at this time.

4. Conclusions

Levulinic acid or γ-valerolactone have been found to be converted in the presence of formic acid or ethylene glycol in a single process step at atmospheric pressure to an organic product that is significantly deoxygenated and oligomerized. The organic product is a complex mixture of mostly open-chain saturated and unsaturated hydrocarbons. Carbon in the aqueous phase can be further condensed to the organic phase product to improve carbon yield in the fuel range. The catalyst simultaneously carries out several processes, including ketonization, hydrogenation, dehydration, and various condensation reactions, probably including aldol condensation of ketone intermediates.

While further process development is required, this conversion might play an important role in tapping renewable cellulosic resources for supplying transportation fuels to help displace petroleum-based fuels and reduce greenhouse gas emissions. Low-boiling fractions containing high-octane light ketones might find direct use as gasoline blend stocks. Higher boiling fractions following hydrotreatment could be fractionated into jet or diesel fuels. The low pressure needed for these conversions offers hope that a low-capital process can be developed to produce biorenewable fuels.

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