

Use of Gamma-Valerolactone as an Illuminating Liquid and Lighter Fluid

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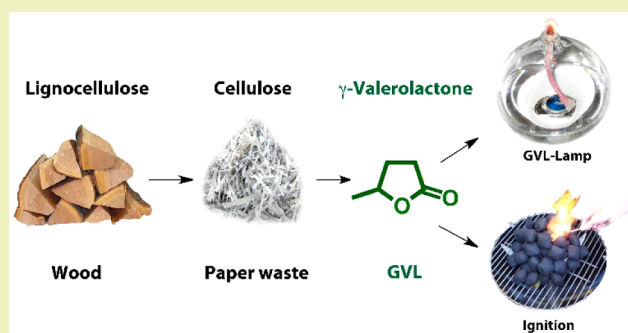
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S Supporting Information

ABSTRACT: The sulfuric acid-catalyzed conversion of paper wastes in gamma-valerolactone (GVL) or dioxane leads to the formation of levulinic acid (LA) and formic acid (FA), which can be converted to GVL by transfer-hydrogenation using the Shvo catalyst *in situ* or separately. The isolation of LA and FA was assisted by the neutralization of the sulfuric acid with ammonia to form a biphasic system. While the ammonium sulfate and most of FA and some of LA were in the aqueous phase, the organic solvent-rich phase contained most of the LA and some of the FA. GVL was used as an illuminating liquid in glass lamps for hours without the formation of noticeable smoke and/or odor even in a small room. While neat GVL can be used for the safe but somewhat slow lighting of charcoal, the ignition with different mixtures of GVL (95 or 90 vol %) and ethanol (5 or 10 vol %) was reduced to a convenient few seconds. Ignition tests of charcoal combined with emission analyses revealed that by increasing the ethanol content to 10 vol % the relative VOC emission can be decreased by 15% compared to the commercial lighter fluids.

KEYWORDS: Gamma-valerolactone, Ethanol, Illuminating liquids, Lighter fluids, Paper wastes



INTRODUCTION

The sustainability of mankind used to be highly dependent on the geographical locations because of the markedly different, and in most areas, seasonal weather conditions limiting the access to water and food.¹ The latter requires the availability of carbon dioxide,² water, and light, the three key components of photosynthesis.³ In addition, fire has been another important tool of maintaining a sustainable and significantly better quality of life.⁴ For example, campfires, torches, and oil and gas lamps have been the light sources after sunset for centuries,⁵ especially before the discovery of electricity and the development of lighting fixtures.⁶ Although there have been a large variety of ready-to-eat vegetables and fruits in many parts of our planet, most cultures have applied cooking with the help of fire.⁷ While early cooking used wood, charcoal, or coal for heat generation, currently most cook stoves operate by either natural gas or electricity.⁸

The use of animal fats, fish, palm, or olive oils as illuminating liquids dates back to ancient civilizations.^{9,10} Small open bowls with a lip or spout to hold the wick have been used as oil lamps from ~5000 BCE. The candles were invented in 3000 BCE and became the primary light source between the 14–17th

centuries.¹¹ Although kerosene was discovered by Muhammad ibn Zakariya Razi, a Persian scholar in 900 BCE,¹² it was not used until much later.¹³ Safer and completely enclosed oil reservoir lamps were used after 500 BCE. Aimé Argand, a Swiss physicist and chemist, greatly improved the performance of oil lamps by using improved oils and glass chimneys to draft the flame in early 1780s.¹⁴ A new illuminant, called *Paraffin Oil*, was patented by James Young in England in 1850.¹⁵ Practically the same illuminating liquid was patented under the name *Kerosene* by Abraham Gesner in the United States in 1854.¹⁶ The next generation of lighting used gas, which was then replaced with electric lighting.⁵

Lighter fluids have also been used for centuries for cooking, especially to start barbecues and cooking fires, all over the world. In general, the role of a lighter fluid is to be distributed on the surface of solid combustibles such as wood,⁴ coal,⁴ or charcoal,^{4,17} readily ignite to combust, and reliably burn to provide enough heat that a bed of the solid combustible will

Received: September 26, 2014

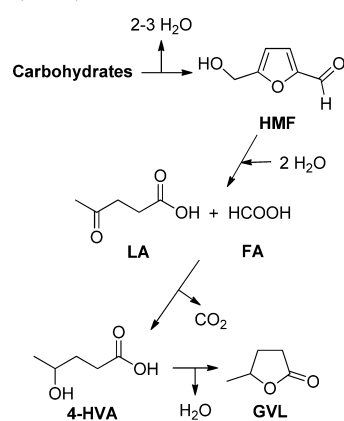
Revised: June 28, 2015

Published: July 30, 2015

start to burn. Traditionally, lighter fluids were made from vegetable oils or lard. Although the use of relatively cheap crude oil-based lighter fluids has rapidly become popular, their use has raised several environmental issues including the emission of volatile organic compounds and carbon dioxide. It should be noted that 41% of households that have a grill in the United States use charcoal as the cooking fuel.¹⁸ Therefore, the development of appropriate biomass-based nontoxic lighter liquids could lower emission and by appropriate selection even the unpleasant smell could be eliminated.¹⁹

We have suggested that gamma-valerolactone (GVL) can be considered as a sustainable liquid because it is renewable and has environmentally friendly physical and chemical properties.²⁰ Since the conversion of carbohydrates^{21–27} including cellulose^{28,29} to GVL has been demonstrated (Scheme 1), the valorization of biomass-based wastes by converting their carbohydrate contents to GVL could become the foundation of a sustainable technology.³⁰

Scheme 1. Conversion of Carbohydrates to Gamma-Valerolactone (GVL)



We report the sulfuric acid-catalyzed conversion of paper wastes to levulinic acid (LA) and formic acid (FA),²⁴ which can be used to produce GVL in the presence of the Shvo catalyst.^{20,24,31} GVL was evaluated as an illuminating liquid and a lighter fluid.

■ SYNTHESIS AND APPLICATION OF GVL

In order to demonstrate the valorization of paper wastes, several pages of white paper (Figure 1a and b) and a local colored newspaper (Figure 2a and b) were cut into small chips by a paper shredder. We have first investigated the conversion of 0.33 g of paper wastes to levulinic acid (LA) and formic acid (FA) in the presence of sulfuric acid in GVL at 130 °C (Figures 1 and 2).

The major content of paper is cellulose, which will undergo acid-catalyzed hydrolysis to glucose. Indeed, glucose (0.15 mmol) was detected by ¹H NMR after 1 h, which completely disappeared after 4 h (Figure S1). The transient formation of 5-hydroxymethylfurfural (HMF) and furfural (FF) from glucose was observed, as expected.³² The concentrations of LA and FA increased for several hours and reached the maximum after 4 h. The yield of LA from the white paper chips were slightly higher (24.5 wt %) than from the colored newspaper (21.1 wt %), indicating a higher cellulose content. It appears that some of the inks from the colored newspaper were dissolved in the mixture of GVL/H₂O/H₂SO₄, but the components of the inks

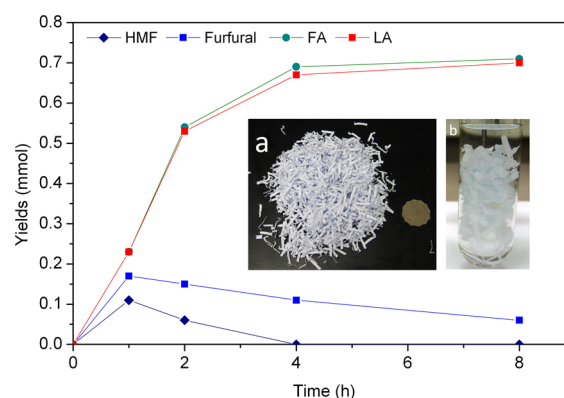


Figure 1. Conversions of white paper chips and the yields of the major products (HMF, LA, FA, and furfural). Insets: (a) white paper chips (with a 2 HK\$ coin) and (b) white paper chips in GVL/H₂O/H₂SO₄ before heating.

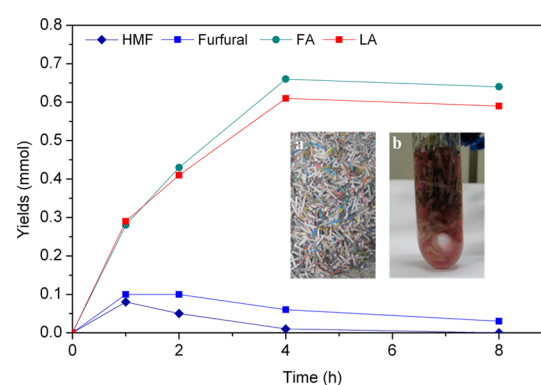


Figure 2. Conversions of newspaper chips and the yields of the major products (HMF, LA, FA, and furfural). Insets: (a) newspaper chips and (b) newspaper chips in GVL/H₂O/H₂SO₄ before heating.

had little impact on the yields. Thus, the white and colored paper wastes could be combined and valorized together—an important factor to develop high volume collection and cheaper processing.

In order to evaluate the possibility to use less GVL, we have investigated the conversion of 0.33 g white paper wastes in 10.0, 5.0, or 2.5 mL of GVL in the presence of 1.5 mL of 5 M sulfuric acid (Table 1). The yields of LA and FA were

Table 1. Conversion of 0.33 g White Paper Wastes to LA and FA in Various Amounts of GVL in the Presence of 1.5 mL 5 M Sulfuric Acid at 130 °C for 8 h

material	GVL [mL]	LA [mmol]	FA [mmol]	LA [wt %]
white paper	10	0.506	0.606	17.8
	5	0.512	0.593	18.0
	2.5	0.538	0.657	18.9

practically the same (around 18 w%), indicating very little solvent effect at the same substrate to acid ratio. However, the use of four times less GVL should significantly lower the cost of the process.

We have also shown that LA (1.82 mmol), obtained by the conversion of 1.06 g of white paper waste in the presence of 3.75 mL of 5 M sulfuric acid in 25 mL GVL at 120 °C for 38 h, can be transfer-hydrogenated *in situ* with FA in the presence of 0.055 g (0.046 mmol) of Shvo catalyst to give an estimated

yield of 1.54 mmol (15 wt %) GVL. Since the *in situ* catalytic conversion of LA and FA to GVL was rather slow, we have evaluated an alternative process by utilizing dioxane and the neutralization of sulfuric acid with ammonia to form a biphasic system (Figure S2). While the ammonium sulfate and most of the FA and some LA were in the aqueous phase, the organic phase contained most of the LA and some of the FA. The final separation of LA and FA from the two phases by distillation could be followed by their conversion to GVL separately according to our reported procedure (Figure S3).³¹ For example, 1 g of white paper chips were converted to 1.55 mmol (18.0 wt %) LA and 1.44 mmol (6.6 wt %) FA.

GVL burns well in glass lamps without noticeable black smoke and odor even in a small room for hours³³ (Figure 3 and



Figure 3. Burning two glass GVL lamps.

Click on [GVL-shaped and -powered glass lamp](#)). It should be noted that similar performance was observed for a sample of GVL, which was isolated by distillation from reaction mixture of the one-pot conversion of waste papers.

The video of the ignition and burning of ethanol (as a biomass-based reference) and GVL was recorded and processed by Windows Media Player to select several snap shots at different times (Figure 4). Thus, 20 mL of EtOH or GVL was placed in a 25 mL porcelain evaporating dish placed on wire gauze on a tripod in a fume hood (Figure 4a). A match-stick was ignited, and its flame was positioned above the liquid (Figure 4b). It was then slowly lowered to just above the liquid, which was considered as the starting time of the ignition. The flame was kept at this position until the liquid was ignited. Ethanol ignited at 0.32 s and burned violently (Click on [EtOH](#)), which could be a significant risk to potential users. The ignition of GVL took about 16 s; the size of the flame grew slowly (Click on [GVL](#)), and the fire remained steady and stable for minutes. These properties could be a great advantage of GVL when it is used as a transportation fuel,²⁰ especially in the case of accidents with fuel spills.

Since the ignition of GVL seemed to be slow for a lighter liquid, we have investigated the ignition and burning of charcoal by using ethanol, GVL, and their mixture to develop not just a green and safe igniting lighter liquid, but a fast igniting lighter liquid. Charcoal was placed on wire gauze on a tripod in a fume hood (Figure 5a). One milliliter samples of the lighter fluids were injected on the top of the charcoal using a syringe. After a few seconds, a matchstick was ignited, and its flame was positioned above the charcoal (Figure 5b). It was then slowly lowered to touch the surface of the charcoal (Figure 5c), which was considered as the starting time of the ignition. While EtOH

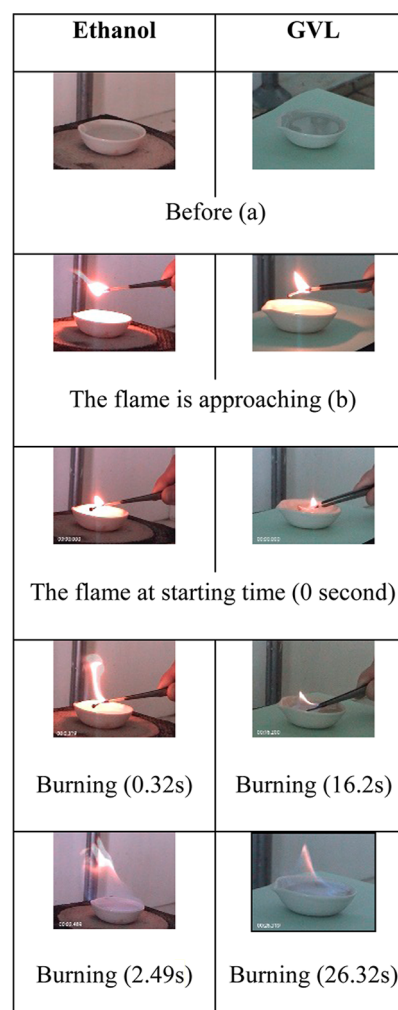


Figure 4. Ignition and burning of ethanol and GVL.

was ignited at 0.12 s and burned violently (Click on [Ethanol](#)), it took about 7 s to ignite GVL (Click on [GVL](#)). The ignition experiments of EtOH or GVL either in the liquid form or on the surface of charcoal have shown that the behavior of these liquids are in accordance with their vapor pressures and flash points. A user-friendly biolighter fluid was therefore developed by testing the mixture of GVL and EtOH in different ratios. Excellent ignition performance was already observed when only 5 vol % EtOH was added to GVL (Click on [a mixture of 5 vol % EtOH and 95 vol % GVL](#)); the ignition time was a few seconds (2.2 s) (Figure 5) due to the lower vapor pressure and flash point of ethanol. The size of the flame grew slowly, and the fire remained steady and stable for minutes due to the excellent performance of GVL. The ignition time was further reduced to 0.1 s by increasing the ethanol content from 5 vol % to 10 vol %. Again, no smoke and unpleasant odor was detected by using the GVL–ethanol mixtures.

■ LIGHTER FLUIDS TEST ON CHARCOAL

The performance of Dunasol, a commercially available lighter fluid, GVL, and the mixture of 90 vol % GVL and 10 vol % ethanol were evaluated according to the ignition experiments described by the U.S. Environmental Protection Agency (US EPA) §59.208 testing protocol.³⁴ The continuously monitored VOC concentrations during the ignition test are shown in Figure 6. In order to verify that the VOC originates exclusively

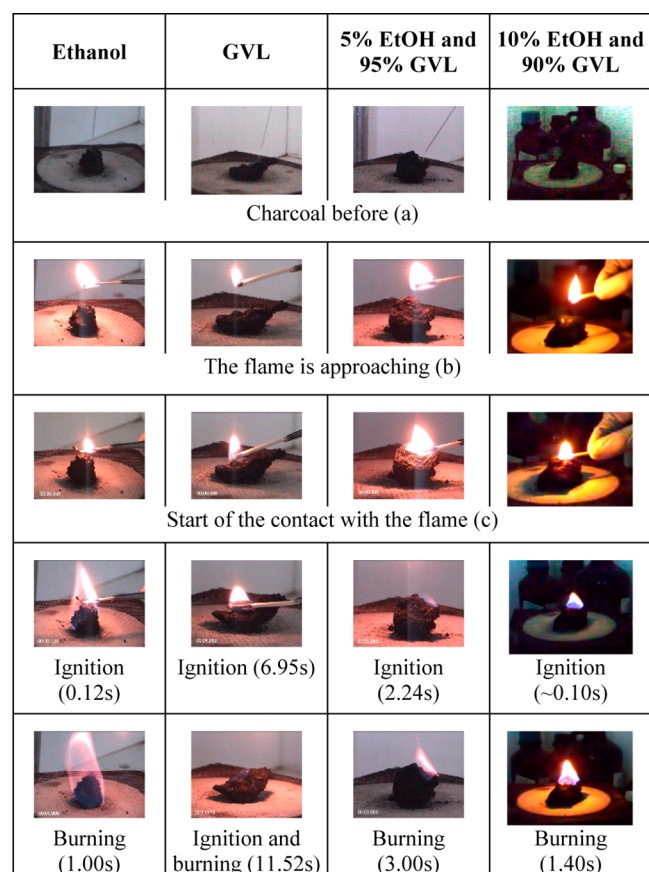


Figure 5. Ignition and burning of charcoal using ethanol, GVL, a mixture of 5 vol % EtOH and 95 vol % GVL, and a mixture of 10 vol % EtOH and 90 vol % GVL.

from the lighter material evaporation and/or combustion, electric ignition was also tested.

While the VOC concentration profiles of GVL and Dunasol were very similar, the latter reached the maximum value a few minutes faster than GVL. Contrarily, the VOC concentration profile of the 90 vol % GVL–10 vol % EtOH revealed the presence of a two component mixture. First, the VOC started

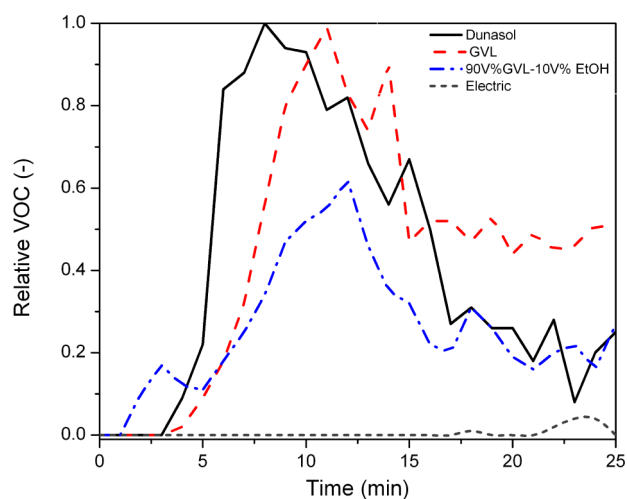


Figure 6. Relative VOC values during ignition and burning of charcoal using Dunasol, GVL, a mixture of 90 vol % GVL and 10 vol % EtOH, and electric ignition.

to increase due to the low vapor pressure of ethanol. After reaching a local maximum and then a local minimum, the further increase was caused by the combustion of GVL. The maximum VOC emission of GVL was approximately as high as that of the Dunasol. However, the addition of ethanol to GVL lowered the overall VOC emission and the maximum as well. All the tested lighter materials fulfilled the requirements of the US EPA §59.208 testing protocol. Finally, the VOC emission data, expressed in $\text{g CH}_2\text{,eq}$ (Figure 7), clearly established that

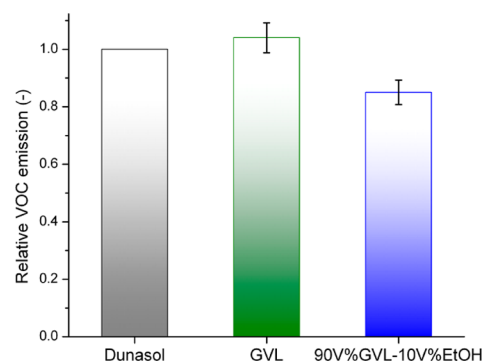


Figure 7. Relative VOC emission of GVL and a mixture of 10 vol % EtOH and 90 vol % GVL related to the commercially available Dunasol.

GVL generated similar VOC emission than that of Dunasol; however, the mixture of 90 vol % GVL and 10 vol % EtOH decreased the VOC emission by $15 \pm 0.75\%$.

A picture taken at the end of the 25 min-long lighter fluid test showed that more than 70% of the charcoal was covered with ash as required by the US EPA §59.208 testing protocol (Figure S4).

CONCLUSIONS AND SUMMARY

GVL was prepared from waste papers and used as an illuminating liquid in two different glass lamps for hours without the formation of smoke and noticeable odor even in a small room. While neat GVL can be used for the slow and safe lighting of charcoal, the mixture of 90 vol % GVL and 10 vol % ethanol accelerated the lighting to a convenient few seconds. Since both GVL and ethanol are renewable and nontoxic, their use can be considered a much more sustainable approach, especially when compared to fossil resources-based illuminating and lighter liquids. In addition, cooking food and/or lighting BBQs with lower toxicity fuels are certainly preferable in a healthy society.

EXPERIMENTAL SECTION

H_2SO_4 (95–97%, Sigma-Aldrich), formic acid (98–100%, Merck), and biphenyl (99.5%, Sigma-Aldrich) were used as received. γ -Valerolactone (GVL, 98%, Aldrich) was distilled before use.

NMR spectra were collected using a Bruker AV III 400 instrument at 20 °C. Quantitative ^1H NMR was carried out using 90° flip angles with a recycle delay of 80 s. Yields were measured using ^1H NMR of the reaction mixture, as calculated from the addition of known amounts of biphenyl as an internal standard.

The videos were recorded with a commercial digital camera and processed by Windows Media Player and Adobe Premiere Pro softwares to select several snap shots at different times on two decimal place accuracy.

Conversion of Paper Wastes Using Sulfuric Acid in GVL. The conversion of white paper and newspaper wastes in GVL was

performed in a 15 mL Ace pressure tube (bushing type, front seal, L × O.D. 10.2 cm × 25.4 mm). The reactions were performed by heating a mixture of 0.33 g of paper waste, 0.1 g of biphenyl as internal standard, 1.5 mL 5 mol/L H₂SO₄, and 10 mL GVL in an oil bath at 130 ± 1 °C. The tube was cooled to room temperature at certain time intervals to take liquid samples (0.3 mL) to monitor the progress of the reactions by ¹H NMR. These experiments were repeated three times.

A total of 1.06 g of white paper chips, 3.75 mL of 5 M H₂SO₄, and 25 mL of GVL was heated in a 150 mL three-necked round-bottomed flask at 120 °C for 38 h. The yields of LA and FA were 20 wt % (1.82 mmol) and 9 wt % (1.9 mmol), respectively. In order to reach FA/LA = 3, the FA was increased to 5.7 mmol, and 0.055 g (0.046 mmol) {[2,5-Ph₂-3,4-(p-MeOPh)₂-(η⁵-C₅O)]₂H}Ru₂(CO)₄(μ-H)} was added. The reaction mixture was heated at 100 °C for 13 h. The concentration of LA decreased to 0.273 mmol, indicating that 85% of LA was converted. Thus, the GVL yield was 1.54 mmol or 15 wt % based on the weight of the white paper waste chips, which was separated from the side-products by fractional distillation. The purity of GVL, collected at 48–50 °C and 3.75 mmHg, was 99.9% according to GC-MS and NMR analysis.

Conversion of Paper Wastes Using Sulfuric Acid in Dioxane.

The conversion of white paper wastes in dioxane was performed in a 15 mL Ace pressure tube (bushing type, front seal, L × O.D. 10.2 cm × 25.4 mm). The reactions were performed by heating a mixture of 1 g of white paper chips, 0.1 g of biphenyl, 4 mL of 5 mol/L H₂SO₄, and 4 mL of dioxane in an oil bath at 130 ± 1 °C for 14 h. The tube was cooled to room temperature, and some solid humins were removed by filtration. The reaction mixture was neutralized with 2.71 g of 25% NH₄OH. The formations of two phases were observed (Figure S2), which were separated and analyzed by NMR. While the upper dioxane phase contained 1.33 mmol LA and 0.34 mmol FA, the lower aqueous phase contained 0.22 mmol LA and 1.1 mmol FA. Thus, the combined yields were 1.55 mmol (18.0 wt %) LA and 1.44 mmol (6.6 wt %) FA.

Transfer-Hydrogenation of LA with FA in Dioxane. The transfer-hydrogenation of LA with FA in dioxane was performed in a 15 mL Ace pressure tube (bushing type, front seal, L × O.D. 10.2 cm × 25.4 mm). The starting biphasic system was obtained by neutralizing a mixture of 2.11 mmol LA, 3.04 mmol FA, 4 mL of 5 mol/L H₂SO₄, and 4 mL of dioxane with 2.71 g of 25% NH₄OH. The upper organic phase was separated, and 0.0068 mmol {[2,5-Ph₂-3,4-(p-MeOPh)₂-(η⁵-C₅O)]₂H}Ru₂(CO)₄(μ-H)} was added. The reaction mixture was heated in an oil bath at 130 ± 1 °C. NMR samples taken at 0, 2, and 3 h have shown the formation of GVL as the only product in solution.

Ignition and Burning of Ethanol and GVL. Twenty milliliters of EtOH or GVL was placed in a 25 mL porcelain evaporating dish placed on wire gauze on a tripod in a fume hood. A matchstick was ignited, and its flame was immediately positioned above the liquid. It was then slowly lowered to just above the liquid to initiate the burning. Since the two experiments were performed within 10 min, it was assumed that the temperature and the humidity was constant during the experiments.

Ignition and Burning of Charcoal Using Ethanol, GVL, a Mixture of 5 vol % EtOH and 95 vol % GVL, and a Mixture of 10 vol % EtOH and 90 vol % GVL. Untreated commercial charcoal stored in a closed bag in the laboratory at 22–23 °C for 72 h was placed on wire gauze on a tripod in a fume hood. One milliliter of the corresponding lighter fluids was injected on the top of the charcoal using a syringe. After a few seconds, a matchstick was ignited, and its flame was positioned above the charcoal. It was assumed that the temperature and the humidity was constant during the experiment since the experiments were performed within minutes after each other.

Ignition Test of Charcoal According to US EPA §59.208 Protocol. The charcoal and lighter liquids were conditioned for 72 h before the test. The relative humidity was 42%, and the temperature of the laboratory was 23 °C. An approximate amount of 900 g of nontreated charcoal was placed on a test grill. A total of 100 mL of each lighter liquid was poured onto the surface of the charcoal and ignited within 30 s. During the 25 min-long test procedure, the emissions were monitored continuously. The sampling ended for each test run when all the following conditions were met: at least 70% of

charcoal surface was covered with ash, the temperature above the pile was at least 93 °C, and the VOC concentration was below 30 ppm_v, CH_{4,eq}. VOC concentration was measured by a Testo 350 combustion and emission analyzer with an accuracy of 10 ppm_v. The VOC sensor was adjusted to methane in the factory.

■ ASSOCIATED CONTENT

Supporting Information

NMR spectra relevant to the sulfuric acid-catalyzed conversion of white paper chips. A picture of the biphasic separation of the reaction mixture. A picture of the charcoal at the end of the ignition test. Video links of illumination and lighting with GVL, EtOH, and 95 vol % GVL and 5 vol % EtOH. The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acssuschemeng.5b00465.

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Author Contributions

The manuscript was written through contributions of all authors. All authors have given approval to the final version of the manuscript.

Funding

This work was partially funded by the Hungarian Scientific Research Fund (OTKA-T047207 and OTKA-CNK 78065), City University of Hong Kong (9380047), and the Innovation and Technology Support Programme of the Innovation and Technology Fund of the Government of the Hong Kong SAR (ITS/079/13). Any opinions, findings, conclusions or recommendations expressed in this material/event (or by members of the project team) do not reflect the views of the Government of the Hong Kong Special Administrative Region, the Innovation and Technology Commission or the Panel of Assessors for the Innovation and Technology Support Programme of the Innovation and Technology Fund. L. T. Mika is grateful for the support of János Bolyai Research Scholarship of the Hungarian Academy of Sciences.

Notes

The authors declare no competing financial interest.

■ ABBREVIATIONS

GVL, gamma-valerolactone; LA, levulinic acid; FA, formic acid; EtOH, ethanol ppm_v, CH_{4,eq}, 1 mL methane in 1 m³ air

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