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Cellulosic Biofuels

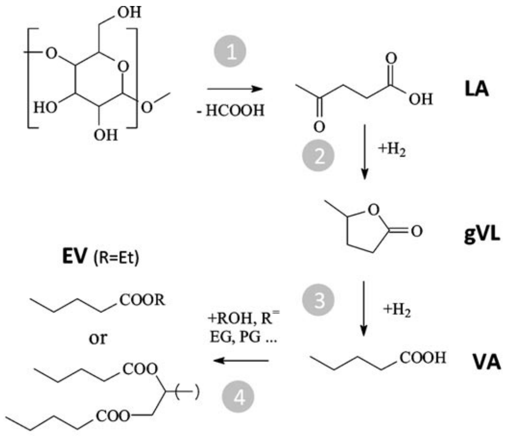
Valeric Biofuels: A Platform of Cellulosic Transportation Fuels**

Jean-Paul Lange, Richard Price, Paul M. Ayoub, Jurgen Louis, Leo Petrus†, Lionel Clarke, and Hans Gosselink*

At the beginning of the 21st century mankind is facing an energy challenge as a consequence of the world's increasing energy demand, the depletion of "easy" oil and gas fields, and the impact of CO_2 emissions on the Earth's climate ("three hard truths").[1] Much research is therefore being devoted to the exploration and development of new, carbon-lean energy sources. These include biofuels, which are the most promising option for the transportation sector in the coming decades.[2] The first generation of biofuels is presently produced from sugars, starches, and vegetable oil. Although instrumental in developing the market, these biofuels are not likely to deliver the large volumes needed for the transport sector because they directly compete with food for their feedstock. A more promising feedstock is lignocellulosic material, which is more abundant, has a lower cost, and is potentially more sustainable.[3]

Lignocellulose is recalcitrant and, therefore, requires complex and expensive processes for upgrading to biofuels.[4] Interestingly, it has been claimed that levulinic acid (LA) can be easily and cheaply produced from lignocellulosic materials by using a simple and robust hydrolysis process.[5] Several LA derivatives have been proposed for fuel applications, for instance ethyl levulinate (EL), γ-valerolactone (gVL), and methyl tetrahydrofuran (MTHF).[5,6] However, these components do not exhibit satisfactory properties when blended in current fuels. Herein, we present a new platform of LA derivatives, the "valeric biofuels", which we have been developing since 2004 and which can deliver both gasoline and diesel components that are fully compatible with transportation fuels.

The manufacture of valeric biofuels (Scheme 1) consists of the acid hydrolysis of lignocellulosic materials to LA, the hydrogenation of the acid to gVL and valeric acid (VA), and finally esterification to alkyl (mono/di)valerate esters. One of these steps, the hydrogenation of gVL to VA (Scheme 1, step 3), has not been reported in the literature and was developed in our laboratory. All the other steps are known but were nevertheless revisited and, wherever possible, improved. This holds for the acid-catalyzed hydrolysis of lignocellulose to LA,[5,7] the hydrogenation of LA to gVL with the use of supported metal catalysts,[8] as well as the familiar esterification of carboxylic acids. Herein, we present the main results of the hydrogenation of gVL to VA (Scheme 1, step 3), key improvements in the hydrogenation of LA to gVL (step 2), options for integrating steps 2–4, and finally a thorough evaluation of the fuel performance of the resulting



	1. Hydrolysis	2. Hydrogenation	3. Hydrogenation	4. Esterification
Catalyst	H_2SO_4	Pt/TiO_2	Pt/ZSM-5	IER
Selectivity	50-60%	>95%	>90%	>95%
Productivity	>0.1 h^{-1}	>10 h^{-1}	>1 h^{-1}	>0.02 h^{-1}
Concentration	<5%	>90%	>50%	>50%

Scheme 1. Platform of valeric biofuels: reaction scheme and key performance factors for the individual process steps (selectivity [mol %], productivity [$t_{product}\,m^{-3}{}_{reactor}\,h^{-1}$], and concentration [wt %]). EV: ethyl valerate; EG: ethylene glycol; PG: propylene glycol; IER: acidic ion-exchange resin.

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[*] Dr. J.-P. Lange, Dr. P. M. Ayoub, Dr. L. Petrus, Dr. H. Gosselink
Shell Global Solutions International B.V.
Shell Technology Centre Amsterdam
Grasweg 31, 1031 HW Amsterdam (The Netherlands)
Fax: (+31) 20-630-3010
E-mail: jean-paul.lange@shell.com

Dr. R. Price, Dr. L. Clarke
Shell Global Solutions (UK)
Shell Technology Centre Thornton
Pool Lane, Ince, Cheshire CH2 4NU (UK)

Dr. J. Louis
Shell Global Solutions Germany
Produkte, Anwendung und Entwicklung
Hohe Schaar Strasse 36, 21107 Hamburg (Germany)

[†] Deceased

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valeric biofuels. Details of the experimental procedures and secondary results are available in the Supporting Information.

gVL is a relatively stable product under hydrogenation conditions. It was, nevertheless, hydrogenated to VA in the presence of bifunctional catalysts that contain both hydrogenation and acidic functions. An evaluation of about 150 catalysts in a continuous high-pressure plug-flow reactor identified Pt-loaded SiO_2-bound H-ZSM-5 as a very effective catalyst (Figure 1 a). However, good yields were also achieved with other zeolites and hydrogenation metals. Promising zeolites included the small-pore TON, the medium-pore PSH-3 (also called MCM-22), and the large-pore mordenite and Beta. The acidic zeolites can be replaced by other strong or weak solid acids, such as W/ZrO_2 and amorphous silica–alumina (ASA). Clearly, the conversion of gVL to VA is not very demanding in terms of "shape selectivity" or acid strength. Pt, Pd, and Rh from among the noble metals are all particularly active; however, Rh was not desirable because it co-produced significant amounts of gas. Alloying Pt or Pd with other noble metals did not deliver measurable improvements.

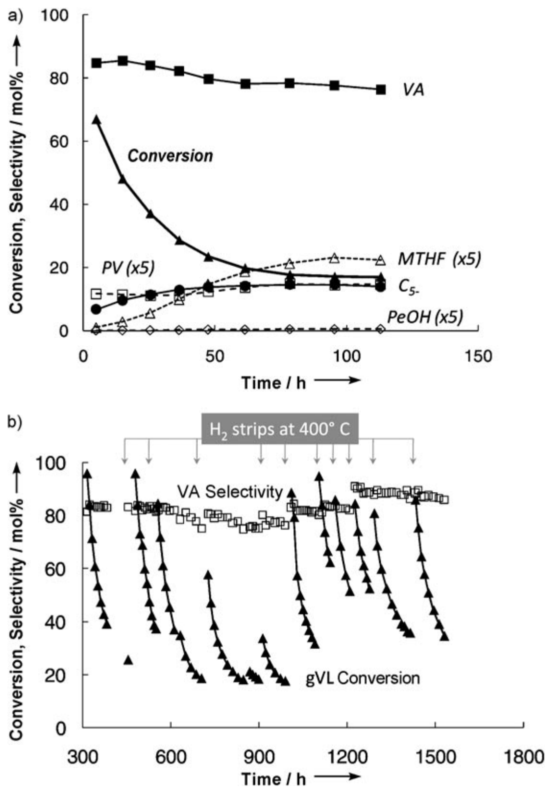
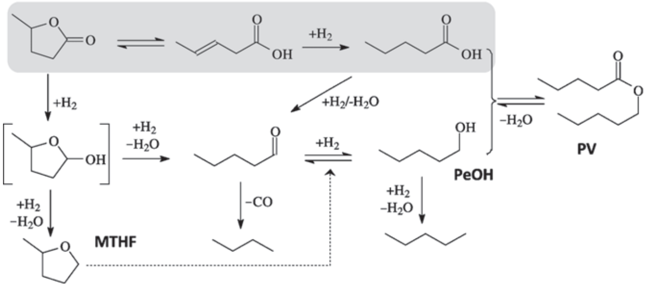


Figure 1. Conversion of gVL to VA over Pt/H-ZSM-5/SiO_2 catalysts. a) Conversion and selectivity; b) long-term operation with multiple regeneration by hot H_2 strips at 10 bar H_2 and 400°C (0.7% metal loading; run conditions: 250°C, 10 bar, H_2/gVL molar ratio 9:1, weight hourly space velocity (WHSV) = 2 h). C_{5-}: C_1–C_4 hydrocarbons, PV: pentyl valerate, PeOH: 1-pentanol.

The reaction mechanism of step 3 (Scheme 1) is believed to proceed by acid-catalyzed ring opening of gVL to pentenoic acid and subsequent hydrogenation to VA (Scheme 2). The production of VA requires a balancing of the acidic and hydrogenation functionalities of the catalyst: changing the metal/zeolite ratio either increases the co-production of pentenoic acid (low metal loading) or favors the formation of MTHF, pentanal/pentanol, and/or pentane/butane (high metal loading). Pentyl valerate (PV) was observed as a minor co-product (Figure 1 a) and is likely to have formed by the esterification of VA with an over-hydrogenation product, such as 1-pentanol or MTHF. For instance, co-feeding MTHF to the gVL feed resulted in a significant increase in PV production.



Scheme 2. Probable reaction mechanism for the conversion of gVL to VA over bifunctional catalysts.

Catalyst extrudates of Pt/ZSM-5 bound with SiO_2 (1.6 mm diameter) were operated with high activity (differential VA productivity of approximately 2 $g_{VA}\,g_{cat}^{-1}\,h^{-1}$) and high selectivity (> 90 mol%). This performance could be maintained for more than 1500 h with intermittent catalyst regeneration under hot H_2 and/or airflow at 400°C (Figure 1 b). Once unloaded, the spent catalyst showed marginal loss of Pt and Al (from the zeolite framework), marginal decrease in support surface area, and no measurable loss of mechanical strength of the catalyst extrudates. Pt/ASA catalysts were also very promising candidates. Although they had a lower initial activity, they showed no sign of deactivation over runs of 200–300 h. Their stability is tentatively attributed to their weaker acidity, which may facilitate the desorption of reactive intermediates, such as pentenoic acid, and thereby depress their tendency to form oligomeric deposits that poison the catalyst surface.

The literature available on the hydrogenation of LA to gVL (Scheme 1, step 2) provides no information on the long-term stability of the catalysts or their resistance to leaching when operating in liquid LA.[8] These issues were addressed through leaching tests of various supports, catalyst evaluation over > 100 h, and analysis of spent catalyst samples. Carbon supports are known to resist aggressive aqueous media but do not survive frequent regeneration by coke burn-off. Preference was therefore given to SiO_2, TiO_2, and ZrO_2 supports, which are stable to "decoking" conditions and appeared to retain their integrity after a week's exposure to hot carboxylic acid (LA or VA). This contrasts with other oxidic materials (e.g., alumina, silica–alumina, and oxides of magnesium, barium, and antimony) that are leached or even dissolve under these conditions.

Evaluation of some 50 catalysts showed the best performance was with Pt supported on TiO_2 or ZrO_2: LA was hydrogenated with high activity (differential productivity 10 $g_{gVL}\,g_{cat}^{-1}\,h^{-1}$), high selectivity to gVL (> 95 mol %), and marginal deactivation over 100 h (Figure 2). The main by-products, VA and MTHF, were formed with < 0.5 mol % selectivity. Carbon and SiO_2 supports provided a tenth of the activity observed with TiO_2 and ZrO_2 supports (see the Supporting Information). Pd-based catalysts also showed a much lower activity and selectivity than their Pt counterparts. Alloying the Pt with other noble metals did not improve catalytic performance (see the Supporting Information). Finally, the resistance to leaching was further confirmed by X-ray photoelectron spectroscopy analyses of spent Pt/TiO_2 and $PtRe/ZrO_2$ catalysts, which showed no significant decrease of Pt/Ti or Pt/Re/Zr ratios, and thereby no significant loss or sintering of active metal.

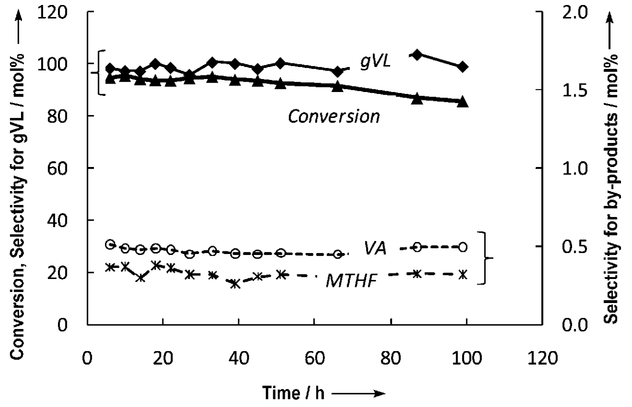


Figure 2. Hydrogenation of LA to gVL over Pt/TiO_2 (1 wt % metal, 200 °C, 40 bar H_2, H_2/LA molar ratio 5:1, WHSV = 9 h).

The four-step process discussed so far provides flexibility and robustness, which are invaluable in work toward deploying a novel technology. However, options for future cost reductions through process integrations have additionally been identified; for example, combining the LA and VA hydrogenation steps with the possibility of even integrating the esterification step. These schemes are described in the Supporting Information; however, one of them is worth presenting here. This is the single-step conversion of gVL to PV, which is a promising diesel component (see below). PV was indeed produced with 20–50 % selectivity upon passing gVL over Pt or Pd/TiO_2 catalysts at 275–300 °C (see the Supporting Information). Pt-based catalysts tend to provide higher PV/VA ratios but also produce more undesired light hydrocarbons. VA can be recycled to the reactor for further conversion to PV. Note that PV can also be co-produced over bifunctional VA catalysts (e.g., Pt/ZSM-5) upon increasing the hydrogenation activity to produce more MTHF and/or pentanal, and recycling these co-products over the reactor for upgrading to PV.

Beyond developing the manufacturing route, we also carried out a thorough study of the fuel properties of the "valeric biofuels". In a first step, we focused on their compatibility with current fuels. The components that fail on these criteria would require modifications of vehicles and/or the distribution network and would, therefore, suffer from a slow and costly deployment. Fuel compatibility was assessed against a few basic properties such as polarity, (volumetric) energy content, boiling point, and ignition indices, for example octane or cetane number (CN) for gasoline and diesel, respectively (Figure 3). The components that successfully passed this screening were then evaluated against additional properties, such as oxidation stability, fouling tendency, corrosion, lubricity, water affinity, and response to conventional fuel additives.

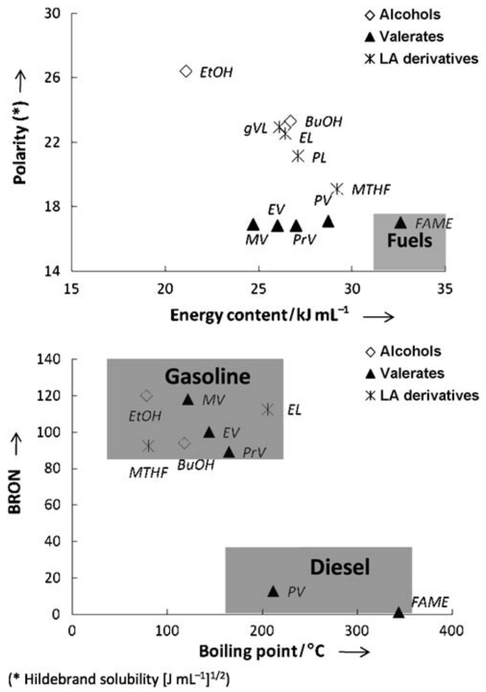


Figure 3. Screening parameters for fuel performance (MV, EV, PrV, and PV: methyl, ethyl, propyl, and pentyl valerates, respectively). The blending research octane number (BRON) values of PrV, PV, and fatty acid methyl ester (FAME) are estimated from a CN–RON correlation;[10] gray shading represents the property windows of hydrocarbon fuels.

Valeric biofuels passed all these tests (Figure 3). They have acceptable energy densities and more appropriate polarities than current and alternative candidate biofuels (ethanol, *n*-butanol, EL, gVL, and MTHF). Their volatility–ignition properties make them compatible for either gasoline or diesel applications, depending on their alkyl chain length. For example, regular gasoline splash blended with ethyl valerate (EV) at 10 and 20 vol % still meets the research (RON) and motor octane number (MON) specification for European gasoline (EN 228; see the Supporting Information). The relatively low polarity of EV makes it less sensitive to elastomer swell or water pickup than EtOH or EL (Figure 4). EV also offers the advantages of a higher energy density and lower blending volatility (dry vapor pressure equivalent, DVPE) than EtOH. This eliminates the need to

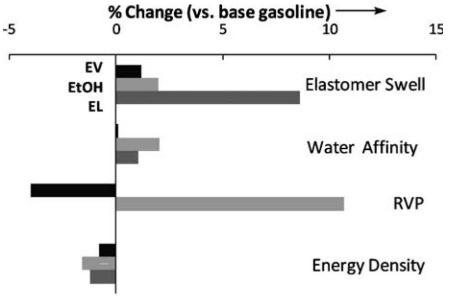


Figure 4. Fuel performance of EV, ethanol (EtOH), and EL blended at 5% in gasoline (the water affinity is measured for neat biofuel). RVP: Reid vapor pressure.

remove light hydrocarbons from the base fuel prior to introducing the biocomponent. Interestingly, ethyl pentenoate (EP), which is readily produced from gVL,[9] is also a promising gasoline component; it presented better octane properties than its saturated analogue EV without showing detrimental effects on other properties.

Heavier esters, such as butyl and pentyl valerates, showed polarity, volatility, and ignition properties that are suitable for diesel (Figure 3). PV has better volatility and cold-flow property match with diesel than FAME. However, this is at the cost of a lower energy density. Di- and trivalerates, which can be produced by esterifying VA with ethylene and propylene glycols as well as glycerol, are compatible with diesel with respect to solubility and volatility. However, their modest cetane properties become limiting to the blend ratio at which they can be used in diesel. All these heavy valerate esters are soluble in diesel to high concentrations, a feature that does not apply to heavy levulinates (e.g., pentyl levulinate, PL). Valerate esters, such as FAME, provide lubricity benefits to diesel.

The fuel evaluation was complemented by a road trial run on a blend of 15 vol% EV in regular gasoline. The trial was based on ten vehicles (both new and used cars) that are representative of current market technologies. Mileage was accumulated by contract drivers who followed a mixed driving pattern (500 km day^{-1}) for a cumulative distance of 250000 km. Attention was paid to exhaust emissions, performance, drivability, oil quality, status of engine and fuel lines, and information from the engine management system (see the Supporting Information). The presence of EV in gasoline showed no measurable impact on engine wear, oil degradation, vehicle durability, engine deposits, or regulated tailpipe emissions (EURO 4 and 5 specifications). Some power benefits were realized as a result of the good octane properties of EV. However, the lower energy density did result in a small loss in volumetric fuel economy compared to non-oxygenated gasoline. The 15 vol% EV blend was stable over the four-month period of the test and had no negative impact on the fuel storage and dispensing equipment (tanks, pipes, pumps, and filters).

In summary, valeric esters represent a new class of cellulosic biofuels that can outperform previously identified candidate molecules in terms of both their manufacture and fuel properties. The initial production step, LA manufacture, is simple and robust. However, it is the advance in the conversion of LA to VA that has opened up the complete manufacturing process. The valeric platform potentially offers cellulosic biofuels that can be used as components in both gasoline and diesel up to high blend ratios.

Note added upon revision: The potential of LA and gVL as intermediates for biofuel manufacture is further confirmed by a paper that appeared during revision of this communication. It reports the conversion of gVL to kerosene- and diesel-range hydrocarbons through decarboxylation to butenes and subsequent butene oligomerization.[11]

Experimental Section

The catalysts were prepared by incipient wetness impregnation of various supports with soluble salts of noble metals, followed by drying at 120 °C and calcination at approximately 450 °C. The supports were commercial extrudates, where available, or based on commercial powders that were extruded in our laboratory.

The catalytic tests were carried out in high-pressure steel or Hastelloy reactors equipped with liquid feed pumps, gas manifold, and cold gas–liquid product separators. The catalysts were loaded either as full extrudates or as 0.2–0.5 mm crushed particles, diluted with inert particles of SiC. The catalysts were reduced under H_2 flow at atmospheric pressure and 300 °C prior to operation. The liquid product was collected and analyzed off-line by means of gas chromatography. The gaseous products were analyzed on-line by gas chromatography. More details of the procedures are reported in the Supporting Information.

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