Raney-Ni catalyzed conversion of levulinic acid to 5-methyl-2-pyrrolidone using ammonium formate as the H and N source

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ABSTRACT

Renewable biomass based levulinic acid was converted to 5-methyl-2-pyrrolidone in 94% yield by a Raney-Ni catalyzed process using ammonium formate in aqueous medium and heating at 180 °C for 3 h. The Raney-Ni could be reused for four catalytic cycles with about 10% loss in catalytic activity. In a similar reaction levulinic acid could be converted 1-substituted-5-methyl-2-pyrrolidones in 90–95% yield by using a mixture of formic acid and the corresponding primary amine.

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The current interest in sustainable carbon based chemical feedstocks and fuels has resulted in a vast expansion in research activities around cellulosic biomass derived C5-6 range compounds. Some of the highly promising compounds in this series are furfural, 5-hydroxymethylfurfural (HMF), levulinic acid (LA) and γ-valerolactone (GVL); most importantly these compounds can be obtained via a series of catalytic transformations from the abundant polysaccharide fraction of the lignocellulosic biomass.[1]

4-Oxopentanoic acid or levulinic acid (LA) is a particularly notable compound in this inventory due to its stability and potential to convert to many other useful feedstocks.[2–4] In addition, LA was listed as one of the top 12 most promising value added chemicals from biomass by the Biomass Program of the US Department of Energy (DOE) in 2004[5] and also continues to rank highly in more recent reviews of major bio-refinery target products.[6] These value added chemicals are molecules with multiple functional groups that possess the potential to be transformed into new families of useful molecules.[5] The twelve sugar-based building blocks in the DOE analysis are: 1,4-diacids (succinic, fumaric and malic), 2,5-furan dicarboxylic acid, 3-hydroxy propionic acid, aspartic acid, glucaric acid, glutamic acid, itaconic acid, levulinic acid, 3-hydroxybutyrolactone, glycerol, sorbitol, and xylitol/arabinitol.[5] Although the current global LA production is around 2600 tons/year, it is expected to grow in the coming years, particularly due to the introduction of the Biofine process, which has been projected to lower

the production costs to as low as US $ 0.04–0.10 per lb.[7] This versatile C-5 keto-acid can be used in the synthesis of a range of useful chemicals such as γ-valerolactone, 2-methyl tetrahydrofuran, acrylic acid, 1,4-pentanediol, β-acetylacrylic acid, α-angelica lactone, δ-amino levulinic acid, etc.[7,8] and some of these compounds have been used for the preparation of polymers and fuel precursors.[9–11] Additionally, our recent studies have revealed a new route for the preparation of a renewable C-7 polymer building block by aldol condensation between LA and glyoxylic acid as well.[12]

The catalytic reduction of LA using noble metal catalysts and hydrogen gas is the well established route for the preparation of another widely studied feedstock γ-valerolactone. The analogous noble metal catalyzed process using a mixture of hydrogen and ammonia gases is known to give the nitrogen analog of GVL 5-methyl-2-pyrrolidone (MPD). Similar to GVL the pyrrolidones are also useful compounds, especially *N*-alkyl-5-methyl-2-pyrrolidones have a wide diversity of applications, such as an alternative to common solvent *N*-methyl-2-pyrrolidone (NMP), surfactants, and important intermediates in the synthesis of agricultural bioactive compounds and pharmaceuticals.[13,14] In addition, MPD is used as an important constituent in many cleaning agents, refrigerants, air conditioning lubricants, inks and in aerosol formulations.[15] The patented method for producing MPD from LA using H_2-NH_3 mixture and noble metal catalysts have several drawbacks such as the requirement of a high excess of H_2 gas, expensive noble metals, hazardous organic solvents, and limited selectivity for the formation of the expected product when aryl amines are used in place of ammonia.[13,14] The most widely used noble metal catalysts in
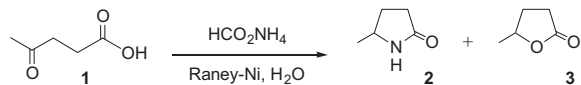
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this technique are Pt/C, Pd, Ru,[16] Ru/C,[14] Ir,[17] and [Ru(p-cymene)Cl$_2$]$_2$.[18,19] The polymeric ruthenium porphyrin-functionalized carbon nanotubes (Ru-PP/CNTs) prepared by the metalation of polymeric porphyrin-functionalized carbon nanotubes with Ru$_3$(CO)$_{12}$, have also been used in the synthesis of pyrrolidone derivatives from ethyl levulinate, primary amines and hydrogen gas.[20]

A few research groups have studied the possibility of reductive amination of levulinic acid using transfer hydrogenation, without using hydrogen gas as the H atom source, especially using Ru and Au based catalysts.[19,21] Du and co-workers developed the use of gold deposited on ZrO$_2$ as the catalyst, where they reported a one pot process requiring only formic acid, ammonia or primary amines, and the Au catalyst to convert levulinic acid directly into the corresponding pyrrolidones.[21] In another example of transfer hydrogenation, Sun et al. used Ru based catalyst fabricated via self-assembly from a p-phenylene-bridged bis-benzimidazolium salt with metal precursors, where ammonium formate was used

Fig. 1. Raney-Ni catalyzed conversion of levulinic acid (1) to 5-methyl-2-pyrrolidone (2) and γ-valerolactone (3) using ammonium formate as the hydrogen and nitrogen source.
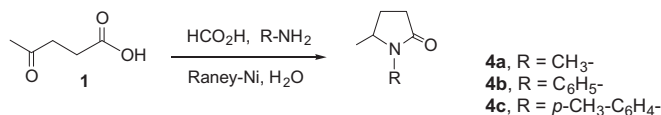
Fig. 2. Raney-Ni catalyzed conversion of levulinic acid (1) to 1-substituted, 5-methyl-2-pyrrolidones (4a–c) using formic acid and primary amines.

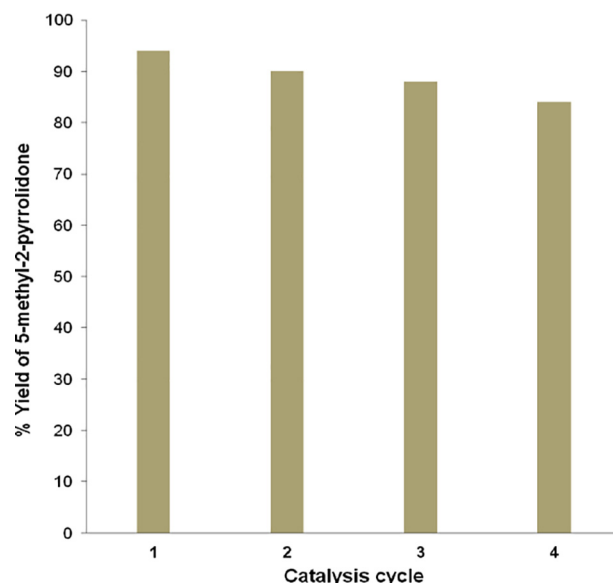to prepare 5-methyl-2-pyrrolidone at a 0.15 mol% catalyst loading.[22]

Our interest in upgrading biomass derived renewable feedstocks to value added chemicals, polymeric materials and renewable fuels[23,9,24] has led us to study the use of ammonium formate and Raney-Ni as the catalyst in reductive amination of levulinic acid to produce 5-methyl-2-pyrrolidone. This method has certain advantages since ammonium formate is attractive as a convenient H, N source; avoids the use of hydrogen, ammonia gases and relatively abundant, inexpensive Ni is used in comparison to expensive Au or Ru noble metal catalysts used in earlier studies. In this pub-

Fig. 3. The percent yields of 5-methyl-2-pyrrolidone (2) produced in reusing Raney-Ni catalyst in conversion of levulinic acid to 5-methyl-2-pyrrolidone (2) using ammonium formate as the H and N source.

Table 1
The LA: HCO$_2$NH$_4$ used, catalyst, reaction condition, levulinic acid conversion (%), product yield based on LA reacted (%) and carbon balance (%) in Raney-Ni catalyzed conversion of levulinic acid to 5-methyl-2-pyrrolidone (MPD, 2) and γ-valerolactone (GVL, 3).

| Entry	LA:HCO$_2$NH$_4$	Raney – Ni catalyst (mg/mmol of LA)	Reaction condition	LA conversion[a] (%)	Product yield based on LA reacted (%)[b]		Carbon balance[c] (%)
					MPD (2)	GVL (3)	
1	1:1	20	Oven, 120 °C, 20 h	40	48	36	84
2	1:2	20	Oven, 120 °C, 20 h	63	52	30	82
3	1:4	20	Oven, 160 °C, 3 h	100	60	28	88
4	1:4	20	Oven, 180 °C, 3 h	100	94	-	94
5	1:4	-	Oven, 180 °C, 3 h	15	68	23	91
6	1:4	20	MW (920W), 5 × 10s	11	80	-	80

1.0 mmol levulinic acid (LA) and 2.00 mL of water were used in all experiments. [a]levulinic acid conversion % = (levulinic acid used − levulinic cid unreacted)/ levulinic acid used × 100; [b]Yield was calculated using: Yield % = (products detected/levulinic acid reacted) × 100; [c]Carbon balance determined on the basis of 5-methyl-2-pyrrolidone (MPD, 2) and γ-valerolactone (GVL, 3) products.

Table 2
The LA: HCO$_2$H: R-NH$_2$ used, reaction condition, levulinic acid conversion (%), product, yield (%) and carbon balance (%) in Raney-Ni catalyzed conversion of levulinic acid to 1-substituted-5-methyl-2-pyrrolidones (4a–c) under oven heating conditions.

Entry	R-NH$_2$ (R−)	LA:FA:R-NH$_2$	Reaction condition	LA conversion[a] (%)	Product yield based on LA reacted (%)[b]	Carbon balance[c] (%)
1	CH$_3$-	1:1:1	120 °C, 20 h	46	4a, 48	48
2	CH$_3$-	1:4:1	180 °C, 3 h	100	4a, 95	95
3	C$_6$H$_5$-	1:1:1	120 °C, 20 h	62	4b, 55	55
4	C$_6$H$_5$-	1:4:1	180 °C, 6 h	100	4b, 92	92
5	p-CH$_3$-C$_6$H$_4$-	1:4:1	180 °C, 6 h	100	4c, 90	90

Levulinic acid (1.0 mmol), 20 mg Raney-Ni and 2.00 mL of water were used in all experiments. [a]levulinic acid conversion % = (levulinic acid used − levulinic acid unreacted)/ levulinic acid used × 100; [b]Yield was calculated using: Yield % = (products detected/levulinic acid reacted) × 100; [c]Carbon balance determined on the basis of 1-substituted-5-methyl-2-pyrrolidone products (4a–c).
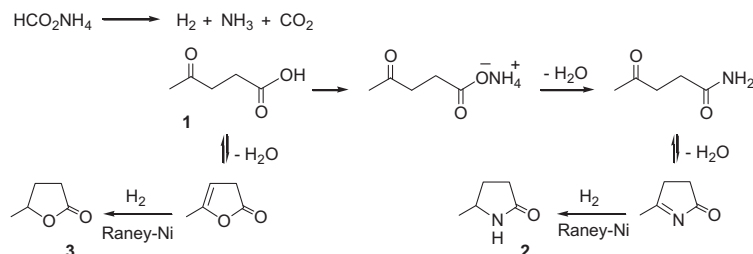
Fig. 4. The proposed reaction pathways for the Raney-Ni catalyzed conversion of levulinic acid (**1**) to 5-methyl-2-pyrrolidone (**2**) and γ -valerolactone (**3**) using ammonium formate.

lication we report the use of Raney-Ni catalyst in reductive amination of levulinic acid under thermal and microwave conditions to produce 5-methyl-2-pyrrolidone as shown in Fig. 1; where the Ni catalyst could be reused without appreciable loss in activity as well. In addition we have studied the possibility of using a mixture of primary amines and formic acid to produce 1-substituted-5-methyl-2-pyrrolidones from levulinic acid by Raney-Ni catalyzed reactions under thermal conditions as shown in Fig. 2.

In our initial experiment (Table 1, entry 1) on Raney-Ni catalyzed reductive amination of levulinic acid we have heated equimolar amounts of LA and HCO_2NH_4 at 120 °C for 20 h in a closed high pressure Teflon reactor. The experimental details are in the Supplementary data (SD) associated with the article. This experiment gave only a low 40% conversion of levulinic acid and produced a mixture of 5-methyl-2-pyrrolidone (48%) and γ -valerolactone (36%). Then increase in the amount of ammonium formate to two equivalents improved the levulinic acid conversion to 63% as shown in entry 2. The complete conversion of LA was possible with four equivalents of HCO_2NH_4 at 160 °C, but gave a mixture of **2** and **3** (entry 3). Further increase in temperature to 180 °C and a reaction time of 3 h gave the complete suppression of the γ-valerolactone (**3**) formation, giving 5-methyl-2-pyrrolidone (**2**) in 94% yield (entry 4). This reaction producing **2** as the sole product may be due to the rapid decomposition of four equivalents of HCO_2NH_4 to NH_3, H_2 and CO_2 at 180 °C and complete conversion of LA to its ammonium salt at the initial stage of the reaction. As a comparison, we have tested the reaction without adding any Raney-Ni catalyst as well (entry 5); this experiment gave only a low 15% conversion of LA after 3 h at 180 °C. Furthermore, we have studied the possibility of heating the reaction mixture using microwaves as shown in entry 6. This experiment gave a poor 11% conversion after heating over five 10s microwave pulses, but producing only 5-methyl-2-pyrrolidone (**2**) as the sole product.

The results from Raney-Ni catalyzed synthesis of 1-substituted-5-methyl-2-pyrrolidones (**4a–c**) from levulinic acid are shown in Table 2. The initial experiments using LA: HCO_2H: CH_3-NH_2 1:1:1 gave only a low 46% conversion of levulinic acid as shown in entry 1 in Table 2. However the increase in formic acid (FA) content gave the complete conversion of levulinic acid and an excellent yield of 1,5-dimethyl-2-pyrrolidone as shown in entry 2. As with methylamine the experiment with aniline using LA: HCO_2H: CH_3-NH_2 1:1:1 gave a low LA conversion and a product yield (entry 3). However, an increase in formic acid content produced high yields of the corresponding 1-substituted-5-methyl-2-pyrrolidones from aniline as well as from *p*-toluidine as shown in entries 4 and 5.

The percent yields of 5-methyl-2-pyrrolidone (**2**) produced in reusing the Raney-Ni catalyst in reductive amination of LA with ammonium formate under thermal conditions is shown in Fig. 3. This experiment shows that catalyst can be reused for four cycles with about a 10% loss in catalytic activity of the Raney-Ni without any special cleaning or regeneration of the catalyst surface. The reuse experiment details are in the Supplementary data (SD).

The proposed reaction pathways for the Raney-Ni catalyzed transformations of levulinic acid with ammonium formate are shown in Fig. 4. The ammonium formate may decompose to a gas mixture of H_2, NH_3 and CO_2 at the reaction temperature[25] and the ammonia formed reacting with levulinic acid gives the ammonium salt. The dehydration of the salt can lead to the amide, which undergoes a reversible cyclization to 3,4-dihydro-5-methyl-2*H*-pyrrol-2-one. The Raney-Ni catalyzed reduction of this intermediate product by hydrogen present in the reactor may give the 5-methyl-2-pyrrolidone (**2**). The alternative path of reversible cyclization of levulinic acid to 5-methyl-2(3*H*)-furanone and reduction of this intermediate gives the γ-valerolactone byproduct, especially at lower temperatures.

In conclusion, we have shown that levulinic acid can be converted to 5-methyl-2-pyrrolidone in 94% yield by using four equivalents of ammonium formate and Raney-Ni as the catalyst in water at 180 °C. Under similar reaction conditions levulinic acid could be converted to 1-substituted-5-methyl-2-pyrrolidones in 90–95% yield by using a mixture of formic acid and corresponding primary amines. This technique provides a simple, single reactor process to produce 5-methyl-2-pyrrolidone and its *N*-substituted derivatives from levulinic acid under mild conditions and the new method has certain advantages such as: no external hydrogen source or expensive noble metal catalysts are required. The Ni-catalyst could be reused for four catalytic cycles with a small loss in catalytic activity. In addition the presented method has certain safety advantages over the patented method, which requires the heating of a H_2-NH_3 gas mixture at high pressures of 7–9 MPa.[13,14]

A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at https://doi.org/10.1016/j.tetlet.2018.03.087.

References

1. Corma A, Iborra S, Velty A. *Chem Rev*. 2007;107:2411.
2. Mukherjee A, Dumont MJ, Raghavan V. *Biomass Bioenergy*. 2015;72:143.
3. Pileidis FD, Titirici MM. *ChemSusChem*. 2016;9:1.
4. Amarasekara AS, Animashaun MA. *Catal Lett*. 1819;2016:146.
5. Werpy T, Petersen G, Aden A, et al. In Top value added chemicals from biomass. Volume 1-Results of screening for potential candidates from sugars and synthesis gas; DTIC Document, **2004**.
6. Bozell JJ, Petersen GR. *Green Chem*. 2010;12:539.
7. Bozell JJ, Moens L, Elliott DC, et al. *Resourc Conserv Recycl*. 2000;28:227.
8. Rackemann DW, Doherty WO. *Biofuel Bioproduct Biorefin*. 2011;5:198.
9. Amarasekara AS, Hawkins SA. Europ. *Polym J*. 2011;47:2451.
10. Zhang Y, Wu L, Li F, Li B. *Huagong Xuebao/J Chem Ind Eng (China)*. 2006;57:992.
11. Zhang Y, Guo Z, Cheng J, Fang Z. *Acta Polym Sin*. 2009;180.

12. Amarasekara AS, Ha U. *Tet Lett*. 2016;57:2598.
13. Werpy T, Frye JG, Wang Y, Zacher AH. In *Methods of making pyrrolidones*; US Patent, US6603021B2, **2003**.
14. Manzer LE. In *Production of 5-methyl-n-aryl-2-pyrrolidone and 5-methyl-n-alkyl-2-pyrrolidone*; US Patent, US6818593B2, **2004**.
15. Du XL, He L, Zhao S, et al. *Angew Chem*. 2011;123:7961.
16. Touchy AS, Hakim Siddiki SMA, Kon K, Shimizu K-I. ACS Catal. 2014;4 :3045
17. Wang S, Huang H, Bruneau C, Fischmeister C. *ChemSusChem*. 2017;10:4150.
18. Ledoux A, Sandjong Kuigwa L, Framery E, Andrioletti B. *Green Chem*. 2015;17:3251.
19. Huang YB, Dai JJ, Deng XJ, Qu YC, Guo QX, Fu Y. *ChemSusChem*. 2011;4:1578.
20. Zhang T, Ge Y, Wang X, Chen J, Huang X, Liao Y. *ACS Omega*. 2017;2:3228.
21. Du X-L, He L, Zhao S, et al. *Angew Chem Int Ed*. 2011;50:7815.
22. Sun Z, Chen J, Tu T. *Green Chem*. 2017;19:789.
23. Amarasekara AS, Wiredu B. *BioEnergy Res*. 2014;7:1237.
24. Amarasekara AS, Razzaq A. *ISRN Polym Sci*. 2012;2012 532171.
25. Sridhar M, Ferri D, Elsener M, van Bokhoven JA, Krocher O. *ACS Catal*. 2015;5:4772.