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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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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.

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 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-

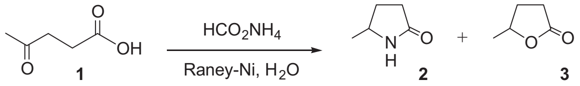

Fig. 1. Raney-Ni catalyzed conversion of levulinic acid (**1**) to 5-methyl-2-pyrrolidone (**2**) and γ-valerolactone (**3**) using ammonium formate as the hydrogen and nitrogen source.

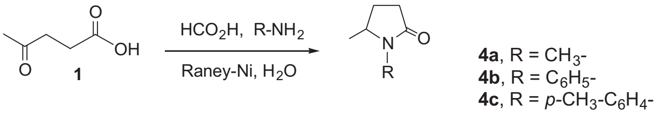

Fig. 2. Raney-Ni catalyzed conversion of levulinic acid (**1**) to 1-substituted, 5-methyl-2-pyrrolidones (**4a–c**) using formic acid and primary amines.

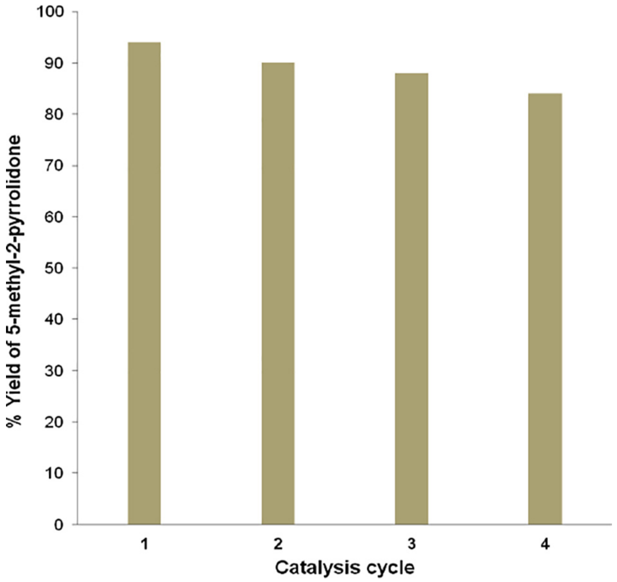

Fig. 3. The percent yields of 5-methyl-2-pyrrolidone (2) produced in reusing Raney-Ni catalyst in conversion of levulinic acid to 5-methyl-2-pyrrolidone (2) using ammonium formate as the H and N source.

Table 1

The LA: HCO_2NH_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_2NH_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_2H: 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_6H_5-	1:1:1	120 °C, 20 h	62	**4b**, 55	55
4	C_6H_5-	1:4:1	180 °C, 6 h	100	**4b**, 92	92
5	*p*-CH_3-C_6H_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**).