

# Green Chemical Methods for Reduction of Levulinic Acid

Poonam Ojha<sup>1</sup> P.S. Verma<sup>2</sup> and I.K. Sharma<sup>2</sup>

<sup>1</sup>Department of Chemistry, SKIT, Jaipur 302 017, Rajasthan, India

<sup>2</sup>Department of Chemistry, University of Rajasthan, Jaipur, Rajasthan, India

(Received 19 January, 2022; Accepted 21 February, 2022)

## ABSTRACT

This paper reports the production of ethyl 4-hydroxy valeric acid by Green synthetic routes by using two ecofriendly techniques of biocatalytic and electrochemical reduction of levulinic acid. For biocatalytic reduction Baker's Yeast was used. Conditions for electrochemical reduction were explored by the use of cyclic voltammetric investigation in different pH and scan rates. Electrochemical reduction was carried out by electrolysis method using stainless steel (SS-316) electrodes galvanostatically. The reduction products were isolated and purified by chromatographic techniques and characterized on the basis of spectral analysis.

**Key words:** Levulinic acid, Baker's yeast (BY), Biocatalytic reduction, Cyclic voltammetry, Galvanostatically, Stainless steel Electrode (SS-316).

## Introduction

Unforeseeable resources of fossil fuels and their rising demands have directed researchers towards the search of alternative feed stocks for chemical industry and fuels. In recent years, use of renewable biomass for production of chemicals and fuels has attracted much attention. The biomass based chemical production is considered as sustainable and environmentally benign process. In this regard, transformation of lignocelluloses into platform molecules, which can be then further, converted into a variety of valuable chemicals or fuels under desirable mild conditions. Researchers, from past many years are working for production of glucose and levulinic acid through hydrolysis of cellulose in aqueous medium.

Levulinic acid on reaction gives  $\alpha$ -hydroxy valeric acid which is a versatile building block with high chemical reactivity and can be catalytically converted into valuable chemicals and fuels like  $\alpha$ -valerolactone (GVL), 5-aminolevulinic acid, diphenolic

acid etc that can be used in flavoring, fragrance industries and additives in diesel and biodiesel. Among them  $\gamma$ -valerolactone is promising C5-building block has variety of applications like as a fuel additive, lighter fluid as solvent etc. Thus production of GVL from lignocelluloses biomass is in much interest in recent years. Generally, GVL can be produced through selective hydrogenation of biomass derived levulinic esters on either homogenous or heterogeneous catalysts. Use of homogeneous catalysts has drawbacks of catalyst synthesis, recovery and recycling. While use of heterogeneous catalysts like supported hydrogenation based on noble metals like ruthenium, palladium and gold have disadvantages like high cost, hard manufacture and vulnerability to poison. Thus, search of environmental friendly green methods is very essential.

Thus, present study focuses on most active areas of Green Chemistry research and development i.e. application of biocatalysts and electro analytical methodology developments in conventional organic

synthesis. Biocatalysts are known to possess many interesting features like high efficiency, mild environmental friendly operation conditions, versatility and production of enantiopure chiral compounds. Secondly, use of electrochemical technique in organic synthesis can be used for reduction and oxidation of substrate. Here, electron plays an important role and acts as reagent. This avoids undesirable byproducts and simplifies cumbersome work-up procedures and also reduces pollution problems.

In this paper, use of Baker's Yeast for biotransformation of levulinic acid to ethyl  $\gamma$ -hydroxy valeric acid was carried out, as use of whole cell is preferred over using pure enzymes. Further, electrochemical reduction was carried out. At first, cyclic voltammogram of levulinic acid was recorded at various scan rates at different pH. On the basis of results obtained from cyclic voltammetry, conditions were determined for electrolysis at a stainless steel electrode (SS-316) galvanostatically.

## Experimental

### Reduction using Baker's Yeast

A suspension of Baker's Yeast (10 g) in 50 ml of glycerol was shaken gently in a magnetic stirrer for 20 minutes. Then 25 ml isopropanol was added and shaken for 10 minutes more. Then 1 g of levulinic acid was added and the reaction mixture was shaken for 96 hr. After that product was filtered using celite (HIMEDIA GRADE) and dried over sodium sul-

phate. Product ethyl  $\gamma$ -hydroxy valeric acid was isolated and purified by thin layer chromatography and characterized by spectroscopic techniques (IR, NMR, Mass spectra).

### Reduction using electroanalytical Technique

Computer based Basic Electrochemistry system ECDA-001, supplied by Con-serv enterprises, Mumbai was used for recording cyclic voltammograms of compounds in aqueous solution using 1M potassium chloride as supporting electrolyte and BR buffer of different pH (5, 7, and 9) at a platinum electrode to determine the optimum conditions for electrochemical reduction. And then electrochemical reduction was carried out at a stainless steel electrode (SS-316) galvanostatically using a conventional H-type cell with two limbs separated by a G-4 disc was used for electrolysis.

The voltammographic curves were recorded for compounds in aqueous solution using 1M potassium chloride as supporting electrolyte and BR buffer of different pH (5, 7, and 9) at a platinum electrode to determine the optimum conditions for electrochemical reduction. These conditions were subsequently applied for carrying out electrochemical reduction at a stainless steel electrode (SS-316) galvanostatically.

The conventional H-type cell with two limbs separated by a G-4 disc was used for electrolysis. The reactants (0.001M) were dissolved in water and placed in the cathodic chamber and the pH of the cathodic solution was 9. The constant current of 1 amp was

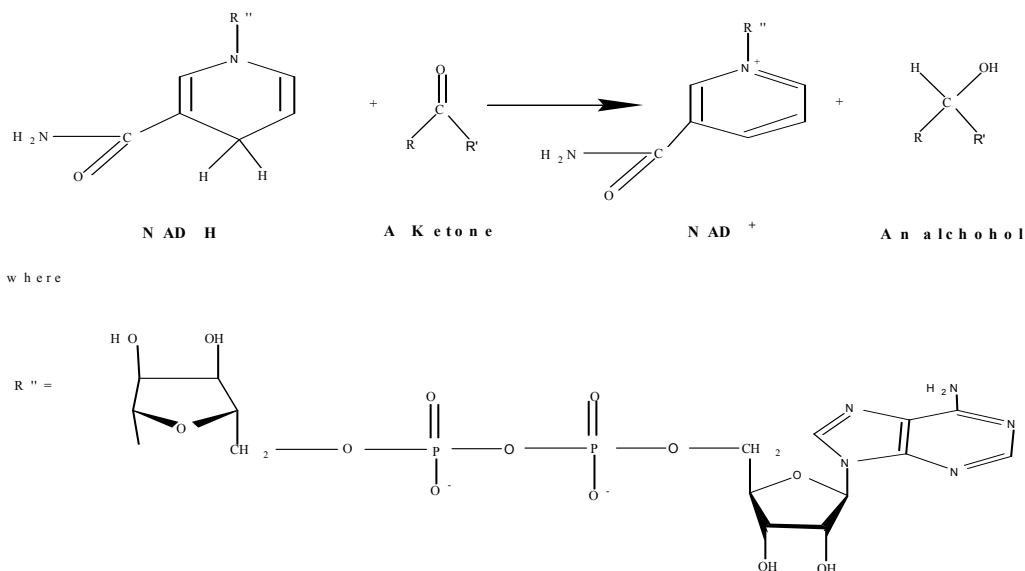


Fig. 1. Scheme of the reduction

passed through the electrolyte for suitable period for 8 hr. There after the working up of the reaction mixture involved extracting the aqueous solution with diethyl ether (3×25ml). The organic extracted were dried over anhydrous  $\text{Na}_2\text{SO}_4$  and than characterized done on the basis of IR, NMR & Mass spectral analysis.

## Result and Discussion

### Baker's Yeast mediated reduction

Baker's Yeast (BY) is a common microorganism can be easily used for synthesis of optically pure alcohols. In case of baker's yeast mediated asymmetric reduction of carbonyl compounds not only enzyme catalyzing the asymmetric reduction of prochiral carbonyl compounds to chiral alcohols, i.e. carbonyl reductases is involved but the cofactor regeneration system to supply NADH or NADPH through the oxidation of the energy source is also involved. The reducing agent, NADH (Nicotinamide Adenine Dinucleotide phosphate hydride) reduces the substrate and itself oxidises to  $\text{NAD}^+$ . Thus to continue reduction process, isopropanol is added to the reaction mixture, which is oxidized to acetone and regenerates NADH from NAD and it ensures an increase in the enantiomeric excess of the product.

### Cyclic Voltammetric Study

#### Effect of PH

The reduction of carbonyl compounds in aqueous solution depends on the pH of the system. From the study of cyclic voltammograms shown in Fig. 2 it

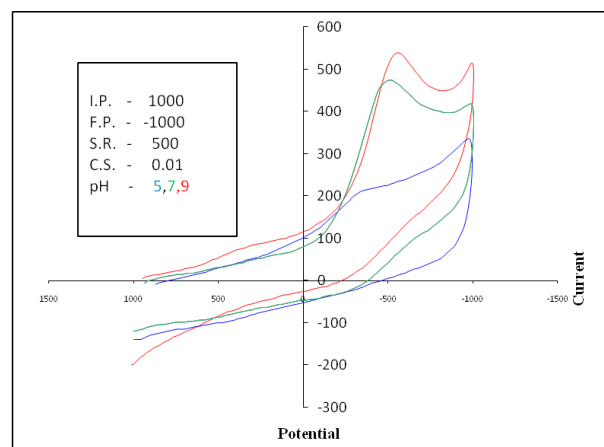


Fig. 2. Effect of pH on reduction of Levulinic acid

can be clearly seen that at pH 5.0, there is no appearance of peak, at pH 7.0, slight peak appears and at pH 9.0, the peak shows prominent appearance. Thus, it can be concluded that the process of reduction is easier in basic media as compared to acidic and neutral media.

#### Effect of scan rate

From cyclic voltammograms (Fig. 3), it is clear that as the scan rate was gradually increased to 100,200,300, 400 and 500,800 and 1000 mV/sec, peak potential ( $E_p$ ) gradually shifted towards higher values. The cathodic peak current ( $I_p$ ) increases with increasing scan rate.

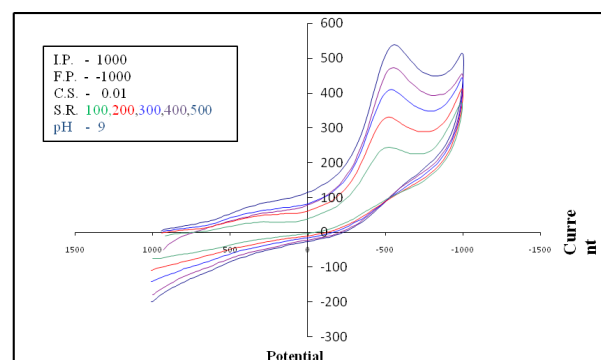


Fig. 3. Effect of Scan rate on reduction of levulinic acid

### Proposed Mechanism for Electrochemical Reduction

Cyclic voltammogram (Fig. 2-3) clearly indicates that in all cases the reduction is ir-reversible and involves transfer of two electrons.

### Conclusion

The present research work focuses on environmental friendly approach using biocatalytic and electrochemical reduction of substrates into useful products. These methods are not only green but also have merits like specificity & cost effectiveness. It is expected to reduce the ever-increasing problem of pollution caused by hazardous, corrosive chemicals and harsh reaction conditions.

### Spectroscopic results

**Product:** Ethyl 3-hydroxy valeric acid (Yield 97%, B.P. 2070C)

**IR ( $\text{cm}^{-1}$ ):** 3450-3600 (O-H str), 3060 (C-H str), 1765 (C=O str), 1470 (C-H def), 1140 (C-O str)

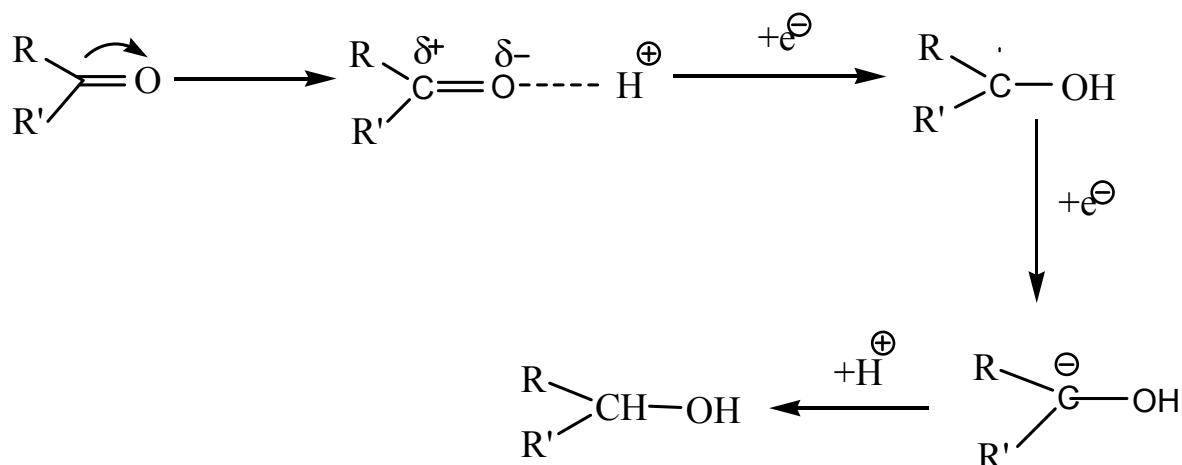


Fig. 4. Mechanism of electrochemical reduction

**NMR (d-Value):** 11.0(OH), 3.39(CH), 2.23(CH<sub>2</sub>), 2.0(OH), 1.71(CH<sub>2</sub>), 1.21 (CH<sub>3</sub>)

**Mass Spectra (m/z):** 118, 117, 103, 101, 73, 60, 59, 55, 45, 31

## References

- Boojlet, K. and Simonet, J. 1979. On the electrochemical reduction of  $\alpha$ -diketones in the presence of oxygen. *Tetrahedron Lett.* 20 (12) : 1063-1066.
- Brown, H.C. and Ramachandran, P.V. 1991. The Boron Approach to Asymmetric-Synthesis. *Pure Appl. Chem.* 63 : 307-316.
- Ikunaka, M. 2003. A Process in Need is a Process Indeed: Scalable Enantioselective Synthesis of Chiral Compounds for the Pharmaceutical Industry. *Chem. Eur. J.* 9 : 379-388.
- Mark, A. K. 1997. Interaction of Optically Active Tartaric Acid with a Nickel-Silica Catalyst: Role of Both the Modification and Reaction Media in Determining Enantioselectivity. *Langmuir.* 13 : 41-50.
- Martina, C. H. and Prather, K. L. J. 2009. High-titer Production of Monomeric Hydroxyvalerates from Levulinic acid in *Pseudomonas putida*. *J. Biotechnol.* 139(1) : 61-67.
- Nakahata, M. 1982. The Preparation of Optically Pure 3-hydroxyalkanoic acid—The Enantioface Differentiating Hydrogenation of the C=O Double-bond with Modified Raney-nickel. *Bull. Chem. Soc. Jpn.* 55 : 2186-2189.
- Noyori, R. 1994. *Asymmetric Catalysis in Organic Synthesis*, John Wiley, New York.
- Wang, Z. 1999. Enantioselective Synthesis of  $\beta$ -hydroxycarboxylic acids: Direct Conversion of  $\beta$ -oxocarboxylic acids to Enantiomerically Enriched  $\beta$ -hydroxycarboxylic acids via Neighboring Group Control, *Tetrahedron: Asymmetry.* 10 : 225-228.
- Wolfson, A. 2001. Enantioselective Hydrogenation of Methyl Acetoacetate Catalyzed by Nickel Supported on Activated Carbon or Graphite. *Appl. Catal.* 208 : 91-98.
- Wolfson, A. 2003. The Role of the Solvent in the Asymmetric Hydrogenation of  $\beta$ -Keto Esters with Ru-BINAP. *J. Mol. Catal. A: Chem.* 198 : 39-45.