**Novel Multistep Process for Production of N-Methyl-2-Pyrrolidone from Renewable Resources**

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**Introduction**

The continued use of petroleum for chemical feedstocks, transportation fuels, and other energy demands is not sustainable. It is important that new processes and catalysts are developed that utilize renewable sources to reduce US dependence on petroleum and especially on foreign oil. The US is especially well suited to be a major contributor to the use of renewable resources due to its very large supply of biomass and its large and well developed agribusiness sector [1].

The production of N-methyl-2-Pyrrolidone (NMP) from fermentation derived succinic acid offers an economically viable route which can be competitive with current processes based on current petrochemical routes [2], which are ultimately based on maleic anhydride from oxidation of butane. To a significant extent, a succinic acid based route to NMP depends on efficient fermentation. These fermentations and those also leading to the corresponding acid, fumaric, have and are being improved and developed by several groups [3,4,5] and will not be discussed in this paper.

Workers at the Pacific Northwest National Lab (PNNL) have developed a simple multi-step process involving both catalytic and non catalytic events which efficiently converts succinic acid into NMP. This process scheme is particularly adaptable to use of succinic acid derived from fermentation in that high levels of costly purification are not required. The process consists of two essential steps, non-catalytic (thermal) conversion of diammonium succinate (DAS) and methanol to n-methyl succinimide (NMS) followed by hydrogenation of the NMS to NMP.

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\begin{align*}
\text{DAS} + \text{CH}_3\text{OH} & \rightarrow \text{NMS} + \text{H}_2\text{O} \\
\text{NMS} + \text{H}_2 & \rightarrow \text{NMP}
\end{align*}
\]

**Materials and Methods**

Non-catalytic steps in the process were carried out in 300cc Parr Autoclaves equipped with stirring, an internal thermocouple, automated temperature control, gas addition and pressure regulation capability and liquid sampling via a dip tube. Catalytic hydrogenations were also conducted in a similar 300cc Parr Autoclave. Since succinate fermentations require pH adjustment to pH levels around 6-7, we used synthetic diammonium succinate (DAS) as feedstock. Commercially supplied Corn Steep Liquor was used as an additive to simulate feed compositions which would be expected from fermentations. Hydrogenation of succinimide intermediates to NMP was conducted with either synthetic succinimide or with succinimide recovered from distillation of product mixtures from experimental runs which produce succinimide in intermediate steps in the overall process. Hydrogenations were typically done by loading feedstock, solvent if required, and catalyst into the autoclave, purging with N2 and then H2 and finally heating to reaction pressure and temperature before sampling. Analysis of products was done with HPLC. Gas chromatography was used for confirmation of selected HPLC results.

**Results and Discussion**

PNNL workers had conducted prior successful efforts in the production of NMP from renewables [6]. To improve on these past results, we devised an overall process scheme that conceived the use of fermentation derived but unpurified diammonium succinate in a series of four basic steps [7]. These are (1) thermal, non-catalytic removal of a portion of the ammonium content, (2) non-catalytic reaction of the ammonia-deficient intermediate with methanol to form n-methyl succinimide (NMS) (3) distillation the NMS and (4) hydrogenation of NMS to n-methyl-2-pyrrolidone with high selectivity. The experimental work involved several series of experimental designs to select the optimal conditions. Catalyst selection was conducted in a similar manner. Steps 1 and 2 were found to occur in high efficiency without catalyst. A Rhodium based catalyst was found to give very high selectivity in the hydrogenation of NMS to NMP. The catalyst was easily recyclable without activity or selectivity loss. The hydrogenation of NMS may also be controlled to vary the ratio of NMP to 2-pyrrolodone (2P) product. Water content of the feed is one route to control the NMP to 2P product ratio.

Most importantly, the overall process was essentially unaffected by large amounts of corn steep liquor which was added to simulate the use of unpurified DAS from fermentation.

Overall molar yields of NMP in excess of 90% of theoretical were observed in when the complete process was simulated at lab scale.

**Significance**

Efficient utilization of renewable resources is likely to involve fermentations and catalytic and non-catalytic steps judiciously combined into a single process scheme. Processes which are able to utilize fermentation derived intermediates without significant purification will be of high value in the overall use of renewables as chemical feedstocks. This work describes such a process scheme.

**References**