ECUT–BIOCATALYSIS RESEARCH ACTIVITY GENERATION OF CHEMICAL INTERMEDIATES BY CATALYTIC OXIDATIVE DECARBOXYLATION OF DILUTE ORGANIC ACIDS

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Generation of Chemical Intermediates by Catalytic Oxidative Decarboxylation of Dilute Organic Acids

S. Di Stefano, A. Gupta, and J.D. Ingham
ABSTRACT

Dilute streams of organic acids are byproducts of fermentation processes, paper and pulp industry waste streams, and processed urban waste. Currently, these are dumped since no method exists to extract the acids unless the streams are first concentrated. A catalytic process which would convert these dilute acids to useful chemicals such as alcohols and hydrocarbons would allow their utilization as a high volume non-fossil feedstock. The catalyst should cause loss of carbon dioxide from these dilute acids without heating to convert them to hydrocarbons which are not soluble in water and can be separated at high energy efficiency. A rhodium-based catalyst was prepared and preliminary experiments were completed where the catalyst appeared to decarboxylate dilute acids at concentrations of 1-10 vol%.

Electron spin resonance spectroscopy was used to characterize the catalyst as a first step leading toward modeling and optimization of rhodium catalysts. Also, a hybrid chemical/biological process for the production of hydrocarbons has been assessed. These types of catalysts could greatly increase energy efficiency of this process.
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SUMMARY

Dilute streams of organic acids are byproducts of fermentation processes, paper and pulp industry and processed urban waste. Currently, these are dumped since there is no method to extract the acids unless the streams are first concentrated. A catalytic process which would convert these acids to useful chemicals such as alcohols and hydrocarbons would open up their utilization as a high volume alternate, non-fossil feedstock of ~10^6 tons/year for the chemical industry, providing up to 10^{13} Btu's annually. Energy conservation at the quad level could be obtained by replacing petroleum-based feedstocks in new, more energy efficient hybrid chemical catalytic-biocatalytic processes.

The desired conversion pathway involves loss or expulsion of carbon dioxide from each molecule of the acid, i.e., decarboxylation to generate alcohols and hydrocarbons which are widely used as intermediates in the chemical industry. Currently there are no catalysts available for this process which can efficiently convert dilute acid streams, although Ce^{4+} promoted with I_2 slowly decarboxylates concentrated acids.

Previous studies have indicated that transition-metal catalysts and catalyst-modified electrodes can be developed that would be effective on dilute acid streams. Therefore, work was initiated at JPL to develop new catalysts for decarboxylation of acids in aqueous solutions.

Accomplishments to date include the preparation of rhodium-based catalysts for which preliminary qualitative experiments were conducted. The catalysts appeared to decarboxylate dilute acids at concentrations of 1-10 volume %; however, the results were not consistently reproducible at 1% concentration, and no kinetic measurements have been made. Further work is required to more completely define the catalyst systems, mechanisms, and practical limitations,
and to determine decarboxylation rates, yields, and susceptibilities to poisoning or inhibition.

The use of diagnostic techniques such as electron spin resonance (ESR) spectroscopy and electrochemistry leading to some initial characterization of reactive intermediates in these systems has been examined. This type of characterization will lead to reactivity models which may be used to optimize the chemical structure of certain rhodium-based catalysts for the best turnover rate/stability trade-off.

Some novel hybrid chemical/biological processes for the production of hydrocarbon chemicals have been examined. An example of a hybrid process proposed by Levy, et al. (10) is conventional electrolysis (i.e., Kolbe synthesis) of dilute acid from a fermentation reactor. However, state-of-the-art technology would require about 5,000 Btu/lb or nearly 25% of the energy of the product for conversion of the acids to hydrocarbons. New catalyst systems could decrease the decarboxylation energy requirement to <2,000 Btu/lb of product by eliminating the most energy-intensive process steps, which are separation of the acids, and Kolbe electrolysis. The significance of this decrease in energy consumption is that it could increase the ratio of product energy/process energy for the overall hybrid process to approximately 10, compared with the value for conventional production of hydrocarbon fuel which has been estimated to be ~6. Thus, it should be practical to produce low molecular weight hydrocarbons from renewable resources with significantly less process energy consumption than for production from non-renewable petroleum.
I. **INTRODUCTION**

The conversion of organic carboxyl compounds to hydrocarbons has been known for a long time; Kolbe first studied the electrochemical oxidation of carboxylic acids to hydrocarbons in 1849, and since then, this topic has been the subject of numerous studies. More recently, a variety of transition metals have been reported as catalysts in the oxidative decarboxylation of carboxylic acids. The application of new catalysts and/or the development of catalyst modified electrodes for oxidative decarboxylation should ultimately give rise to highly efficient conversion processes. The goal of this research is to improve the understanding of the decarboxylation process by determining the mechanism of the decarboxylation reaction, and then optimize catalyst performance. Ultimately this understanding will be used to develop improved and less expensive efficient catalysts.

Improved efficiency would be obtained via new chemical catalytic systems (compared with conventional Kolbe electrolysis) because the overall energy efficiency of thermal catalytic processes is higher than electrolytic processes by a factor of more than two. It has already been shown by Levy, et al. (10), that the process:

\[
\text{Biomass} \xrightarrow{\text{Fermentation}} \text{Carboxylic Acids} \xrightarrow{\text{Kolbe Electrolysis}} \text{Hydrocarbons}
\]

is energy efficient, giving rise to a favorable energy balance of $\sim 4.0/1.0$ (product energy/process energy). This means that processing of the carboxylic acids consumes approximately 25% of the total product energy.
Organic fatty acids are major components of byproducts of pulping operations in paper manufacture and allied industries, the third largest energy user of the major industry groups\(^{(1)}\). This technology can result in more efficient energy use in this industry and in the recovery and conversion of fatty acids which are components of anaerobic digestion of biomass and organic waste materials. Development of more efficient catalysts for oxidative decarboxylation could ultimately result in new hybrid chemical and fuel production processes that would result in energy consumption reduction at the quad level.

II. BACKGROUND

a. Homogenous Transition Metal Catalyzed Oxidative Decarboxylation

Certain oxidants such as Ce\(^{4+}\) and Mn\(^{3+}\) oxidize carboxylic acids via a one electron oxidation process. This process is slow at room temperature but may be promoted by addition of I\(_2\) or strong acids. Scheme I outlines the mechanism for oxidative decarboxylation using Mn\(^{3+}\)\(^{(2)}\). This mechanism involves formation of hydrocarbon radical intermediates. Formation of energetic radicals as intermediates requires that the overall reaction have a large activation energy. Energetic transients tend to result in the formation of a mixture of products, including alcohols and hydrocarbons. Once the radical intermediates are formed, it is difficult to control their reactivity.
In order to avoid these problems, we propose to investigate non-radical pathways to decarboxylation. Suitable transition metal catalysts will be developed which can act as templates for this process.

Thermodynamic data for certain reactions of interest are given below.

Table 1

<table>
<thead>
<tr>
<th>Reaction</th>
<th>Products</th>
<th>ΔH (kcal/mole)</th>
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<tr>
<td>CH₃COOH → CH₄ + CO₂</td>
<td>ΔH = -8.2</td>
<td></td>
</tr>
<tr>
<td>CH₃COOH → CH₃OH + CO</td>
<td>ΔH = +21.2</td>
<td></td>
</tr>
<tr>
<td>CH₃COOH → H₂O + H₂CO</td>
<td>ΔH = +33.6</td>
<td></td>
</tr>
<tr>
<td>CH₃COOH + 1/2 O₂ → CH₃OH + CO₂</td>
<td>ΔH = -46.5</td>
<td></td>
</tr>
</tbody>
</table>

The reaction of interest which proceeds with a small exothermicity (and hence, minimum loss of energy in the form of heat) is the formation of hydrocarbon and carbon dioxide. Although methane is not the desired product (because of its relatively low value as a chemical intermediate) it will be used in this work as a model product since its formation from acetic acid in high yield
would indicate that a non-radical pathway is operative. The applicability of these catalysts for production of higher hydrocarbons (such as ethane or pentane) will be determined in subsequent work.

Three possible non-radical pathways to decarboxylation can be proposed.

b. Non-Radical Decarboxylation Via Extrusion/Insertion

One potential mechanism is via extrusion/insertion:

\[
\begin{align*}
\text{CH}_3\text{COOH} + M &\rightarrow (n-1)^+ M - \text{OOCCH}_3 + H^+ \\
\text{CH}_4 + M &\rightarrow [M - \text{CH}_3] + \text{CO}_2
\end{align*}
\]

However, known examples of CO\textsubscript{2} insertion and extrusion are rare in the literature. For example, insertion of CO\textsubscript{2} into a metal diallylamide turns out to be catalyzed by free amine implying a pre-equilibrium, where L\textsubscript{n}M is a coordinated metal center:

\[
\begin{align*}
\text{R}_2\text{NH} + \text{CO}_2 &\leftrightarrow \text{R}_2\text{NCOOH} \\
\text{L}_n\text{M} - \text{NR}_2 + \text{R}_2\text{NCOOH} &\leftrightarrow \text{L}_n\text{M} - \text{O}_2\text{CNR}_2 + \text{R}_2\text{NH}
\end{align*}
\]

Similarly, the reaction reported by English et al.\textsuperscript{(3)}

\[
\text{Ir}_{\text{I}} + \text{CO}_2 + \text{CH}_3\text{CN} \rightarrow \text{H} - \text{Ir} - \text{O}_2\text{C} - \text{CH}_2\text{CN}
\]

does not involve insertion of CO\textsubscript{2} into H - Ir - CH\textsubscript{2}CN.
Although existing evidence for extrusion of CO₂ is weak, our preliminary results encourage us to attempt to design specific metal complexes capable of CO₂ extrusion.

c. Non-Radical Decarboxylation Via Oxidative Addition

Oxidative addition may also be proposed:

\[
\text{CH}_3\text{COOH} + M \rightarrow_\text{H} M \rightarrow_\text{CH}_2\text{COOH}
\]

\[
M + \text{CH}_4 \rightarrow_\text{H}^+ M \rightarrow_\text{H}^- + \text{CO}_2 + \text{H}^+
\]

The "Carbene" Mechanism

There is some precedence for the possibility of oxidative addition across CH-bonds, exemplified by Shilov(4). In particular, PtCl₂ in aqueous CH₃COOH is a good catalyst for alkane H-D exchange, and the methyl group in acetic acid has been noted to undergo extensive deuteration under the reaction conditions. However, basic conditions may be necessary and an early transition metal catalyst such as Nb or Ti may be more suitable, since carbenes seem to be more common for these metals.

d. Indirect Oxidative Addition

The Monsanto process for synthesis of acetic acid is:

\[
\text{CH}_3\text{OH} + \text{CO} \rightarrow_\text{CH}_3\text{COOH}, \Delta H = -21.2 \text{ kcal/mole}
\]
catalyzed by rhodium iodocarbonyl and believed to proceed via two equilibria:

\[
\begin{align*}
\text{CH}_3\text{OH} + \text{HI} & \rightarrow \text{CH}_3\text{I} + \text{H}_2\text{O} \\
\text{CH}_3\text{COOH} + \text{HI} & \rightarrow \text{CH}_3\text{COI} + \text{H}_2\text{O}.
\end{align*}
\]

The alkyl and acyl iodides are both facile oxidative addends (as CH₃COOH is not), so the following equilibria are set up in the presence of Rh⁺:

\[
\begin{align*}
\text{Rh(I)} + \text{CH}_3\text{I} & \rightarrow \text{Rh}^{\text{III}} \rightarrow \text{CO} \rightarrow \text{Rh}^{\text{III}} \rightarrow \text{COCH}_3 \rightarrow \text{Rh}^{\text{I}} + \text{CH}_3\text{COI}
\end{align*}
\]

Theoretically, if it were possible to remove CO from the system by starting with excess acetic acid, it would be possible to drive methanol formation from acetic acid. A rhodium (I) phosphine complex should be better than Rh(CO)₂ I₂ for this purpose (5) or perhaps a heterogenous catalyst such as rhodium on zeolites (6). It might also be possible to intercept the methyl complex:

\[
\begin{align*}
\text{Rh}^{\text{III}} + \text{CH}_3 & \rightarrow \text{H}^+ \rightarrow \text{CH}_4 + \text{Rh}^{\text{III}} - \text{I}
\end{align*}
\]

Turning CO from acyl elimination into CO₂ and regenerating Rh(I) now simply amounts to the water gas shift reaction:

\[
\begin{align*}
\text{Rh}^{\text{III}} - \cdot \text{I} + \text{CO} & \rightarrow \text{Rh}^{\text{III}} \rightarrow \text{H}_2\text{O} \rightarrow \text{Rh}^{\text{I}} + \text{CO}_2 \rightarrow \text{I}^- + 2\text{H}^+
\end{align*}
\]
III. PROGRESS

a. Homogeneous Systems Using Rh-Isonitrile Complexes

In previous work, we have investigated the reaction of carbon monoxide and other substrates with the inorganic complex $\text{Rh}_2(\text{bridge})_4^{2+}$, where the bridge is $\alpha$, $\omega$-diisonitrilo propane. In aqueous solution, in the presence of an oxidant such as $\text{O}_2$, $\text{Rh}_2(\text{bridge})_4^{2+}$ is oxidized to a stable tetrameric form, $\text{Rh}_4(\text{bridge})_8^{6+}$. This complex, hereafter abbreviated $\text{Rh}_4^{6+}$, contains a linear chain of four rhodium nuclei. Upon the replacement of air by an atmosphere of $\text{H}_2$, $\text{Rh}_4^{6+}$ is partially reduced with corresponding oligomerization to form an insoluble black polymer. The polymer can be reoxidized to the tetrameric form by the reintroduction of air or by pumping off $\text{H}_2$.

If $\text{CO}$ is used instead of $\text{H}_2$, the same qualitative behavior is observed:

$$\begin{align*}
\text{Rh}_4^{6+} + \text{CO} & \xrightarrow{25^\circ\text{C}} (\text{Rh}_4^{4+})_n \text{ black polymer} \\
(\text{Rh}_4^{4+})_n \text{ black polymer} & \xrightarrow{\text{air}} \text{Rh}_4^{6+} + \text{CO}_2
\end{align*}$$

In this case, $\text{CO}_2$ is observed as a product and the polymer cannot be returned to the tetramer by pumping off $\text{CO}$. When re-exposed to air, the regeneration of $\text{Rh}_4^{6+}$ is quantitative. Thus, it appears that the following overall reaction is taking place:

$$\text{CO} + \frac{1}{2} \text{O}_2 \xrightarrow{\text{Rh}_4^{6+}} \text{CO}_2$$

The $\text{Rh}_4^{6+}$ solution may be cycled many times without apparent loss of the characteristic absorption spectrum.

In the presence of acetic acid (10% V/V) with $\text{Rh}_4^{6+}$ removal of oxygen causes the same black precipitate to occur. Gas is evolved which is most likely $\text{CO}_2$. Upon re-exposure to air, $\text{Rh}_4^{6+}$ is quantitatively regenerated. As
in the case of CO, the solution may be cycled many times by alternate
degassing and aeration of the sample with no apparent loss of catalyst. GCMS
analysis of the product mixture showed that simple hydrocarbons (e.g., CH₄)
are formed in addition to CO₂. Isotope labelling experiments using CH₃COOH
produced labelled CO₂ qualitatively. However, quantitative kinetic data have
not yet been obtained.

To accomplish decarboxylation by a non-radical, template pathway, a
heterogenous catalyst system might be more appropriate (vide supra). To this
end we synthesized a two-dimensional coordination polymer of Rhodium(I). The
polymer is of the type [Rh−(bridge)₂⁺Cl⁻·xH₂O]ₙ (bridge = 1,4-diisocyanobenzene), and consists of colinear bridging ligands separating
Rh nuclei by 12Å, forming a one-dimensional planar array. These arrays are
stacked in an eclipsed manner giving an intermetallic distance of 3.31Å, only
slightly longer than those of dinuclear cations (7) (i.e., Rh₄⁶⁺ described
above for homogenous catalysis). See Figure 1.

This polymeric rhodium network polymer is a semiconductor material (κ
~10⁻⁶ Ω⁻¹ cm⁻¹) and shows promising properties for catalysis and
photocatalysis. The new two-dimensional Rh(I) polymer is found to be more
stable than the homogenous Rh(I) dinuclear cations. Preliminary experiments
in which the Rh(I)-polymer reacts with 1% V/V acetic acid indicate the
evolution of CO₂ and there is also evidence of hydrocarbon products from mass
spectral data. However, in some cases, CO₂ evolution higher than that
attributed to the CO₂ background was not observed, which indicates the
possibility of catalyst inhibition (or poisoning) by unknown components.
Further work is required to define the mechanisms and practical limitations of
this catalyst and to determine decarboxylation rates, yields, and
susceptibility to poisoning or inhibition.
b. Characterization of the Electronic Structure of the Catalytic Sites by ESR Spectroscopy

The electron paramagnetic resonance of a model compound (i.e., rhodium trifluoroacetate dimer) was recently determined\(^\text{(8)}\). This compound is a dimer of two Rh(II) atoms (\(d^7\) configuration) with four trifluoroacetate ligands in a square planar arrangement. Since this compound is diamagnetic, the spectrum was studied as a nitrooxide spin adduct. The M.O. diagram consistent with the ESR spectrum is shown in Figure 2 \(^\text{(8)}\).

In its fully reduced state, the rhodium atoms in the rhodium polymer are formally in the +1 oxidation state. However by analogy to the mixed oxidation state of the rhodium isonitrile dimers, there are a number of mixed valence sites in the rhodium polymer. Furthermore, it is probably the sites with a mixed oxidation state that are responsible for the catalytic activity. A quantitative measure of the number of catalytic sites can be obtained by using ESR spectroscopy, since a combination of Rh(I)-Rh(II) sites will result in an unpaired electron and hence an ESR signal. The ESR spectrum of a sample of
[\text{Rh} (\text{bridge})_2^+ \cdot \text{Cl}^- \cdot \text{H}_2\text{O}]_n \quad (\text{bridge} = 1,4'\text{diisocyanobenzene}) \quad \text{is shown in Figure 3. In this figure, traces A and B are duplicate traces of identical samples of Rh-polymer. The two spectral features are assigned to the hyperfine splitting components G_{11} and G_{1} of ^{103}\text{Rh} (I = 1/2), and are consistent with an unpaired electron in an orbital of } \sigma \text{ symmetry. Trace C is the spectrum of the Rh-polymer after having reacted with acetic acid; the decrease in intensity can be accounted for by a decrease in the number of active sites Rh(I)-Rh(II) due to reduction of the active centers in the decarboxylation reaction. Quantitative measurements of the intensity change will lead to a direct method for monitoring catalytic activity.}
Figure 3. ESR Spectra of Isocyanide Network Polymer.
c. Electrochemical and Electrocatalytic Oxidative Decarboxylation

Generally speaking, electrodes act as catalysts and all electrochemical reactions might be viewed as heterogenous catalytic processes under the influence of imposed electric fields. Electrodes have different catalytic activity depending on the electrode material, the surface morphology and the treatment of the electrode. The most widely studied electro-organic reaction is the oxidative decarboxylation of carboxylic acids (Kolbe electrolysis). The Kolbe reaction is usually carried out in solutions of alkali metal salts of carboxylic acids at platinum anodes. The reaction proceeds preferentially as follows:

\[
2 \text{RCO}_2^- + 2e^- \rightarrow 2R^* + 2\text{CO}_2
\]

The mechanistic pathway depends on several parameters such as anode material, pH, nature of medium and concentration of carboxylic acid. Products by both carbonium ion and radical ion mechanisms can be obtained depending on the conditions\(^9\). Kolbe electrolysis has been used as a final step in the development of a process for the conversion of liquid fuels from biomass. A favorable energy balance (product energy/process energy) of about 4.0/1.0 has been estimated for this process\(^10\). This energy balance could be further increased by application of the photo-Kolbe process. This modification would consist of utilizing an anode of an appropriate semiconductor material, and solar radiation as part of the driving force for the decarboxylation reaction. Bard has shown that for n-TiO\(_2\) anodes, the photo-Kolbe oxidative decarboxylation of acetic acid can occur with a quantum efficiency \(-65\%\)\(^11\). The electrolytic process can also be made more efficient by the use of
chemically modified electrodes. In this case, the electrode surface is coated with a thin film of catalyst, and to the extent that the film allows the passage of current, the catalytic reaction proceeds at the surface of the catalyst. Preliminary cyclic voltametric experiments where the $[\text{Rh (bridge)}_2 Cl^- \cdot x H_2O]_n$ polymer was coated on graphite electrodes show several oxidation reduction peaks in the range between 0 to +1.8V vs. SCE. The peaks are consistent with one electron oxidation reduction of mixed Rh(I)-Rh(II) species\(^{(12)}\). This type of electrode modification can lead to the in situ regeneration of the catalytic substance:

$$[\text{Rh(I)-Rh(II)}] \cdot \text{Polymer} + \text{RCO}_2H \xrightarrow{+e^-} \text{R}^+ + \text{CO}_2 + \text{H}^+ + [\text{Rh(I)-Rh(I)}] \cdot \text{polymer}$$

Then at the anode:

$$[\text{Rh(I)-Rh(I)}] \cdot \text{Polymer} \rightarrow \text{[Rh(I)-Rh(II)]-polymer}$$

Additional energy savings could then be realized for an electrolytic process based on this system since minimal recovery of spent catalyst would be required.

Another electrocatalytic hybrid scheme which looks very promising is the electrochemical regeneration of enzymatic cofactors. Recently\(^{(13)}\) a procedure has been developed in which the regeneration of NAD(P)H from NAD(P) is accomplished by the electrochemical reduction of oxidized to reduced methyl viologen ($\text{MV}^{+2} \rightarrow \text{MV}^{+1}$) followed by flavoenzyme catalyzed reductions of the nicotinamide cofactor by this MV\(^{+1}\). This combined electrochemical enzymatic scheme is more convenient than classical methods and gives rise to much higher turnover numbers. This scheme is schematically shown in Figure 4.
TUNGSTEN CATHODE
E ~ 0.7 V (SCE)

FDR (for NADP)

Lip DH (for NAD)

NAD(P)H

NAD(P)

\[ 2e^- \]

\[ 2\text{MV} + 2 \]

\[ 2\text{MV} + 1 \]

Figure 4. Electrochemical Regeneration of NAD(P)H from Ref. 13.

\[ \text{MV} = \text{Methyl viologen} \]
\[ \text{FDR} = \text{ferredoxin-NADP reductase} \]
\[ \text{LipDH} = \text{lipoamide dehydrogenase} \]
\[ \text{D-LDH} = \text{D-lactate dehydrogenase} \]
\[ \text{GluDH} = \text{glutamic dehydrogenase} \]

It has been estimated that energy consumption expressed as the ratio of product energy to process energy for ethanol production by fermentation is 0.65 (10) to about 1.8 (14), depending on assumptions used in the analysis. This ratio is a reasonable measure of energy consumption because it indicates that if the product was burned as fuel, there would be no net energy benefit if the ratio is one or less. Furthermore, it provides a measure that can be
compared with hydrocarbon production from petroleum, where the ratio is approximately six (14).

For the hybrid biocatalytic-chemical process for production of hydrocarbon previously proposed and investigated (10) the ratio is about four. Essentially all of the process energy is utilized to separate the carboxylic acids and then convert them to hydrocarbons by Kolbe electrolysis. A comparison of this process with an advanced process that would be based on utilization of wood and waste, and advanced biocatalyst and chemical catalyst systems is shown in Figure 5. The values for energy consumption were estimated as follows. Energy for wood/waste production or collection was assumed to be 50% of the energy required for corn production. The net process energy for enzymatic hydrolysis and fermentation was zero, based on an analysis by Chem Systems, Inc. (15) for n-butanol production. The total energy for decarboxylation using a new catalyst was estimated to be 2000 Btu/lb, but could be less, depending on reactor conditions and process constraints.

The significance of this estimate is that it shows that advances in catalysts could yield energy benefit ratios that are more favorable than for hydrocarbons from non-renewable resources, and the ratios would be much higher than previously estimated values for ethanol production. The ratios (product energy/process energy) are: ethanol by fermentation, 0.7 to 1.8; hydrocarbons by fermentation and Kolbe electrolysis, 4.0; hydrocarbons from petroleum, ~6.0; and hydrocarbons by fermentation, using advanced catalysts, >10.2. An additional advantage of such a process is that most of the existing infrastructure and process operations for conversion of hydrocarbons to other chemicals could be effectively utilized.
A. PREVIOUSLY PROPOSED PROCESS (BY LEVY, ET. AL.)

B. ADVANCED CATALYTIC PROCESS

A.\{ Ratio of Product Energy: Total Energy Used = 2.7;

B.\{ Ratio of Product Energy: Total Energy Used > 6.3;

* Per pound of final product

Figure 5. Comparison of Hybrid Processes.
IV. REFERENCES


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