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I. INTRODUCTION

Biomass fermentation and high temperature pyrolysis processes are the classical methods of producing gas or liquid fuels. Each has certain disadvantages, but both are deficient in the extent of carbon conversion to product. For example, the theoretical limit of ethanol production is 67% due to the loss of one third of the available carbon as carbon dioxide gas during the fermentation. Pyrolytic reactions usually lose carbon as char and gases, including carbon dioxide, but may achieve up to 80% carbon conversion.¹ A new strategy was selected to prepare liquid fuels from biomass by a chemical process so as to achieve 100% carbon conversion.

We have developed an efficient multistep chemical process² for the conversion of the principle components of biomass, namely cellulose and hemicellulose, into hydrocarbon fuels and chemicals. The use of selective reduction reactions allows for 100% carbon conversion by keeping the carbon chain intact. Furthermore, initial reactions are conducted in an aqueous medium, which allows the use of wet feedstock. Overall, for example, a six-carbon sugar polymer such as cellulose or starch affords a single pure hydrocarbon product such as hexene. Similarly, other products are now available.

A. GENERAL PROCESS SCHEME

This chemical process consists of four separate reactions. Scheme I shows the main reaction steps that initially achieved the strategic objectives of the organic portion of the
Scheme I

**Biomass** (Cellulose + Hemicellulose + Lignin)

**Step 1**

94% → 1 hr, 165°

H⁺/H₂O, Ru/H₂ (600 psi)

**Step 2**

100% → H₂O₂, 117°

H₃PO₃, 2 hr

**Step 3**

100% → RCH
KOH
heat, 0.5 hr

**Step 4**

Zn/heat

(lodine Free)
process. For clarity, Scheme I shows only the reaction products of cellulose. Starch and hemicellulose aldoses react similarly. Each reaction step is briefly presented to explain the strategy of the process. Detailed discussions then follow.

**Step 1** is a reductive depolymerization of carbohydrate biopolymers. Cellulose\(^3\) or starch\(^4\) is converted into sorbitol in essentially quantitative yield. Hemicellulose aldoses are similarly converted into sorbitol, mannitol, xylitol, etc. The distribution of polyols obviously mirrors the biomass source of the hemicellulose. Lignin, if present in the starting biomass, is separated from the resulting solution of polyols by simple filtration. Thus, Step 1 uniquely provides the polyols required for the next reaction and simultaneously provides a facile separation of lignin.

**Step 2** of the process is the key reaction: the chemical conversion of polyhydric alcohols to liquid hydrocarbons (or chemicals). The major part of all reduction requirements occurs here. Polyols react with aqueous hydriodic acid (HI) and phosphorous acid (\(\text{H}_3\text{PO}_4\)) to afford iodoalkanes and alkene oligomers. The immiscible products, hydrocarbons and halocarbons, are simply removed as a separate phase from the aqueous acid solution in essentially quantitative yield. Reaction conditions can be controlled to afford mainly alkyl iodide (\(\text{C}_6\)) or mainly hydrocarbons (\(\text{C}_{12}\) and \(\text{C}_{18}\)). These groups represent fuels in the range of gasoline, kerosene, and diesel fuel, respectively.

**Step 3** converts the remaining halocarbons (ranging from 10% to 90%) in the mixture from Step 2 to alkenes by an elimination reaction with base (\(\text{KOH}\)) in boiling alcohol.
After reaction, the salts and alcohol solvent are easily removed from the products with simple water washing.

**Step 4** is a cleanup of remaining trace iodides. Boiling the crude hydrocarbon mixture from Step 3 with activated zinc dust provides complete removal of iodine from the 100 ppm range to less than 2 ppm.

**Step 5** does not involve a reaction; it is listed as a unit operation for distillation of the products. Vast differences in boiling points of hexenes (68 °C) from the other higher mass hydrocarbons, 200 °C and 300 °C, allow facile separation of these fuel groups.

**B. OTHER PROCESS STEPS**

The main process is thus defined in three major reactions, a trace cleanup, and a distillation. Recycle of the reagents, solvents, etc. are considered branching steps from the main process. The recovery/recycle of solvents and reagents are analogously listed using the same Step number as above but with a B, C, etc., notation. Some of these will be discussed in detail. The intermediate iodoalkanes and simple alkene products also provide for the syntheses of several oxygenated fuel additives and important industrial chemicals. Separate reaction schemes and detailed discussions for these value-added products will also be presented.
II. RESULTS AND DISCUSSION

A. SUITABLE FEEDSTOCKS FOR NEW CHEMICAL PROCESS

1. Steam Explosion

At the onset of this project, steam-explosion fractionation of biomass was viewed as a means to provide relatively pure cellulose and hemicellulose streams for Step 1 of this process. Generally, wood chips can be fractionated into three streams by the steam explosion process: 1) water soluble hemicellulose contaminated with small amounts of low MW lignin, 2) cellulose pulp containing about 4% lignin, and 3) lignin in an alkaline extract. Peroxide bleaching is required to remove the remaining lignin from the cellulose pulp, an expensive but environmentally friendly process. Typical cellulose pulp via steam explosion from wood chips provides approximately 50% yield. This yield, steam processing, separation, and expensive peroxide bleaching all contribute to a cost of about $150-$170/dry ton ($0.075-$0.085/lb), which includes the cost of the raw biomass. However, any other fraction of the biomass is at this point free of cost. Obviously, recovery and use of any portion of these streams will reduce the overall cost for processing biomass by steam explosion. For example, if this cost were to be spread over a 75% yield which includes the hemicellulose stream, then the cost range is $100 to $113/ton ($0.05 - 0.0567/lb). While there is no cost attributed to the lignin, this was still considered to be too expensive for the fuel process, especially when the lignin content in the cellulose was still several percent and while the hemicellulose stream was also contaminated with lignin phonemics.
However, if just processing costs for the steam explosion and separation of the three streams noted above are considered, which include utilities, chemicals, and labor, this cost would be about $13.48/ton ($0.00674/lb). Note that this cost is presented for the entire biomass, not just the cellulose pulp. It also does not include the cost of the raw biomass, which depending on the selection will vary as a commodity price. It does not include the peroxide bleaching cost, but does include the cost of concentrating the lignin and hemicellulose streams to about a 50% strength.5

Perhaps the best way to present the cost of steam-explosion is as an incremental cost in the overall process. Therefore, it may be advantageous to consider using steam-explosion to initially fractionate raw biomass. This would allow several options:

1) using the hemicellulose as a separate feedstock stream,

2) recombining the hemicellulose and cellulose for larger yield of mixed carbohydrates

3) recovering the lignin for fuel value, or

4) processing the lignin by a totally different manner for chemicals or fuels.

2. Acid Hydrolyzed Biomass

Like steam-explosion, raw biomass may be fractionated by “pre-treatment” with acid whereupon the hemicellulose is readily dissolved. Both “dilute acid and concentrated acid” procedures have been developed.6 Digestion then yields a glucose solution and a pentose solution. Costs are usually quoted as comprising about 2/3 of the cost of making
ethanol or about $0.60 per gal of ethanol. The large expense of acid methods is due to the non-recycling or of expensive recycling of acid and base in the process.

3. Commercially Available Starch Provides Pure C$_6$ Feedstock.

Starch costs about $0.045/lb, and while still relatively expensive is actually less than steam-exploded biomass. Starch solutions may cost somewhat less.

4. Raw Biomass

Ladisch$^7$ as well as others have published that cellulose (42.0%), hemicellulose (26.5%), lignin (28.6%), and ash (0.4%) account for 97.5% of spruce wood. The “extractives such as waxes, starches, oils, gums and cytoplasmic constituents account for part of the difference” (2.5%). Obviously there are different constituents in different feedstocks. Tables of constituents for hardwoods, softwoods, newsprint, corn stover, grasses, etc. are readily available for other feedstock composition information. Costs of biomass will vary from municipal waste streams subsidized with tipping fees to future tree farms or even to starch and refined sugar.
B. DETAILED DISCUSSION OF THE CHEMISTRY OF EACH STEP

STEP ONE (A):

\[
\text{WOOD} + H_2(900 \text{ psi})/\text{Ru(C)} + 0.7\% \text{H}_3\text{PO}_4/\text{H}_2\text{O} \rightarrow \text{POLYOLS (C}_6 \& \text{ C}_3) + \text{LIGNIN/CATALYST (slurry)}
\]

1 hour, 165° C

For example:

\[
(C_6H_{10}O_5)_n + H_2O + H_2 \rightarrow C_6H_{14}O_6 \text{ (Sorbitol)}
\]

\[
(C_3H_8O_4)_n + H_2O + H_2 \rightarrow C_3H_{12}O_5 \text{ (Xylitol)}
\]

One of our goals was to compare a Russian method for fractionation of raw biomass by the direct reduction to a polyols solution. A unique fuel process may well justify a uniquely matched feedstock process. Thus, a facile biomass to polyols (BTP) fractionation is perfectly suited for our process. Lignin is removed by simple filtration. In this manner, a mixed-size polyols solution is obtained directly from raw biomass. Or a pure C_6 polyols may be obtained directly from starch. Indeed, polyols are the required substrate for conversion to hydrocarbons via Step 2 of our process.

Russian researchers demonstrated that cellulose can be converted to sorbitol in >94% yield. They also converted acetone-extracted sawdust to a clean polyol solution, hexitols and pentitols, in 95% yield. Two high-pressure reactors for evaluation of this step were acquired via the DOE-ERLE program. About 100 such reactions have been conducted in this manner in our labs. Many variables have been studied. The typical amounts of pentitols and hexitols expected from spruce wood for example are 26.5% and 42.0%, respectively, and therefore 68.5% total. Hardwoods (Aspen) approach 80% holocellulose
due to increased hemicellulose (xylans, 25%) and less lignin. There is also less volatile oil (extractives) in hardwood. Softwoods have a larger mannan content (C₆ sugars) and as a result only about 10% of C₅ content.

In our study of this biomass to polyol (BTP) fractionation, results are in line with the Russian literature but vary somewhat with biomass source and type of catalyst used. About 20-60 ppm of reducing sugars is present in the resulting polyol solution (after 1-2 hr at reaction temperature). We have used some of these mixed size polyols directly in Step 2 of the process with reasonable success (85% yields). As it turns out the are a few complications when both C₆ and C₅ substrates are run simultaneously. The products are much more volatile and are therefore more difficult to quantitate. We have also discovered that some of the products (carboxylic acids and lactones) from actual reactions of holocellulose are fairly water soluble and have not been recovered well from these initial tests. However, not even a trace of a phenolic by-product, which might have resulted from some lignin degradation, has been detected.

There is some slow hydrogenation and/or hyrogenolysis of reactive lignin functional groups (e.g., aldehydes, alkenes, and benzylic ethers). This is determined by the continuing slow reaction of hydrogen. A computer-controlled reactor was used to optimize the polyol conversion while minimizing the slower lignin reaction. There may also be some reduction and cleavage of 3-carbon components from lignin to afford glycerol in the polyols solution. However, GC/MS and HPLC analyses of several polyol solutions have not shown much, if any, glycerol. This has not yet been determined.
The lignin and powdered catalyst (Ru/C) are filtered from the aqueous solution. Standard lab grade filter paper suffices. No further removal of any particles could be determined with filtration through 0.45 micron filter paper. Alternatively, pelletized catalyst is simply screened from the slurry and the lignin is centrifuged or filtered from the polyol solution. Such facile catalyst recovery was deemed very important for industrial scale use.

One important question for this step arose very early: Is it necessary to extract the wood with acetone as per the Russian literature? The Russian investigators used “spruce (or pine) sawdust” and “extracted with acetone to remove resins.” The actual components extracted have not yet been assessed in this laboratory. Repeating this reaction, which was only briefly described in the literature, has been our first concern. While some extraction experiments were done, this extraction process is now not deemed necessary. The present task to just produce a fuel does not require a highly purified polyol. In fact, the presumed extraction of terpenes (pine oils) which was reported in the literature was probably to eventually provide a clean, crystalline polyol. In our case, any terpene impurities carried through would be very much like the fuels produced from the process. It was also considered possible for these oils and/or waxes to absorb onto the catalyst and to perhaps interfere in some way with subsequent catalyst activity. This does not appear to be the case.

A two-stage hammermill fed with one-inch wood chips will provide minus 10-mesh material and requires about 60 hp hr/dry ton. Feed size of the raw biomass is not deemed critical, it simply relates to the speed of the hydrolysis and convenience of slurrying in
the reactor. There seems to be little difference between the reaction time required for minus 60-mesh sawdust versus minus 10 mesh.

We have extended the catalytic hydrogenolysis reactions of lignocellulosic biomass to apply to low rank coals (lignite) that also have high oxygen content. In a few preliminary reactions we have found that 90% of lignite can be extractively solubilized in aqueous base, as was lignin after subjection to these same reaction conditions. We are presently writing another paper about this novel prospect for coal liquefaction at much less severe conditions than has been done in the past.

**STEP ONE (B): Recycle of Ru/C Catalyst**

Powdered Ru/C catalyst can only be recycled several times before treatment becomes necessary. Lignin can be extracted (90%) into aqueous base from the powdered catalyst. A Hastelloy C reactor equipped with a basket for pelletized catalyst afforded an even better method for lignin separation. The pelletized catalyst was simply screened from the solution. Lignin is easily centrifuged or filtered from the polyol solution and completely recovered. However, the catalyst shows the same degree of deactivation when reacted with raw biomass or even with pure starch. With pure starch there was no terpenes, protein, or lignin to blame for the loss of activity. Therefore, some reaction with oxygen, mineral acid, or with trace metals may be giving the gradual catalyst deactivation. While this will be a phenomenally simple and inexpensive method to obtain both a separation of lignin from biomass and simultaneously prepare a mixed size polyol solution, a suitably
stable catalyst system must yet be devised. Recently however, a patented process for
similar polyol production was found in the literature.\textsuperscript{4} This process uses Ru on a zeolite
catalyst which requires no extra mineral acid co-catalyst. Perhaps this catalyst system
will maintain activity over many uses as is reported.

Ultimately, the easily recovered lignin is then available as a value-added product, used as
feedstock for subsequent upgrading reactions, or perhaps in a less valuable way simply
burned for cogeneration power.

\textbf{STEP TWO (A): Polyols to Halocarbons and Hydrocarbons}

\begin{align*}
C_6H_{14}O_6 + 5 H_3PO_3 + 9 HI & \rightarrow C_6H_{13}I + 5 H_3PO_4 + 8 HI + H_2O \\
2 C_6H_{14}O_6 + 9 H_3PO_3 + (HI) & \rightarrow C_{12}H_{22} + 9 H_3PO_4 + 3 H_2O \\
3 C_6H_{14}O_6 + 13 H_3PO_3 + (HI) & \rightarrow C_{18}H_{32} + 13 H_3PO_4 + 5 H_2O
\end{align*}

Tables presented in our U.S. Patent show reactions conditions of several polyols versus
product ratios and yields.\textsuperscript{2} Yields of total products are essentially quantitative. However,
this reaction is highly tunable, i.e., by simple dilution, a 1:4 mixture of halogen
compounds to hydrocarbon compounds is obtained. Optimum production of hydrocarbon
compounds, which require significantly less reduction, occurs with 43 - 48\% water
content. Without dilution, about 90\% is $C_6H_{13}I$ and the remainder is mostly $C_{12}H_{22}$.
Progressively smaller amounts of each higher oligomer $C_{18}$, etc. are also produced.
The reaction fails if the ratio of HI to sorbitol (a C₆ polyol) is not greater than 6 to 1, or if water content is greater than 50%. As one might expect, the ratio may be smaller for a C₅ polyol or for a mixture of C₅ and C₆ polyols. Please note that HI is the reagent; the H₃PO₃ should be viewed as a coupled redox reagent. H₃PO₃ instantly converts incipient iodine (I₂) into hydriodic acid (HI). This maintains the high concentration and ratio of active HI. For mechanical, sequential batch additions, and dilution reasons, an initial 9/1 ratio is typically used. To the extent that halogen products form, this ratio is diminished with each sequential batch reaction. As each batch of sorbitol is reacted, the products simply float on top as a separate layer. Then, another batch of sorbitol and H₃PO₃ is added to the pot and the reaction continued. Each time the organic layer gets bigger but the ratio of acids to unreacted polyols stays about the same. We have developed a detailed spreadsheet calculator for this reaction to help maintain the optimum ratios of reagents for both the batch as well as a continuous drip mode. Since the original grant proposal, this reduction step with hydriodic acid has been increased in scale by a factor of 100-200. Sorbitol is converted into hydrocarbons (major products) by up to three sequential additions of about 1-1.5 mole to the same 3 L flask. This scale provides 0.5 to 1 L of products per workup. An example of a preparative experimental procedure is:

**Production of C₆, C₁₂, C₁₈ Products from Sorbitol (Sequential Batch Method)**

Using a 3 neck (ST 24/40), 3 L flask with two Freidrich's condensers, D-sorbitol (150.1 g, 98 %, 0.8 mol), hydriodic acid (HI, 980 mL, 57 %, 7.2 mol), and phosphorous acid (H₃PO₃, 372.3 g, 97%, 4.4 mol) and deionized water (200 mL) were refluxed (118 °C) under a nitrogen atmosphere for 2.5 hours. The solution
was allowed to cool for approximately 20 minutes. D-Sorbitol (150.1 g, 98%, 0.8 mol), H₃PO₃ (338.5 g, 97%, 4.0 mol) and H₂O (260 mL) were then added and the solution refluxed overnight. The product (top layer) was then separated from the aqueous acid (bottom) using a separatory funnel. The total product was 149.8 g.

Mass spec analysis allowed an estimation of the production yields. The recovery of C₆I was 6.57%; C₁₂ was 42.69%; C₁₈ was 46.11% and C₂₄ was 5.43%. The additional water added to the reaction limits the reaction to 2.4 moles of sorbitol per 3 L flask. This run used only 1.6 moles. Each run is limited to the amount of sorbitol per batch due to the exothermic nature of the initial reaction.

Such sequential batch additions also makes for more efficient use of the HI before water and H₃PO₄ has to be removed. This engineering allows for the instantaneous ratio of HI to be high but finally results in a 3:1 to 1:1 range versus starting carbohydrate overall. This simple reuse of expensive HI is made possible by the fact that HI is regenerated in situ by the iodine reaction with phosphorous acid.

The reaction is highly adjustable. We are inclined to push the direction towards a high ratio of hydrocarbon fuels rather than to C₆H₁₃I. While preparation of mostly C₆H₁₃I is cleaner and can easily be made to be a continuous process, it requires more reduction.

**STEP TWO (B): Recovery of HI**

\[
\text{H}_3\text{PO}_3 \, + \, (\text{I}_2) \rightarrow \, \text{H}_3\text{PO}_4 \, + \, (\text{HI})
\]
The acid solution after the above reaction consists primarily of HI and H₃PO₄. One of our most important tasks was to actually reconstitute the somewhat diluted hydriodic acid (HI) from the spent reagents in Step 2. Initial distillations of HI were partially successful but resulted in several pyrophoric decompositions of phosphorous moieties that led to several small but nonetheless disturbing fires. The problem was solved in a simple manner by monitoring the phosphorous species in this strong acid solution directly with the new NMR spectrometer purchased by the grant. Traces of unreacted phosphorous acid remaining in the HI solutions are easily oxidized to stable phosphoric acid by a stream of air during the early stages of the distillations. The distillations can then be completed safely and show recovery of 99.99% of the HI. The presentation at the Dallas ACS meeting was drafted into a paper submitted but not yet published.

**STEP THREE (A): Conversion of Halocarbons to Hydrocarbons**

\[ C_6H_{13}I + C_6H_{12}I_2 + (KOH) + (ROH) \rightarrow C_6H_{12} + C_6H_{10} + (KI) + H_2O \]

This step represents a classical elimination (E2) of hydrohalic acid equivalents from the substrates by reaction in hot alcoholic base. 2- and 3-Iodohexane thus give *trans*-2- and 3-hexenes. Small to trace amounts of dihalo compounds presumably give dienes. The use of less expensive NaOH rather than KOH in Step 3 was the initial choice but the eventual electrochemical recovery proved more efficient with KOH. It is used in excess mole quantities than actually required in the above equation. In the same step, any mechanically entrained HI will be recovered to KI as well.
Furthermore, we have addressed the glucuronic type carboxylic acids that are part of the hemicellulose. Of course the content varies with different species of wood having various but small amounts. Hardwood and softwood have about the same amount (3%). These polyhydroxy acids are reduced to the gluconic type acids and subsequently converted in Step 2(A) to water-soluble lactones and isomers of iodojexanoic acid, which are in turn converted into hexenoic acids. Such medium length (6 carbon) chain acids, or their conjugate base salts, can be electrochemically coupled to decane by well-known reactions. Alternatively, these acids may have more value as chemicals rather than as fuels. Therefore, each feedstock may have to more carefully evaluated as to the extent of glucuronic acids present. On the other hand, if starch or only the cellulose fraction of steam exploded wood is used in this process then such problems from these hemicellulose components would not be a factor.

**STEP THREE (B): Solvent Recovery**

Several solvents have been used for this step, methanol, ethanol, propanol, and 2-hexanol. The smaller alcohols are deemed the better choice. The small alcohol can be efficiently washed from the hydrocarbon products and then does not interfere with the distillation process. For example, ethanol and the hexenes form an azeotrope with a 46-66 °C boiling range that cannot be separated by distillation. If steam explosion is used to prefractionate biomass for this process, then the methanol byproduct (about 1-3%) will be available. The alcohol is eventually recovered for reuse from water by flash distillation.
STEP THREE (C): Hexenoic Acid Recovery

Hexenoic acids are extracted as their conjugate base into the basic layer of this present Step 3. These may build in concentration, as the base layer is recycled. At some point, the base layer will be reacted with a dilute acid stream from Step 2 and these organics recovered. They may have some chemical value or value as a fuel additive, rather than just btu value. Again, this step would only be necessary if the hemicellulose is included in the feedstock.

STEP THREE (D): Electrochemical Regeneration of HI

\[ \text{KI} + \text{H}_2\text{O} \rightarrow \text{KOH} + \text{HI} \]

This regeneration of dilute acid and base from salt water is a viable commercial process for NaCl streams. It is accomplished electrochemically with a bipolar membrane cell. Aqualytics\(^8\) cells are used commercially for regeneration of neutralized pickling acid and spent battery acid recovery. It has also been documented for NaBr but not with an iodide salt. Therefore, an Aqualytics electrochemical cell stack was ordered and a pilot scale processing plant was constructed. The study of the recycle of NaI and KI salts back into HI and NaOH or KOH was completed. The choice of K cation versus Na cation for base in Step 3 has now been made because the K ion gives such better electrochemical results when recycled. KI gave about 90-95% total current efficiency versus about 75-80% efficiency for NaI (see Fig 1). The expensive nature of HI, because of scarce natural
resources, requires that it be recycled from each part of the process. While these iodide salts result from the elimination of the alkyl halide to the alkene (hexene), they may be only a minor amount of the overall products from the process. However, if hexene or compounds produced from hexene, such as hexane, are desired as the major route then this recycle of salts has a greater impact.

**STEP FOUR (A): Trace Iodide Removal**

Results by GC/MS instrumentation clearly indicated that less than 1% levels of iodine had been obtained in Step 3 by the simple treatment with base. Upon actual analysis however, there remained small amounts of iodide impurities (15-350 ppm) in the respective low to high boiling hydrocarbon products. It was desirous to remove these trace levels of iodine for two reasons:

a) the corrosive character of the combustion by-product, hydriodic acid, and

b) potentially expensive iodine replacement costs.

The latter is also no trivial matter because even a hundred ppm of iodine in a fuel for about 5% of the nations fuel needs for about one year might exhaust the natural resource supply of iodine and negatively impact market price of the required hydriodic acid.9

There seems to be some correlation of trace iodide remaining in the organic layer that varies with the bp range of the products. For example, the hexene fraction ranges from 15 - 50 ppm, if the NaOH treatment is only done one time, while the C12 fraction is typically in the 100 - 350 ppm range, etc. While this level of iodine was almost 4 orders of
magnitude better than previous reports by Canadian researchers (30 %),\textsuperscript{10} it was not sufficient. Repeated base treatments gave little improvement because there is also the statistical problem of finding the last few molecules to react within a given amount of time, i.e., the iodine concentration approaches zero with time. To optimize time and yet overcome this infinite dilution problem, either a scavenger reagent with a strong affinity for halogen (a dissolved electron) or another strong reducing agent is necessary to remove all traces of iodine. Several reagents were investigated. Indeed, it is necessary for even further reasons to chemically remove the last traces of iodine from the C\textsubscript{12} and higher homologues before they can be easily distilled. Iodine vapors from thermal decomposition of iodides occur and severe foaming cause problems on distillation.

Finally, the problem was solved as mentioned earlier in the introduction to the general process scheme (Scheme I). The Step 4 reaction was incorporated into the process. The hydrocarbon product mixture after Step 3(A) containing iodine impurities is simply boiled with activated zinc dust for about one hour. After separation of the solids, unreacted zinc dust and salts, the fuels were washed with water. The dried hydrocarbon layer is then filtered through Celite filter aid. Fine filtration of the treated fuels apparently removed some colloids or salts that may have been partly responsible for the foaming during the distillation. It is likely that the water wash is not required.

\[
\text{C}_6\text{H}_{13}\text{I} + \text{C}_6\text{H}_{12}\text{I}_2 + (\text{Zn}) \rightarrow \text{C}_6\text{H}_{12} + \text{C}_6\text{H}_{10} + (\text{ZnI}_2)
\]
Liters of fuels were produced as reactions were scaled up by a factor of several hundred. Analyses of these fuels for iodine content by an outside commercial laboratory, Galbraith Labs, was conducted. Their method for trace iodine analysis in an organic substance uses an oxygen bomb combustion and subsequent selective ion electrode measurement of the liberated ion. The limit of detection of iodine by this method is 2 ppm for a 0.2 g sample.

**STEP FOUR (B) : Zinc Iodide Recycle**

The small amount of zinc iodide that is washed out with water will probably have to be ion exchanged with potassium ion, and eventually a reasonably sized batch of zinc ion can be reduced back to zinc dust. This will be combined with any acid solution that is used to activate the zinc dust so that all traces of zinc and iodide are accounted for. This small amount of iodide solution can be returned to the Step 3(D) KI stream for recycling.

**STEP FIVE : Distillation and Separation of Fuel Groups**

This is not a reaction step as was presented in the general introduction scheme (Scheme I); it does requires some energy cost. The hexenes are distilled easily, generally 64-68 °C. The C_{12} fraction may be distilled at about 180-210 °C without vacuum or between 75-82 °C at 5 mm. It is preferred to distill the higher oligomers at reduced pressures, C\textsubscript{18} bp = 145-150 °C at 3.75 mm, C\textsubscript{24} bp = 160-190 °C at 1.25 mm, and C\textsubscript{30} bp = 200-212 °C at 0.65 mm. A blend of C\textsubscript{18}s + C\textsubscript{24}s, etc., might be kept together for a fuel oil and not
distilled. Marketing choices for such product blends have not been made. The higher oligomers are obtained in progressively smaller amounts.

C. OPTIONAL REACTIONS TO VALUE ADDED PRODUCTS

With the very low prices for fuels in the current marketplace, it is logical to seek more valuable products from the process, particularly for the near term. Therefore high purity solvents, oxygenate additives for fuel, and other value-added chemicals for industrial use were also sought. Intermediate iodoalkanes as well as the hexenes fraction both provide for the syntheses of several oxygenated fuel additives and an important industrial solvent. Three of these reactions, Step 6(A-C), are shown in Scheme II. While similar syntheses from iodoalkanes have been proven, these result in additional streams from which iodine must be recovered. For this and other reasons, only hexenes are used in these syntheses.

**SCHEME II**

\[
\begin{align*}
1) & \quad H_2SO_4 \\
2) & \quad H_2O \\
\text{ROH} & \quad H^+ \\
\text{H}_2 & \\
\end{align*}
\]

\[
\begin{align*}
\text{OH} & + \quad \text{HO} \\
+ & + \\
\text{R-R} & \\
\end{align*}
\]
OPTION STEP SIX (A): High Purity Solvent Hexane

\[
\text{Hexenes} + \text{H}_2 + (\text{Pd/C}) \rightarrow \text{Hexane}
\]

This optional step (Scheme II) does not produce a fuel. But it does show the capability to produce hexane, a value added industrial solvent. Hexane only has an average octane number of 25.\textsuperscript{11} Hexane sells for about $0.85/gal to $1.25/gal as an industrial, polymer grade solvent. Hexane for seed oil extraction may be less pure. This reduction is an easy classical type of catalytic hydrogenation. For example, Pd/C at ambient temperature and only about 100 psi of hydrogen will give essentially quantitative conversion. On a larger scale, a countercurrent trickle tower provides for a continuous flow reactor.

OPTION STEP SIX (B): Hexanols as Oxygenate Fuel Additives

\[
\text{Hexenes} + \text{H}_2\text{O} + (\text{H}^+) \rightarrow \text{Hexanols} + \text{R-R}
\]

A mixture of 2- and 3-hexanol is formed by the addition of water to the hexenes (Scheme II).\textsuperscript{12} The extent of conversion to alcohols is only moderately good. Some oligomerization to noncyclic hydrocarbon fuels occurs. This step has not been optimized. Sulfuric acid must be reconstituted for reuse. Commercial methods may be more efficient as well as selective with catalytic hydration at high temperature and pressure (250 °C @ 500 psi).\textsuperscript{13}
This alcohol mixture may be suitable as a fuel additive. The value of this natural blend of isomers as an octane booster with low vapor pressure needs to be established. However, information for one of the isomers, 2-hexanol, appears suitable as a good octane fuel \((R+M/2 = 84)\). It is not high enough for fuel blending. Table I lists and compares pertinent data for several commercial oxygenates.

**OPTION STEPS SIX (C): Hexyl Ethers as Oxygenate Fuel Additives**

Hexenes + Alcohol(s) + \((H^+)\) \(\rightarrow\) Hexyl ethers

Methyl, ethyl, isopropyl, and bis-2-hexyl ethers have been made by a variety of means of adding the alcohol to the alkene (Scheme II).\(^{14}\) The 3-hexylethers have not been investigated. The value of each as a fuel additive was determined.\(^{15}\) The blending octane numbers for these additives were not as good as known tertiary ethers (see Table I). Octane numbers are about half what is desirable.

Thus, we now recommend that one of several published/patented procedures be first used to rearrange our hexenes (and pentenes) into tertiary olefins as shown in the following equation.\(^{16}\) These tertiary alkenes are even easier (acidic resin catalysis) to convert by commercial methods directly into TAME (tertiary amyl methyl ether, Table I) and THME (tertiary hexyl methyl ether) both of which are used today as commercial fuel additives. This will be the focus of near term future work. But rather than repeat their
work, our task will be to show the scale, continuous flow, and efficiency necessary to provide the simple alkenes to these facilities.

\[
\text{WO}_3 / H_2/H_2O \\ 250^\circ/320^\circC \\
\rightarrow \text{conversion} \quad 58\%
\]

Similarly, bis-2-hexyl ether was made by adding 2-hexanol to 1-hexene and by simple dimerization of 2-hexanol. Such heavy oxygenates may prove to be useful for cetane enhancement. However, the secondary bis-2-hexyl ether gave only fair to good cetane enhancement (Cetane # = 67). Linear ethers like 1,1-dipentyl ether are required for excellent (109) cetane values for fuel blending.\(^\text{17}\)

D. PREPARATION OF SPECIAL JET-A AND DIESEL FUELS

\(^1\)H and \(^{13}\)C NMR data that classify n-alkanes, branched and cyclic alkanes, and aromatic content has been used successfully to predict important fuel properties and thus determine whether a particular fuel will meet physical specifications such as Cetane Index. Cookson and coworkers,\(^\text{18}\) in a series of papers, used HPLC, GC, and NMR techniques to express fuel property values in terms of chemical composition. Through their work it is now possible to represent a specified property constraint as a composition constraint. These authors showed the chemical compositional requirements for jet fuels that fell within the narrow bp range of 190-230 °C. The C\(_{12}\) fuels produced in the present process would be classified from a theoretical percent hydrogen of 13.338% and an actual specific gravity
of 0.84 to be right on the edge of the "specification domain" for jet fuels. Predicted values for smoke point, freezing point, and net heat of combustion being 18, -66 °C, and 42.64 MJ/kg, respectively. For this fuel it can be argued that the relatively high heat of combustion per unit volume would significantly extend aircraft range. The olefinic character, almost exclusively tetrasubstituted sp² carbons, may suffice as an equivalent for the aromatic content of typical jet fuels. A good portion of these isomers are bycyclics, i.e., naphthenes.

The compositional requirements for diesel fuels of bp 230-320 °C are, much to our surprise, also predominately branched and cyclic alkanes (BC). The "specification domain" runs from 100% branched and cyclic (BC) up to a 40% aromatic content with 40% n-alkanes and only about 20% BC. The maximum amount of n-alkanes is 40-55% where it is bounded by cloud point line of -4 °C. Cetane Index provides the opposing "specification domain" boundary. Thus the C₁₈ fuel which consists solely of branched and cyclic compounds should fit within this "specification domain." Continued efforts to isolate individual components of the C₁₂ and C₁₈ range of isomers are in progress. NMR data required to support these predictive property correlations are in progress. However, with the current market prices for hydrocarbon fuels being so low, these tests and data are not a high priority.

Some data is now available for the novel hydrocarbon fuels (see Table II). While hexenes have a good octane number, alkenes are not desirable in gasolines for other reasons. Hexane is too linear and would have to be cracked to branched alkanes to be useful as a
gasoline fuel. Hexane could serve as a conventional feedstock to a crude oil refinery which takes low valued straight run gasoline today and cracks it to a higher valued fuel. However, the dimers showed an unexpectedly high octane number (78) versus cetane number (24). The branched and cyclic nature of these dimers obviously imparts this characteristic while typically a straight chain affords higher cetane number. The trimers (C\textsubscript{18}) also are branched and cyclic (cetane \# = 25). Not enough “cross products,” arising from a C\textsubscript{5} blend with C\textsubscript{6} feedstocks, have been isolated to obtain fuel data.

E. Demonstrations of Alternative Reductive Recycle of Iodine to HI.

One of the major goals of this DOE grant was to study the economics and to improve the prospects for eventual use in industry. In order to achieve this measure of economics and eventual acceptance a method was sought that would be less expensive than the current consumed phosphorous acid and phosphoric acid byproduct. Several approaches were investigated:

a) methods to recycle the H\textsubscript{3}PO\textsubscript{4} back to H\textsubscript{3}PO\textsubscript{3},

b) direct hydrogenation of incipient iodine during Step 2,

c) direct electrochemical conversion of I\textsubscript{2} during the Step 2 reaction.

Using \textsuperscript{31}P NMR analysis, we found that between 2-3\% H\textsubscript{3}PO\textsubscript{3} could be achieved by direct electrolysis of H\textsubscript{3}PO\textsubscript{4} in HI solution. Greater success was not to be. Apparently, the electrodes polarize, the mechanism changes, and the progress stops. Similarly, we had only very low successes with Indium or Vanadium iodide salts as co-reduction couples to
reduce the $\text{H}_3\text{PO}_4$ to $\text{H}_2\text{PO}_3$. However, both (b) the direct use of catalytic hydrogenation as well as (c) the direct reduction of iodine electrochemically have been demonstrated. Both these methods thus achieve **major milestone** goals of this grant. Both are still continuing to be studied.

**F. Direct Use of Hydrogen for the Reduction of I$_2$ Generated in Step 2.**

A stated **major milestone** and an alternative for the electrochemical couple discussed above, is the use of direct catalytic hydrogenation of the *in situ* generated I$_2$ during Step 2. Upon upgrading our Teflon lined (Berghof) reactor, this task was addressed during the final year. $\text{H}_3\text{PO}_4$ could not be hydrogenated in concentrated HI. Indeed, no reaction occurred even at 150 °C at 50 atm. However, as expected, when I$_2$ was also dissolved in the solution, catalytic hydrogenation did occur. Hydrogenations during a Step 2 reaction of sorbitol to hexane have also begun. However, only 67% of the expected amount of product has been found. It is likely that the reaction really gave near quantitative conversions but because of the “tree of sensors and gauges” needed to monitor reaction progress a fair amount of material was lost. Such mechanical losses can be overcome with different arrangements in the future. Our use of Rh/C and Ir/C catalysts may be the reason why greater conversions were achieved than those of a Japanese Patent. While the goal has been met in this sense, further work of product distribution and catalyst recycle are planned. Continuous drip of sorbitol solutions directly into the hydrogenation reactor via HPLC pump should give products weighing a total of more than 1 g and thus be easier to gain accurate material balances, etc. This area looks very promising. The
reaction has the same sort of controls to provide either mostly hydrocarbon dimers and trimers or alternatively mostly haloalkane. However, the C\textsubscript{12}S did have mass of 168 rather than MW = 166 typically obtained in previous methods, indicating that the cyclic dimers had no unsaturation.

G. Electrolytic Reduction of I\textsubscript{2} in HI Using a Membrane Divided Cell

In a procedure similar to an earlier patent,\textsuperscript{20} iodine was reduced to HI using a membrane divided cell. A simple electrolysis “H” cell was constructed that would accommodate a Nafion\textsuperscript{®} membrane clamped between Viton\textsuperscript{®} washers between the two half-cells. The cathode compartment was filled with 40 mL of 1 M hydriodic acid (HI). Carbon rods were used as the working electrode and together with the Ag/AgCl reference electrode were placed in the cathode cell. The anode compartment was filled with 40 mL of 1 M phosphoric acid solution (H\textsubscript{3}PO\textsubscript{4}) and fitted with a platinum coil as the auxiliary electrode. An EG&G Princeton Applied Research Model 363 potentiostat/galvanostat held the working electrode at –0.001 V until the solution was clear. The background current was measured to be 4 mA. Iodine (1.539 g, 6.064 mmol) was added to the cathode cell. The voltage immediately rose to 600 mV and the current was held constant at 200 mA. After 1.69 h the voltage dropped sharply to 0 V. This “end point” for reduction thus calculates a 96% (±2%) current efficiency.

Similarly, the cell was established with concentrated HI (35 mL of 7.57 M) and H\textsubscript{3}PO\textsubscript{4} (40 mL of 3.78 M). Then iodine (2.5676 g, 10.116 mmol) was reduced for 328 min
beginning at 150 mV briefly rising to 825 mV before returning to 150 mV, all the while held at a constant 100 mA. This calculates to a 99.2% (+2%) current efficiency.

This method of reduction of iodine was also conducted simultaneously on the iodine generated in a reaction of sorbitol (5 g) refluxed in 250 mL of concentrated HI analogous to the sorbitol reduction outlined in our US Pat. 5,516,560. Alkyl iodides and hydrocarbons as described in our patent were similarly produced. These coupled reduction reactions represent a practical use for this method. Indeed, the incipient iodine formed during the organic reaction is reduced electrolytically rather than by added H₃PO₃ or by catalytic hydrogenation. This reduction is much less expensive than either previous method. It has added advantages of not 1) having to occasionally recycle/redistill HI to remove H₃PO₄, 2) having to sell or dispose of potentially large quantities of this mineral acid, and 3) requiring a sister plant for large amounts of hydrogen.

H. Novel Reactions for Chemicals from Biomass.

Now that the polyol system has been well characterized, other more oxidized carbohydrates, e.g., gluconic acid, were examined. While this type of substrate occurs in small amounts in a natural hemicellulose, it could be scaled to the major reaction of biomass carbohydrates by initially oxidizing carbohydrates rather than reducing them to polyols. Model studies were thus done with gluconic acid. After the first reaction with HI/H₃PO₃, we were surprised to learn that caprolactones were a major product with some iodoheptanoic acids.
Such caprolactones may be valuable as chemicals or may be converted into other value added products. Therefore we examined several variables to try to drive the reaction to primarily lactones. As before, we used different ratios of HI and H₃PO₃, hypophosphorus acid instead of phosphorus acid, time of reflux, and the percent water in the reaction. These reactions are still not conclusive as to the optimum conditions. However, the extraction of lactones has been greatly improved, so now perhaps material balances and yields may be improved. A procedure that does afford good yield and a 4/1 lactone/acid mixture has been established.

Solid H₃PO₃ (21.13 g, 250 mmol) was dissolved in gluconic acid solution (50% in H₂O, d = 1.234 g/mL, 16 mL, 50 mmol) and HI (57%, d = 1.701 g/mL, 73 mL, 550 mmol) in a 250 mL round bottom flask. This mixture was refluxed under nitrogen for 5 h. The resulting mixture was extracted with CH₂Cl₂ (usually 3 x 100 mL). NOTE: 4-ethyl-γ-butyrolactone is fairly soluble in water, therefore, multiple extractions are required for efficient separation. Each portion was agitated for 5 minutes to ensure thorough partitioning. The combined extracts were dried with Na₂SO₄. Solvent was removed under vacuum to afford 6.734 g. Spectral analysis confirmed that one of the products is a butyrolactone. GC/MS analysis of this material allowed an estimation of 74.8% yield of lactones(s) and
18.5% iodohexanoic acids giving a total yield of 93.3%. The lactone percentage consists of two isomers, probably the gamma and delta lactones.

The iodic acid products are currently undergoing reaction with alcoholic base to afford hexenoic acids, analogously to the iodide removal in the polyols sequence.

Also at this time reactions with glucose are being re-examined. Preliminary evidence indicates that the results are a very complex mixture and that this reaction is much more dependent upon the variables. Product separation and structure identification, and variables are continuing to be studied.

I. ECONOMIC PROJECTION

This multistep chemical process for reduction of biomass to liquid hydrocarbon fuels is the first of its kind. It stands in sharp contrast to other research areas that follow classical lines of bio- (fermentation) or thermal (pyrolysis) conversion. In fact, uncoupling the reduction process to a series of mild selective chemical reactions was the key to the problem. As a result, economic advantages abound. One particular advantage of this chemical process is that both Step 1 and Step 2 reactions take place in water as solvent, which allows the use of wet biomass. The water immiscible organic products of Step 2 simply coalesce as an upper layer facilitating their separation by mere decantation. Another benefit of the process is that the cyclic alkene dimers and trimers produced directly in Step 2 may require less reduction, 10% and 13%, respectively, than hexene.
Nor do these oligomeric hydrocarbons require base treatment and subsequent reagent regeneration costs as do the haloalkanes. Step 2 is highly tunable, which allows a choice of product distribution. Each step of the process can be driven to essentially quantitative yield resulting in the same high yield for the entire process.

There are five major economic concerns of our Biomass to Fuel Process:

1) The cost of a multi-step process
2) The cost of the feedstock and its preparation for the process
3) The cost of reduction.
4) The recycle efficiency of expensive hydrogen iodide and other reagents.
5) The value of the products

Each will be addressed.

J. Multistep Complexity

Any multistep process is more complex (interrelated) so the benefits and the advantages that accrue with each successive step must outweigh the alternative. However, this should not be construed to mean more difficult. By using more steps (complexity) in this process it is actually less difficult to achieve a high yield of specific and valuable compounds. And there are no major separation problems. A difficult to engineer solids handling problem such as occurs with shale oil extraction or most biomass pyrolyses have delayed if not prevented these methods from becoming broadly commercial. There are on the other hand many petrochemical, chemical, pharmaceutical, and biogenetic-chemical
companies that have succeeded in engineering intricate plants to provide multistep paths
to a variety of industrial products and consumer goods. So engineering presently existing
in industry can be directly used for this process. Feedstock materials for this process are
already handled by the pulp and paper industry, distilling industry (alcohol), and waste
disposal companies. Conventional distillation, transportation, storage, and sales easily
handle the liquid fuel and chemical products. The middle of this process should be
relatively easy for the chemical industry engineers who are accustomed to handling
corrosive liquids in glass lined reactors, Teflon lined pipes, etc., which are today simply
off-the-shelf items. Yes, there will have to be extensive attention to details of plant
design, but there is no step that does not have an analogously engineered counterpart in
industry today.

In such a new versatile process there are several options for processing pathways that
have not been determined. When improved economic data in any one area is obtained, the
entire process must be updated. For now, only one economic model may be considered:
one using starch. The other models, one using steam exploded cellulose and one using
raw biomass as feedstock, must await catalyst recycle studies. But does the steam
explosion cost more than all the benefits that result from its use to prefractionate raw
biomass? If just steam-exploded cellulose is used in the process then the low lignin
content results in less catalyst recycle in Step 1, and Step 3C is now moot. But is there
enough market to absorb the entire hemicellulose stream? If there is, then the C₆ and C₆-
oligomers will not be crossed with any C₅ components in the products, i.e., not any C₁₁,
C₁₆, or C₁₇’s. This steam explosion route also gives isolation of a conventional
unmodified lignin. There is some market for this material. It could also be used as a fuel for cogeneration for the process or enter into a separate plant for value added phenolic chemicals. There are also specific product questions to answer: e.g., what are the most valuable products that can be easily marketed? When there is quite a variety of valuable products possible from this new process, then greater resources must be used to gain the information required to rank these decisions. However, it is appropriate that some attempt be made to estimate the costs associated with the main reactions of the process even at this stage.

2. Feedstock Cost Contribution:

The acquisition of values of the products and the cost database of a variety of feedstocks are continually being updated. In particular, this economic analysis was part of the tasks in this Advanced Energy Projects grant. What really exists is a very complex economics picture that must be developed and investigated to obtain a more realistic view.

Cornstarch, lignocellulosic biomass, glucose, newsprint, and mixed paper represent a variety of feedstocks readily available for this process. However, this process does not require glucose as an intermediate between the biopolymer and the next step, in this case to sorbitol. Shortening the process one step makes it less complex as compared to a biomass to glucose to ethanol process. Thus the cost of sorbitol directly from biomass or cellulose should be less than through the unrequired but usable intermediate, glucose.
A few quoted prices represent a range of both quality and price of commodities, which could be used as feedstock. NREL typically uses a renewable biomass (wood) cost of $40/ton. Most newsprint in the U.S. is produced by chemithermomechanical pulping and contains about 48% cellulose, 18% other C5-C6 sugars, 28% lignin, and 6% other components, including ash. Combining the cellulose and other sugars it is possible that about 66% of the newsprint (holocellulose) could be utilized by this process. Other forms of paper may range from 90 to 99% cellulose but their current commodity prices are higher because of demand for recycled materials. Off spec corn sells at about half the price of regular commodity corn, perhaps making the cornstarch to sorbitol a more economic route. A very wide variety of feedstocks such as aquatic biomass, corn stover, or other waste streams such as mixed office paper (MOP) or municipal solid waste (MSW) can also be used. The cost of mixed paper is monitored by Pulp & Paper magazine. Prices vary considerably with "clay-coat" content. For example, the national average costs for 1990-1993 were $3.86, $3.24, $2.21, and $4.90 per ton, respectively. During this period actual local price ranged monthly from -$15 to $17.50. It is presently not known how the clay would interfere with this process. In many areas, disposal of MSW even involves a tipping fee and that definitely tips the economics in a favorable direction!

Separation of the holocellulose from raw biomass by the steam explosion process was investigated as presented above. But ideally, Step 1 of the process separates lignin from the raw biomass simultaneously with the reaction of holocellulose to mixed size polyols. Comminution of the starting biomass to fine sawdust speeds the reaction due to increased
surface area. The lignin may then be recovered and burned as fuel in an efficient (80%) cogeneration system; steam as well as inexpensive electricity ($0.02 to $0.04/kWh) is produced. The costs of this separation and use thus offset the prorata percent of lignin in the feedstock.

Calculations are made for feedstock contributions from glucose (@ $0.049/lb) as well as for lignocellulosic biomass and newsprint. Holocellulose content is used instead of just cellulose; if steam explosion is not used then all the holocellulose will be reacted. To simplify the calculations, all polyols are calculated as sorbitol. Adjustment is also made for the weight gain in the hydrolysis of the carbohydrate polymer and simultaneous reduction to sorbitol (water and hydrogen). It can be shown that 2000 lb of cellulose could theoretically give 183.87 gal of hexene, which gives a conversion factor of 0.09184 gal/lb. Using the costs of $40/dry ton for lignocellulosic biomass and $25/ton and $10/ton for ranges of waste paper cost, then the following feedstock cost contributions to a gallon of hexene are shown. Again, if all of the feedstock cost, e.g., $40, is attributed to just the holocellulose, then the lignin for cogeneration would have zero cost! Instead, it is preferable to divide the cost of the biomass proportionally to each component so that regardless of which biomass is used each component carries the same price rate, i.e., $40/ton. Accordingly, the feedstock price rate contributes to the cost of product:

<table>
<thead>
<tr>
<th>Feedstock &amp; Price Rate</th>
<th>Cost per gal of Hexene</th>
</tr>
</thead>
<tbody>
<tr>
<td>from cornstarch via glucose @ $98/t</td>
<td>$0.534/gal</td>
</tr>
<tr>
<td>from lignocellulosic biomass: @ $40/t</td>
<td>$0.218/gal</td>
</tr>
</tbody>
</table>
from lignocellulosic biomass: @ $25/t $0.136/gal
from lignocellulosic biomass: @ $10/t $0.054/gal

3. Reduction Costs:

To convert one mole of a C₆ carbohydrate into hexene requires 6 moles of reduction. This represents the most expensive case. The C₁₂ hydrocarbons require only 5.5 moles of reduction per mole of aldohexose. Similarly, the C₁₈ hydrocarbons require only 5.33 moles of reduction per mole of hexose. Since about 80 - 90% of C₁₂ & C₁₈ hydrocarbons may be produced directly by the end of Step 2, then this hydrocarbon production would cost less. Hexene not only requires more reduction but also requires two extra steps. The halocarbons (i.e., 10%) are converted in Step 3 to hexene. This in turn requires some extra cost to recover the iodine content after elimination. All materials are thus converted to hydrocarbons by the end of Step 3.

Step 2 occurs with a mixture of HI and, for example, H₃PO₃. HI for the most part is not consumed in the reaction, except for what becomes part of the halocarbon compounds. As I₂ is produced during the course of this reduction reaction, it is instantaneously reduced to HI by the H₃PO₃, which is consumed (oxidized to H₅PO₄). Thus the real costs of 6 equivalents of reduction required for the conversion of a glucose equivalent into a hydrocarbon fuel is the cost of 6 equivalents of H₃PO₃ less the sale value of byproduct H₅PO₄. The main goal of the DOE-BES-ARP grant was to thus find a better-cost alternative to the use and consumption of H₃PO₃. Even though the cost of using H₃PO₃ is
about 15-20 times less than the cost of HI it may still lead to quite expensive products. Since bulk price of a 70% solution of H$_3$PO$_3$ was quoted as $1.10/lb of solution, this equates to $0.2841/mole. Byproduct phosphoric acid would probably sell as agricultural grade for about $0.20/lb as a 75% solution and with adjustment for weight gain would recover $0.32/lb for a difference of $0.78/lb or $0.20145/mole. Using a factor of 30.49 mol/gal for hexene, and 6 mole of reductant per mole of sorbitol, the reduction cost calculates to $36.85 per gal. There is some “waste H$_3$PO$_3$” resulting from other industries that typically sells for $0.40/lb or 36.4% of new cost. Even using “waste H$_3$PO$_3$”, the reduction cost alone would be $13.41/gal. Clearly this reduction cost was prohibitive and about 100 times the typical biomass cost.

Alternatively, a better reduction cost is calculated for the direct catalytic hydrogenation reaction by simply using the cost of 6 equivalents of hydrogen. Currently the cheapest means of producing hydrogen comes from reforming of fossil methane. A large methane reforming plant (10 MM SCFD) can produce H$_2$ for $0.40/lb or $0.0017739/mol. Thus, the cost of H$_2$ required is $0.010644/mole of hexene, and times 30.4923 mol/gal gives a total reduction cost of $0.32455/gal of hexene. Reduction with hydrogen then costs about two orders of magnitude less than the cost of using H$_3$PO$_3$.

There is also some incremental cost that should also be attributed to the cost of hexene and that is the cost of regeneration of the HI (and KOH) from the byproduct salt after Step 3 ($0.81/gal of hexene). The entire cost of reduction including the regeneration of acid and base is thus $1.25. This cost is about 10 times the cost of a biomass feedstock.
Combining the costs of feedstock, hydrogen, and HI recovery, then hexene costs are:

<table>
<thead>
<tr>
<th>Source &amp; Price Rate</th>
<th>F'stock +</th>
<th>H-Redn +</th>
<th>HI Rec =</th>
<th>Total/gal</th>
</tr>
</thead>
<tbody>
<tr>
<td>glucose @ $98/t:</td>
<td>$0.534</td>
<td>$0.325</td>
<td>$0.81</td>
<td>$1.669/gal</td>
</tr>
<tr>
<td>biomass @ $40/t:</td>
<td>$0.218</td>
<td>$0.325</td>
<td>$0.81</td>
<td>$1.353/gal</td>
</tr>
<tr>
<td>biomass @ $25/t:</td>
<td>$0.136</td>
<td>$0.325</td>
<td>$0.81</td>
<td>$1.271/gal</td>
</tr>
<tr>
<td>biomass @ $10/t:</td>
<td>$0.054</td>
<td>$0.325</td>
<td>$0.81</td>
<td>$1.189/gal</td>
</tr>
</tbody>
</table>

The total cost of hydrogen reduction, including acid recovery, to hexene is still greater than the cost of even the most impractical feedstock. Nevertheless, the range of costs for hexene are shown to be $1.19 - $1.67. This would be too expensive for a fuel but does compare with the cost of ethanol by fermentation. It might be a fair cost for a chemical use of hexene. If the cost of regeneration of HI can be diminished, then hexene by this new chemical conversion of biomass may become a viable process.

However, if one considers the cost of perhaps the preferred major products for fuel purposes, namely the $C_{12}$ and $C_{18}$ hydrocarbons, then the reduction costs are even less. The $C_{12}$'s reduction cost using the $H_3PO_3$ method is only 5.5/6 (91.67%) and the $C_{18}$'s are 5.33/6 (88.83%) that of hexene. Unfortunately, this apparent advantage in reduction requirement is lost when catalytic hydrogenation is used. The unsaturated sites in the $C_{12}$s are also hydrogenated and the consumption of hydrogen gas remains the same as for hexene. Furthermore, alkyl iodides can be produced in about 10% yield. So only about 10% additional HI recovery costs are required ($0.08).
Some biomass feedstocks would thus allow a more competitive picture and produce fuels in the $0.46 – $0.62 range. Even though the estimated cost of hydrogen reduction and acid recovery is lower ($0.405) for these fuels, it is still the major cost.

Considering now the cost of direct electrochemical reduction, a comparison to the above methods can be made. Using $0.03/KWH (from co-generation) and the data from the two experiments listed earlier, calculations show that electrochemical reduction costs are $0.177 and $0.046, respectively, for the dilute versus the concentrated acid experiments.

Less current density across the membrane, less overpotential with lower voltage, and greater concentration of protons required for mass transport across the membrane all contribute to lower costs. Indeed, it is in the concentrated acid where the experiments were also run simultaneously with sorbitol. The effects that higher temperature or longevity of the membrane have on the economics have not been ascertained. Nor have enough reactions been conducted to evaluate the proportional controls to give different products; this one example gave mostly trimers (diesel fuel range). But using this latter figure, the reduction costs are again about an order of magnitude lower than those with

<table>
<thead>
<tr>
<th>Source &amp; Price Rate</th>
<th>F’stock + H-Redn + HI Rec</th>
<th>Total</th>
</tr>
</thead>
<tbody>
<tr>
<td>cornstarch/glu, C₁₂’s cost:</td>
<td>$0.534 + $0.325 + $0.08</td>
<td>$0.939/gal</td>
</tr>
<tr>
<td>biomass, $40/t, C₁₂’s cost:</td>
<td>$0.218 + $0.325 + $0.08</td>
<td>$0.623/gal</td>
</tr>
<tr>
<td>biomass, $25/t, C₁₂’s cost:</td>
<td>$0.136 + $0.325 + $0.08</td>
<td>$0.541/gal</td>
</tr>
<tr>
<td>biomass, $10/t, C₁₂’s cost:</td>
<td>$0.054 + $0.325 + $0.08</td>
<td>$0.459/gal</td>
</tr>
</tbody>
</table>
direct catalytic hydrogenation. Revisiting the total costs for hexene as well as for the C_{12} hydrocarbons over a range of biomass types shows now to be quite a different and favorable economic picture.

<table>
<thead>
<tr>
<th>Source &amp; Price Rate</th>
<th>F'stock</th>
<th>E-Redn</th>
<th>HI Rec</th>
<th>Total/gal</th>
</tr>
</thead>
<tbody>
<tr>
<td>glucose @ $98/t:</td>
<td>$0.534</td>
<td>$0.046</td>
<td>$0.81</td>
<td>$1.390/gal</td>
</tr>
<tr>
<td>biomass @ $40/t:</td>
<td>$0.218</td>
<td>$0.046</td>
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<td>$1.074/gal</td>
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<td>$0.81</td>
<td>$0.992/gal</td>
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<tr>
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<td>$0.054</td>
<td>$0.046</td>
<td>$0.81</td>
<td>$0.910/gal</td>
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</tbody>
</table>

Now the total cost of reduction is lower but the cost of acid recovery is still greater than the cost of even the most impractical feedstock. Nevertheless, the range of costs to make hexene are shown to be $0.91 - $1.39. This would be too expensive for a fuel but does compare with the cost of ethanol by fermentation. It might be a fair cost for a chemical use of hexene (further reactions). Again, if the cost of regeneration of HI can be diminished, then hexene by this new chemical conversion of biomass may become an even more viable process. We are continuing to work in this direction.

The C_{12} hydrocarbons now have quite a different and very favorable economic picture.

<table>
<thead>
<tr>
<th>Source &amp; Price Rate</th>
<th>F'stock</th>
<th>E-Redn</th>
<th>HI Rec</th>
<th>Total</th>
</tr>
</thead>
<tbody>
<tr>
<td>cornstarch/glu, C_{12}'s cost:</td>
<td>$0.534</td>
<td>$0.046</td>
<td>$0.08</td>
<td>$0.660/gal</td>
</tr>
<tr>
<td>biomass, $40/t, C_{12}'s cost:</td>
<td>$0.218</td>
<td>$0.046</td>
<td>$0.08</td>
<td>$0.344/gal</td>
</tr>
</tbody>
</table>
biomass, $25/t, C_{12}$’s cost: $0.136 + $0.046 + $0.08 = $0.262/gal
biomass, $10/t, C_{12}$’s cost: $0.054 + $0.046 + $0.08 = $0.180/gal

All biomass feedstocks now show a competitive price because these hydrocarbon fuels (e.g., Jet A) can be produced for a very low $0.18 - $0.66 range! Even though the price of starch is twice that of other biomass types, this readily available super-clean feedstock can be used for these fuels economically. Whereas other typical biomass feedstocks would produce a fuel that compares favorably with the current rack price for diesel in Houston with today’s extremely depressed prices for fossil fuels. Finally, as can be seen above, the cost of the biomass has become the major cost. Viola!

4) The Recycle Efficiency of HI and Other Reagents

A high ratio of HI allows for reaction to the more desirable C_{12} fuel as shown in Table 1. With a typical use of a 9 mole ratio, a 40-57% yield of C_{12} is achieved. Almost all of the HI is simply regenerated in situ. A quote from Deepwater Iodide (OK) for 57% HI in drums was $6.75/lb, or $3.33/mole. One gallon of hexene is produced from 30.5 moles of sorbitol using 275 moles of HI (9:1 ratio) which would cost $916/gal of hexene, if HI was either consumed or wasted and not recycled. But as we have indicated earlier, the HI is not consumed. As long as this is recycled efficiently then it becomes more of a capital investment. The question then becomes how well is it recycled. We have given it some thought for two reasons: 1) iodine must be completely removed from the fuel so that when the fuel is burned there is no corrosion or pollution due to HI formation and 2) an
efficient iodine recycle precludes potentially expensive replenishment costs of HI. The same data answers both concerns. As presented above, all iodine is recovered either in situ in Step 2, as KI in Step 3, and as a few ppm of ZnI_2 in Step 4. Clearly, this goal has also been accomplished.

There is a cost associated with the bipolar membrane regeneration of KOH and HI from the KI recovered from Step 3. This cost is proportional to the amount of iodo compounds produced, not to the amount of HI used originally in the Step 2 reaction. Thus, hexene will cost more, as indicated earlier, because of the added cost ($0.81/gal) for HI and base recycling. Aqualytics bipolar membrane units are commercially used for regeneration of acid and base. Payback for such installations, including about 30% profit, has been about 2-2.5 years. Rapid payback demonstrates that this type of electrochemical water splitting can be economically successful. Indeed, KI is regenerated into both HI and KOH for about $0.15/L electricity cost. Adding about $0.05/L distillation cost for concentrated HI shows that this expensive acid can be regenerated for about 125 times less than the original cost, $0.76/gal versus $95/gal.

The lignin part of biomass feedstock may be available as a value-added product. The cost of lignin is prorata the same price rate as the original feedstock cost ($40 to $10/t range). The value of lignin, described in the literature at about $50/t with 40% water content, or about $80 on a dry weight basis, is well above this. At the very least, the lignin value can be recovered by cogeneration. Cogeneration furnishes both the heat for the plant and an efficient, inexpensive power. Alternatively, the lignin might be further hydrolyzed and
reduced as per the Russian references to the more value added phenols. Credits from such a suite of possible value added products may help pay for the costs associated with other parts of the process. A further multiple step process will undoubtedly cost more than a one step process. However, if the process has many advantages, then one must take into account the accrued values that occur with each step in regards to extremely high conversion efficiency, selectivity, ease of separations, and quality of product(s).

Producing phenols in this way might be lucrative.

Physical values, H/C ratio, and octane numbers are known for individual hexenes. For example, *trans*-2-hexene, has a RON of 93, density of 0.68, and a H/C ratio of 2, all ideal for gasoline. But alkenes are not desired in fuels for other reasons. This fact together with the present cost of producing hexenes probably demand they are converted into more value added compounds, i.e., hexane solvent or oxygenates for fuel additives.

The versatility of this process which allows syntheses of several value added product is very attractive. Synthesis of an optional product requires further reaction of hexene, e.g., hydrogenation to hexane. Pure hexane has more value as a solvent than as a fuel. For comparison, the current petroleum based hexane spot price range is $0.85/gal to $1.25/gal. The price range for hexane from this biomass reduction process is calculated to be in the same range. The incremental cost for the additional reduction together with adjustment for density difference results in a $0.0515/gal hexane cost. Thus, hexane would cost:
While the high purity of hexane from this new chemical process should bring a premium price, the cost is perhaps almost competitive. Improved costs for acid recovery are required to make this biomass to hexane route truly economically feasible. However, it does demonstrate that there is now a method to provide polymer solvent grade hexane from renewable resources.

The C_{12} hydrocarbons have several desirable properties (less volatile, highly branched, cyclic, partially unsaturated, density of 0.84, and a H/C ratio of 1.8) that should contribute to a high RON. But since these values are also similar to the values of kerosene, these isomers appear to best fit as a narrow boiling point range jet fuel. The C_{18} isomer mixture falls right into the diesel fuel specifications and are sulfur free! The C_{24} oligomers can be used as fuel oil or cracked back to smaller molecules.

It appears that the area of oxygenate fuels, which have a higher value, would better utilize the near term market. Our developments allow us to synthesize hexanols and quite a variety of mixed ethers, i.e., ethyl 2-hexyl ether and dihexyl ethers for potential diesel blending and TAME, TAEE, as well as the C_6 analogues, THME and THEE. Costs for
these optional products may be estimated by using a similar incremental reaction cost to the cost for pentene or hexene. Indeed while there would be some additional cost for the isomerization to tertiary alkenes and subsequent reaction with alcohols, just including the material cost of the alcohol (~$1.10) with the cost of hexene gives a total cost for tert-oxygenates in the range of $2.01 - $2.49. If present commercial prices are in the range of $4 to $6 per gal for these tert-oxygenates appear to make this process viable, presently, even with no further improvements in the process! This is especially important since even when this process is “tuned” to give mainly hydrocarbons (Jet-A), about 10% C6s can also be marketed as these oxygenates.

III. SUMMARY

Now that we have established a very low-cost method for reduction during this grant, these fuels will always be available from renewable resources while fossil fuels will be even more limited in supply in the future. It is our opinion that cost estimates within the range shown ($0.18-$0.66) for Jet-A fuel and $2.01 - $2.49 for tert-ethers for fuel blending should warrant further scale-up and engineering. This is particularly important with regard to (1) recyclable catalysts for Step 1, (2) optimization of Step 2 with direct electrochemical reduction, and (3) reagent regeneration from Step 3. Any improvement(s) in these three areas will guarantee an even more attractive process.

However, there are other chemical, mechanical and other operating costs as well as capital costs associated with this multiple step process that will definitely contribute to
overall process economics. Establishment of even more accurate economics will take some additional effort. An economically attractive process depends not only upon the exact steps and reagents but also upon the products and precisely how the reagents are recycled. The high quality, high value products available via this process are indeed economically attractive presently, even without a change in the margin of fossil fuels. These projections are viewed as being competitive to alternative biofuels especially considering all the technical, political, and social advantages of this process.

Clearly, we have explored not only a lot of chemistry but also several processing choices that impact the economics of a variety of products possible from renewable resources using this novel chemical reduction process. Presently, we are exploring other fuel and chemical products, means to cut reagent regeneration costs, and stabilization of the catalyst for Step 1.

Finally, the following list of milestones and accomplishments is presented:

1. Facile Separation of Lignin from Holocellulose with Unique Polyol Product
2. Step 2 has been Scaled-Up Several Hundred Fold For Production of Hydrocarbons
3. Demonstrated a Safe Recycle and Recovery of All HI from Step 2.
4. Electrochemically Recycled KI into HI and KOH.
5. Direct Use of Hydrogen for Reduction of I$_2$ Generated in Step 2.
6. Direct Electrolytic Reduction of Iodine in HI Using a Membrane Divided Cell
7. Iodine-Free Fuels and Value Added Oxygenate Fuel Additives Have Been Obtained
IV. PRESENTATIONS AND PUBLICATIONS

Our patent, based on earlier work to establish the basics of the process, finally issued in May 1996: U.S. Patent 5,516,960 (Appl. Aug. 1994). An initial presentation of our research in a Biomass Fuels Symposia in the Fuel Chemistry Section of the 210th National Meeting of the American Chemical Society in Chicago in August, 1995 was followed by five presentations at the 212th ACS National Meeting in Orlando in Aug. 1996. Four presentations were also made at the 214th ACS National Meeting in Dallas March 1998. All papers and presentations are listed in Appendix 1. Copies are attached.

V. REFERENCES


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Demercuration. 11. Alkoxymercuration-Demercuration of Representative Alkenes in


