

October 22, 1995

T. Milne Due: 11/23

National Renewable Energy Laboratory
Attn: Thomas A. Milne
1617 Cole Boulevard
Golden, CO 80401-3393

Dear Tom:

This **Final Technical Report** is for the subcontract, XAC-4-14386-01. This report will cover both Phase I, the "Concept Feasibility Evaluation," and Phase II, the "Fuels Preparation for Evaluation and Preliminary Economics." Each section will address the specific tasks outlined in the "Scope of Work" section of the subcontract. Both the "Objectives" and the detailed "Scope of Work" reflect the single most important goal for this statement of work for which the subcontract was established (see "Introduction"): To determine whether or not the reagents involved in the chemical conversion could be efficiently removed from the product(s).

The original proposal to NREL was planned for May through August, 1994, a 4 month period when the PI was available to work essentially full-time on the project. However, the final NREL subcontract did not begin until Sept. 7, 1994. Release time from the normal Sept. through May teaching duties is almost impossible to arrange during the middle of a semester. While some adjustments were made, it was still necessary to extend the time period of the subcontract. In short, all tasks were essentially completed in about eight months. Samples have been ready to ship for some time. No one at UTPB is licensed to ship hazardous materials. However, personnel at the local Shell Oil refinery have agreed to help ship samples.

This Final Technical Report will show how we have met the major goal of the statement of work and how we have accomplished each specific task designed to meet the objectives. It also presents data that show these fuels are very valuable indeed. Copies of three Cookson papers are attached for your information. One new reference was added to the "steam explosion" bibliography, Fieber's M.S. Thesis, #17. Please advise if there are changes or additions needed in the report. I will be glad to assist.

Respectfully,

J. Michael Robinson, Ph.D.
Ashbel Smith Professor and Chemistry Chair

Final Technical Report
 for the subcontract, XAC-4-14386-01,
**“Preparation of Four Biomass-Derived Transportation Fuels
 for Fuel Suitability Evaluation.”**

I. STATEMENT OF WORK

I. INTRODUCTION

The goal of the BioCrude Project at NREL is to identify and develop cost-competitive and environmentally acceptable technologies for the production of liquid transportation fuels from biomass utilizing direct conversion processes. Historically this project has focused on pyrolytic liquefaction to refinery feedstocks. Other processes have been studied in the past but are currently un-funded. Among these are various types of hydrogenation of carbohydrate solutions.

The hydrogenation or reduction of carbohydrates has not been recently considered a viable option due to inherent problems related to the purification of the fuel products. Specifically, some of the reagents involved in the chemical conversion could not be efficiently removed from the product. These reagents are expensive and limited in supply.

Recent developments in this field indicate that these problems may have been overcome. It is vital that NREL determine whether this has indeed been accomplished. This statement of work allows NREL to make this determination.

II. OBJECTIVES

This work effort has three objectives:

1. Evaluate the removal of and the level of detection of any reagents remaining in fuels derived by the hydrogenation of carbohydrates in aqueous solutions. For the purpose of this work, these fuels will be referred to as Hydrogenated BioFuels, or HBs.
2. Conduct a thorough literature review and find commercial economic information for production of pure cellulose and pure hemicellulose streams by the "steam explosion" route.
3. Produce sufficient quantities of HBs for subsequent evaluation of fuel properties by NREL.

III. SCOPE OF WORK

This subcontract is broken into Phase I and Phase II. The duration of Phase I is to be no longer than 1 month. The duration of Phase II is to be no longer than 3 months.

Phase I Concept Feasibility Evaluation

- Task 1: Produce at least 2 fuels by hydrogenating carbohydrates in an aqueous solution, namely:
- a. undistilled product blend and at least one (1) of the following:
 - b. hexenes, mixture of isomers
 - c. $C_{12}H_{22}$, mixture of isomers
 - d. $C_{18}H_{32}$, mixture of isomers
 - e. 2-hexyl ether

Produce sufficient quantity of each HB to allow analytical determination of impurity levels by both NREL and subcontractor. The subcontractor shall produce these HBs in such a manner as to insure as complete of removal of reagents as possible, including both entrained and chemically bound species. The subcontractor shall produce between 100 mL and 150 mL of each HB. Half of each sample shall be sent to NREL for evaluation, the other half shall be used by the subcontractor for the following task.

- Task 2: Evaluate the removal of and the level of detection of any reagents remaining in each of the HB samples produced in the above Task 1. This shall be done using at least 2 different analytical techniques. The subcontractor shall use techniques which provide the lowest possible detection limits. The subcontractor shall provide information on each of the analytical techniques as to the type of method used and the method's detection limits.

After Phase I is complete, approval from the NREL Technical Monitor must be given prior to starting Phase II. Phase II will not proceed unless Phase I demonstrates economic removal of reagent.

Phase II Fuels Preparation for Evaluation and Preliminary Economics

Task 1: Conduct a thorough literature review and find commercial economic information for production of pure cellulose and pure hemicellulose streams by the "steam explosion" route. Literature will be searched for references in the primary literature. Citations within these will be screened. Direct interface with at least one operating steam explosion plant is required. This will facilitate acquisition of data about actual economics of this method for production of cellulose and hemicellulose streams. Other information as to the utilization of lignin for energy to run the process and to the fate of protein or other soluble fractions will be obtained. This information will be used to prepare preliminary process economics for the preparation of HBs.

Task 2: Produce 4 fuels by hydrogenating carbohydrates in an aqueous solution, namely:

- hexenes, mixture of isomers
- $C_{12}H_{22}$, mixture of isomers
- $C_{18}H_{32}$, mixture of isomers
- 2-hexyl ether

Produce sufficient quantity of each HB to allow fuel property determination by NREL. The subcontractor shall produce these HBs in such a manner as to insure as complete of removal of reagents as possible, including both entrained and chemically bound species. It is anticipated that a total of between 500 mL and 1000 mL will be required for each HB. Each sample shall be sent to NREL for evaluation.

II. PHASE I: RESULTS AND DISCUSSION

The essence of Phase I was a "concept feasibility evaluation." The real question was posed: Could the levels of reagent (iodine) be reduced to a level low enough to warrant further research and development, i.e., continuing with Phase II? To appropriately view the answer to this question, some digression must be made to explain the general process.

A. PROCESS 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.

Our initial goal was to develop an efficient multistep chemical process for the conversion of the principle components of biomass, cellulose and hemicellulose, into hydrocarbon fuels. The use of selective reduction reactions might allow for 100% carbon conversion by keeping the carbon chain intact. Furthermore, if initial reactions could be conducted in an aqueous medium, then the use of wet feedstocks would be possible. Overall, a six carbon sugar polymer, such as cellulose, would afford a single pure hydrocarbon product such as hexene. This is precisely what we have developed, a novel *chemical* process.²

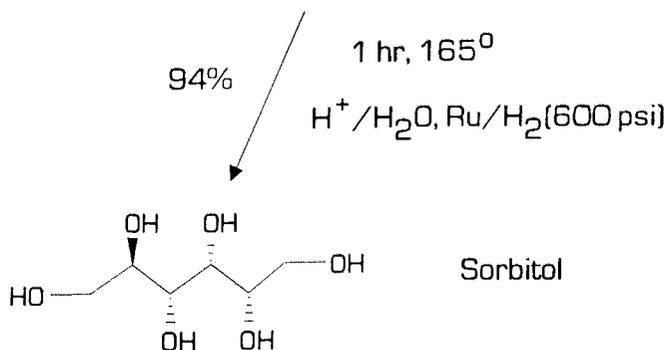
B. GENERAL PROCESS SCHEME

Our use of the term *chemical* implies the typical mild conditions usually employed in glass vessels. This process now consists of four separate reactions. The first two reactions, where the majority of the reduction occurs, uses water as the solvent medium. Scheme I comprises a brief summary of the main reaction steps that achieve the strategic objectives of the organic portion of the process. For clarity, Scheme I shows only the reaction products of cellulose.

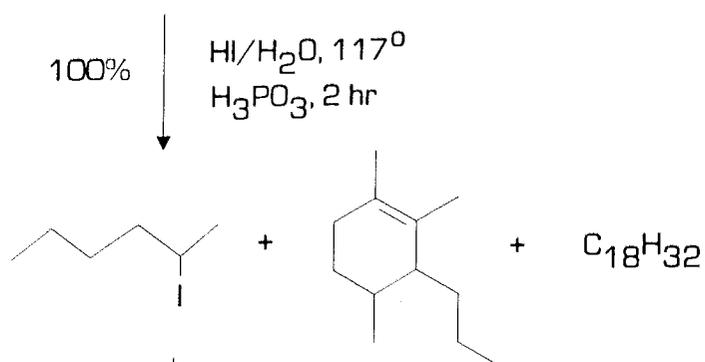
Scheme I

Cellulose (Cellulose + Hemicellulose + Lignin)

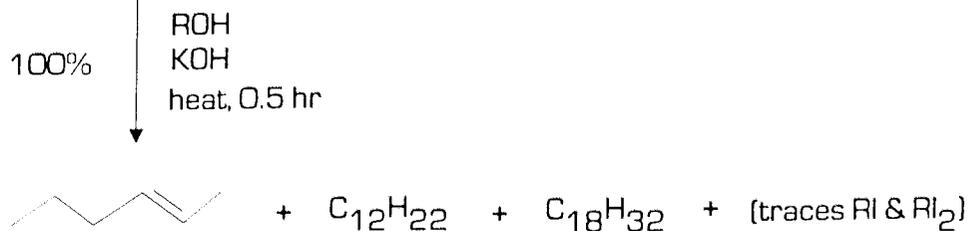
Step 1



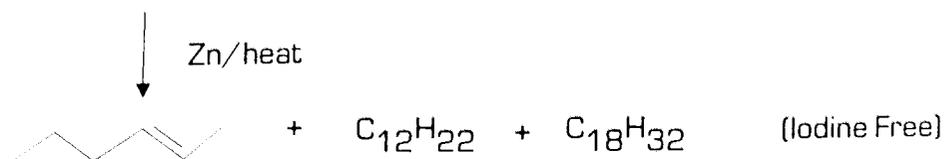
Step 2



Step 3



Step 4



Hemicellulose reacts similarly. Indeed, for this NREL subcontract to produce quantities of certain fuels, only reactions from commercially available sorbitol were conducted. Each reaction is briefly presented here to explain the strategy of the process. Detailed discussions of each Step will then follow.

Step 1 is a reductive depolymerization of carbohydrate biopolymers. Cellulose and hemicellulose are converted into sorbitol and xylitol in essentially quantitative yields.³ Lignin is separated from the resulting solution of polyols by simple filtration. Thus, Step 1 uniquely provides the required polyols required for the next reaction and simultaneously provides a facile separation of lignin.

Step 2 of the process is also a key reaction: the chemical conversion of polyhydric alcohols to liquid hydrocarbons. The major part of all the reduction requirements occurs here. The polyols react with aqueous hydriodic acid (HI) and phosphorous acid (H_3PO_3) to afford iodoalkanes and alkene oligomers. The immiscible products are simply removed as a separate phase from the aqueous acid solution in essentially quantitative yield. Reaction conditions can be controlled to afford mainly hydrocarbons. So Step 2 not only provides a highly reduced C_6 compound but also C_{12} , C_{18} , and C_{24} hydrocarbons. These groups represent fuels in the range of gasoline, kerosene, diesel, and fuel oil, respectively.

Step 3 might be considered a cleanup reaction. All of the remaining halocarbons (about 10%) in the mixture from Step 2 are now also converted to alkenes by an elimination reaction with base (NaOH) in boiling alcohol. After the reaction, the salts and alcohol solvent are easily removed from the products with simple water washing. Vast differences in boiling points of hexenes (68 °C) from the other higher mass hydrocarbons, 200 °C and 300 °C, allow facile distillation for separation of these hydrocarbon fuel groups.

C. IODINE LEVEL IN THE FUEL PRODUCTS

Returning now to the essential question of Phase I, could the levels of reagent (iodine) in the fuels be reduced low enough to warrant further research? Results by GC/MS instrumentation prior to this subcontract clearly indicated that less than 1% levels had been obtained. So, other analytical methods needed to be established that would determine the actual levels at lower detectability. Furthermore, when larger quantities of fuels were produced, what would be the levels and could these be eliminated? Removing all iodine content from the fuels is required for two reasons: (1) potential corrosion due to the HI produced upon combustion, and (2) potentially expensive iodine replacement costs.

During Phase I, fuels were produced in quantity by reactions scaled up by two orders of magnitude. It was determined that the color of the distilled fuels was not related to the iodine content. Analyses of these fuels for iodine content by an outside commercial laboratory, Galbraith Labs, was then conducted. The Galbraith 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 quantitation of iodine by this method is 2 ppm using a 0.2 g sample. The cost is \$50 per sample.

Iodine levels in distilled C₆ and C₁₂ fuels were found to be within a range of 42 to 229 ppm for the fuels, respectively. Since this level of iodine was almost 4 orders of magnitude better than previous reports by Canadian researchers (30 %),⁴ Phase II of the NREL subcontract was continued. At the time, it was envisioned that serial treatments with base, i.e., repeating Step 3, and better distillation equipment with more theoretical plates would reduce these levels even further. These efforts did not completely solve the problem.

Eventually, during Phase II, it was found necessary to chemically remove the last traces of iodine (15-350 ppm) from these fuels, especially the higher homologues, before they could be successfully distilled. Iodine vapors (pink) and severe foaming caused numerous mechanical problems. However, boiling the crude hydrocarbon mixture with activated zinc dust provided complete removal of iodine. Finally, filtration of the treated fuels through Celite analytical filter aid apparently removed some colloids which seemed to be partly responsible for the foaming. This **Step 4 (NEW)** resulted from this NREL subcontract which posed this question. Several fuels have now been analyzed to show less than 2 ppm iodine remaining.

D. OTHER PROCESS STEPS

The main process is thus defined in four reaction steps, the fifth step is the distillation of these fuel products. 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 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.

III. PHASE II: RESULTS AND DISCUSSION

A. SUITABLE FEEDSTOCKS FOR STEP 1

Steam explosion was viewed as a means to provide relatively pure cellulose and hemicellulose streams for Step 1 of this process. A review of the literature for the "steam explosion" route for fractionation of biomass into pure cellulose, hemicellulose and lignin streams was completed and a list of references are separately attached. This review was Task 1 for this Phase II of the subcontract.

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 lignins, 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 phenolics. The level of tolerance of lignins in the carbohydrate streams used in our process has not been completely defined. Most, if not all, lignin is removed in Step 1 of the process.

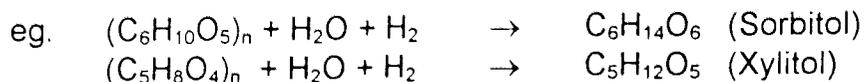
An alternate method of fractionation of steam exploded wood is accomplished by washing with a solvent such as ethanol to remove about 90% of the lignin, but at a replacement cost of about 8 gal of solvent per ton of biomass. This cost must be weighed against the cost of base used for extraction and the acid used to neutralize the solution and reprecipitate the lignin. Of equal importance, but not available at this time, is the extent of contamination in the hemicellulose stream.

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.

Copies of two proposals from Dr. Ernest Yu of STAKETECH are attached to show where these steam explosion figures were quoted. Some idea of the capital equipment costs are also shown therein. In the most recent communication with Dr. Yu, other pertinent information was clarified, such as their use of metric ton. Perhaps this is the best way to present the cost of steam explosion, as an incremental cost when steam explosion is included in the overall process. In light of this new information, it may be advantageous to consider using steam explosion to initially fractionate raw biomass. This would provide for several new options: 1) simply selling the concentrated hemicellulose and alkaline lignin streams, 2) using the hemicellulose as a separate feedstock stream, 3) recombining the hemicellulose and cellulose for the larger yield of mixed carbon length feedstock, 4) recovering the lignin for fuel value, and 5) processing the separated lignin by a totally different manner for chemicals or fuels.

B. DETAILED DISCUSSION OF THE CHEMISTRY OF EACH STEP

STEP ONE (A): WOOD $\xrightarrow[\text{1 hour, 165}^\circ\text{C}]{\text{H}_2(900\text{ psi)/Ru(C) } \rightarrow \text{ 0.7\%H}_3\text{PO}_4/\text{H}_2\text{O}}$ POLYOLS (C₆ & C₅) +
LIGNIN/CATALYST(slurry)



While it was not specified as part of this NREL task, it was our research goal to also compare a Russian method for fractionation of raw biomass by the direct reduction to a polyols solution.³ A unique fuel process may well justify a uniquely matched feedstock process. Thus, the facile biomass to polyols (BTP) fractionation is perfectly for our process. Lignin is removed by simple filtration. In this manner, a clean cellulose fiber fraction as obtained from the steam explosion process may be bypassed as is the need for a clean glucose also bypassed. Instead the clean polyols solution can be converted directly to hydrocarbons *via* Step 2 of our process. So not only is the Russian biomass to polyols (BTP) fractionation process better suited for our process but there also may be obvious economic advantages.

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 thirty such reactions have been conducted in this manner in our labs. Many variables have been studied. The maximum amounts of pentitols and hexitols expected from spruce wood are 26.5% and 42.0%, respectively, and therefore 68.5% total. The Russian researchers isolated solid, recrystallized, polyols in 95% yield based on the theoretical, so we expect at least (68.5% x 95%) about 65.1+% in solution. 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 source and type of catalyst. About 20 ppm of reducing sugars are present in the resulting polyol solution (after 1-2 hr at reaction temperature). However, not even a trace of a phenolic by-product, which might have resulted from some lignin degradation, has been detected.

There is some hydrogenation of reactive lignin functional groups (aldehydes and alkenes). This is determined by the continuing slow reaction of hydrogen. A computer controlled reactor is being used to optimize the polyol conversion while minimizing the slower lignin reaction. There may also be some reduction and cleavage of some 3-carbon components from lignin to afford glycerol in the polyols solution. This has not yet been determined.

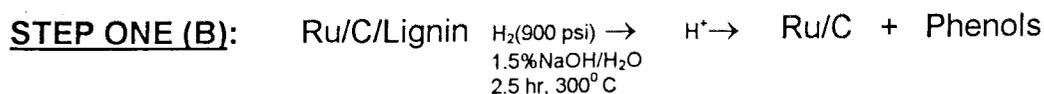
The lignin and catalyst (Ru/C) are simply filtered from the aqueous solution. Standard lab grade filter paper suffices. The slight tackiness of the powder is improved with longer reaction time. No further removal of any particles could be determined with filtration through 0.45 micron filter paper.

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 references 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. Whether these extractives have any impact on the activity of the catalyst used in this step will continue to be addressed.

Ladisch⁵ 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; cornstalk, for example, has much more starch and protein which might be extracted. However, starch should not be removed; it is an ideal feedstock. Tables of hardwoods, softwoods, newsprint, corn stover, grasses, etc. are readily available for other feedstock composition information. Newsprint, for example, contains 48% cellulose, 18% hemicellulose, 26% lignin, and 6% other including ash.

A two stage hammermill fed with 1 inch chips will provide minus 10 mesh material and requires about 60 hp hr/dry ton. Size is not deemed critical, it simply relates to the speed of the hydrolysis and convenience of slurring in the reactor. There seems to be little difference between the reaction time required for minus 60 mesh sawdust versus minus 10 mesh.



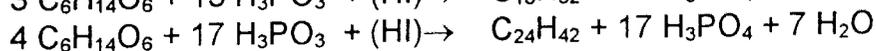
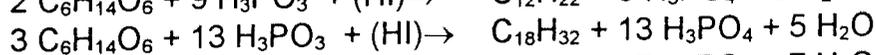
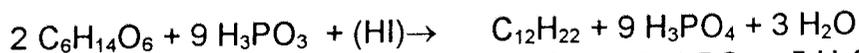
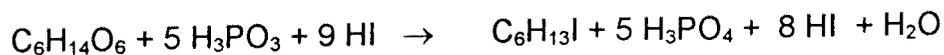
The catalyst/support is reportedly recovered for reuse as shown in the reaction above. It is simply filtered from the solution before acidification. The solution is then acidified to recover the hydrogenolysed lignin products: phenol, cresols, catechols, etc. These phenols are very valuable organic chemicals, which will perhaps more than pay for this step. Presently, a series of reactions is being conducted to learn more about the products and their recovery/yields. At this early stage, the loss, lifetime, or the activity of the recovered catalyst is not known. Presumably, the catalyst can be reused many times. Traces of Ru ion have been detected in the Step One (A) acidic solution; none are expected in this basic solution.

Alternatively, lignin might be easily recovered by base extraction removing the solid catalyst by filtration, and finally precipitating the lignin by acidification. The intact lignin could then be available as a value added product or perhaps in a less valuable way simply burned for cogeneration power. This extraction - recovery method is also being tested. However, after the lignin/catalyst precipitates have been oven dried to get material balances for Step One (A), the lignin is very difficult to extract. Currently only 40-50% is easily removed. Extractions of lignin from the precipitates while they are fresh, i.e., before drying, are in progress.

A study of catalyst effectiveness and regeneration is underway. With sequential additions of sawdust (oak) containing about 25% lignin, the catalyst has remained effective until physically blinded by about a five fold larger amount of lignin. For example 600 g of raw sawdust was processed to leave 150 g of lignin filtered with 20-30 g of catalyst after 2-3 cycles. If low lignin biomass such as China grass or steam exploded cellulose (3-4% lignin) were used, then perhaps 3,750 g of biomass could be treated (12 - 15 reactions) before catalyst separation would be required.

In either of these paths, use of base and acid generate chemical costs. The recycle of dilute acid and base will be done as per Step 3(D). Thus, expenses for waste, new reagents, and freight will be significantly reduced.

STEP TWO (A): Polyols to Hydrocarbons



Tables 1 and 2 show reactions conditions of several polyols versus product ratios and yields.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 occurs with 43 - 48% water content. Without dilution, about 90% is the $\text{C}_6\text{H}_{13}\text{I}$ and the remainder is mostly $\text{C}_{12}\text{H}_{22}$. Proportionately smaller and smaller amounts of each higher oligomer (tetramer and pentamer) are also produced.

TABLE 1

SORBITOL Reactions						Product Yields %											
#	Mole Ratios					HR	R1	RX	R2	RX2	R3	R4	TX	TR	% Y	M	
	HI	H3PO3	H3PO2	H3PO4													
1	(5)	(2.5)				20		99					99	0	99	D	
2	11	5				2	1	53	19	10	7		64	27	91	D	
3	11		2.5			20		30	31	4	35		34	66	100	D	
4	11		2.5			1		19	34	10	31		29	65	94	D	
5	11		5			20	5	9	51	1	24	1	10	81	91	D	
6	11	5			*	20	2	10	20	2	28	21	12	71	83	D	
7	11	5				20		77	9	4	tr		81	9	90	E	
8	11		4			2	7	30	37	4	2		34	46	80	E	
9	11		5			27	1	20	48	4	19	1	24	69	93	E	
10	7	7.5				20	tr	21	12	2	64	5	23	81	104	E	
11	6	5			*	2	1	31	15	6	50		37	66	103	E	
12	11		5			5	13	7	29	45	1	21	30	73	103	E	
MANNITOL Reactions																	
13	11		5			5	12		20	38	3	65	tr	20	103	123	E

TABLE 2

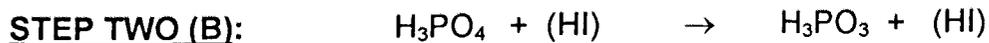
#	Mole Ratios				HR	Product Yields %								% Y	M
	HI	H ₃ PO ₃	H ₃ PO ₂	H ₃ PO ₄		EN	RX	R2	RX2	R3	R4	TX	TR		
14	5.2	4.4			1		44	(33)	6			83	0	83	D
15	6	4.4			24		1	12	tr	32	22	2	67	69	E
16	6		2.5		24		tr	15	tr	24	4	1	43	44	E

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 polyols. Please note that **HI is the reagent**; the **H₃PO₃ should be viewed as a coupled redox reagent**. H₃PO₃ instantly converts nascent iodine (I₂) into hydriodic acid (HI). This maintains the high concentration and ratio of active HI. For mechanical, sequential batch additions, and dilution reasons, we typically now use an initial 9/1 ratio. 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 very detailed spreadsheet calculators for this. An example of a preparative experimental procedure is as follows:

Production of C₆, C₁₂, C₁₈s from D-Sorbitol (Sequential Batch Reaction Method)

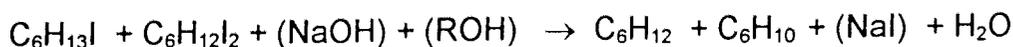
Using a 3 neck (ST 24/40), 3 L flask with two Freidrich's condensers, D-sorbitol (150.1 g, 98 %, 0.8 mol), hydriodic acid (HI, 980 mL, 57 %, 7.2 mol), and phosphorous acid (H₃PO₃, 372.3 g, 97%, 4.4 mol) and deionized water (200 mL) were refluxed (118 °C) under a nitrogen atmosphere for 2.5 hours. The 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 starting material (sorbitol) per 3 L flask. This run used only 1.6 moles of starting material. The runs are limited to 0.8 moles of sorbitol per batch due to the exothermic nature of the initial reaction.

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



The acid solution after the above reaction consists primarily of HI and H_3PO_4 . Some HI can be recovered by distillation but strong CAUTION is necessary as pyrophoric reactions may suddenly occur. Anyone proceeding along this path should first obtain full knowledge of all species present in this mixture. This Step is the major goal of our DOE Basic Energy Sciences, Advanced Research Projects Grant. This research and intellectual property information is not available for release at this time.

STEP THREE (A):



(In same step: Any mechanically entrained HI will be recovered to NaI as well.)

Several solvents have been used for this step, methanol, ethanol, propanol, and 2-hexanol. The 2-hexanol has to be separated by distillation from the hydrocarbon mixture. Of the other smaller alcohols, ethanol may be the better choice because the temperature of reaction is higher. Both methanol and ethanol have to be efficiently washed from the hydrocarbon products or they will interfere with the distillation process. For example, ethanol and the hexenes form a azeotrope with a 46-66 °C boiling range that cannot be separated, even with the very efficient spinning band distillation system. While small amounts of ethanol (in hexene) cannot be detected by the GC/MS system (again these azeotropes coelute), it is easily determined by a ^1H NMR spectrum. If steam explosion is used to prefractionate biomass for this process, then the methanol byproduct (about 1-3%) will be available for this step.

Potassium hydroxide was initially used to effect greater solubility of the base in the organic medium. This solubility was found to not be such a critical factor. Sodium hydroxide works very well and is not only less expensive but probably will be even easier to regenerate. It is used in excess mole quantities than actually required in the above equation.

Any residual extractives were hydrolyzed and hydrogenated and none are expected to provide a problem. There should also be no lignin, as mentioned earlier in Step 1. However we have addressed the glucuronic type carboxylic acids that are part of the hemicelluloses. Of course the content varies with species with wood having the various but small amounts and these have about the same amount (3%) in hardwood or softwood. These polyhydroxy acids are reduced to the gluconic type acids and subsequently converted in Step 2(A) to isomers of iodohexanoic acid, which are in turn converted into hexenoic acids. 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 filtered or perhaps steam distilled from the solution. Such medium length (6 carbon) chain acids, or perhaps their conjugate base salts, can be electrochemically coupled to decane by well known reactions. Therefore, each feedstock may have to more carefully evaluated as to the extent of glucouronic acids present.

On the other hand, if only the cellulosic fraction of steam exploded wood is used in this process then such problems from these hemicelluloses would not be a factor.

STEP THREE (B): Solvent recovery

The solvent alcohol, preferably methanol or ethanol, is recovered by flash distillation from the basic/saltwater layer.

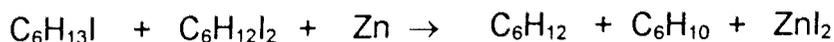
STEP THREE (C): Hexenoic acid recovery

The dilute caustic solution is made acidic and the hexenoic acids are extracted, or perhaps steam distilled. These might be converted to caprolactone(s), acyclic esters (e.g., ethyl ester), or dimerized to decane as mentioned above. 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, i.e., non steam exploded starting material.

STEP THREE (D): $\text{NaI} + \text{H}_2\text{O} \rightarrow \text{NaOH} + \text{HI}$

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. Aquatech⁶ cells are used commercially for regeneration of neutralized pickling acid and spent battery acid recovery. It has also been documented for NaBr. Presently, as part of the DOE-BES grant tasks, we are also doing this for NaI solution and KI solutions. Power consumption of about 1600 kWh/T of NaOH (and an equivalent amount of HCl) allows an estimate of about 1200 kWh/T for this step. However, the use of KOH throughout the entire process will also be evaluated and compared to NaOH. The choice of KOH for Step 3(A) at the onset was based solely on solubility and not on the overall economics.

STEP FOUR (A): Trace Iodide Removal



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. 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 perhaps a fixed bed chromatographic-principle reduction reactor, will be necessary to remove all traces of iodine. Several scavenger reactions were considered to police trace amounts of iodine left in the hydrocarbon mixture after Step 3(A). A non-

aqueous organometallic (sodium metal reacted with naphthalene in dry etheral solvent) scavenger reagent was simply used to titrate the hydrocarbon mixture. This is one method used to decompose organohalogen compounds into water soluble halides that could be analyzed by ion selective electrode. While this was suitable for an analytical scale reaction, much more reagent was required than was really necessary for the true amount of iodine present when this was conducted on a practical scale. Apparently some of the alkene bonds were also susceptible to reduction by the reagent. An additional problem was that the naphthalene reagent also coupled with the alkyl groups to give new organic products. These were not considered desirable for this fuel process.

Finally, the problem was solved as mentioned earlier in the introduction to the general process scheme (Scheme I). The new Step 4 reaction was incorporated into the process. Again, the hydrocarbon product mixture after Step 3(A) which contains iodine impurities is simply boiled with activated zinc dust for about one hour. After separation of the remaining unreacted zinc dust, the salts are removed by water washing. The dried hydrocarbon layer is then filtered through Celite filter aid and distilled.

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 sodium 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. The thus obtained small amount of sodium iodide solution can be returned to the Step 3(D) NaI stream for recycling.

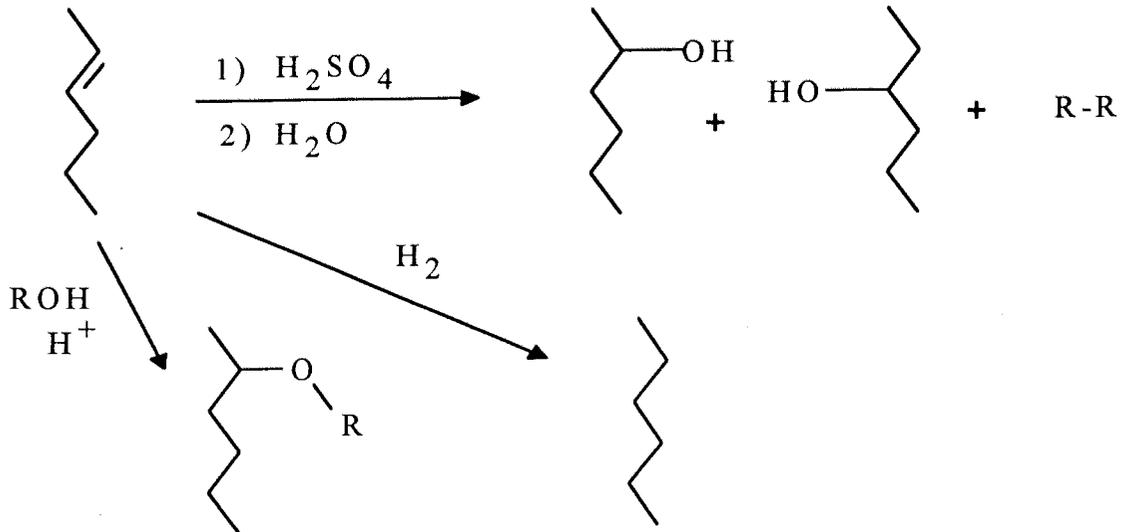
STEP FIVE : Distillation/separation of fuels groups

This is not a reaction step as was presented in the general introduction scheme (Scheme I) but may be an actual processing step that requires some energy costs. The hexenes are distilled easily, generally 64-68 °C. The C₁₂ fraction may be distilled at about 180-210 °C without vacuum or between 75-82 °C at 5 mm. It is necessary to distill the higher oligomers at reduced pressures, C₁₈ bp = 145-150 °C at 3.75 mm, C₂₄ bp = 160-190 °C at 1.25 mm, and C₃₀ bp = 200-212 °C at 0.65 mm. A blend of C₁₈S + C₂₄S, etc., might be kept together for a fuel oil and not distilled. Such product blends for marketing choices have not yet been made.

C. OPTIONAL REACTIONS TO VALUE ADDED PRODUCTS

Intermediate iodoalkanes as well as the hexenes product 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 expensive iodine must be recovered. For this and other reasons, only hexenes are now used in these syntheses.

SCHEME II



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 a RON of 25. Hexane sells for \$0.85/gal as an industrial, polymer grade solvent. Hexane for seed oil extraction may be less pure. This 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.



A mixture of hexanols (Scheme II) may be highly suitable as a fuel additive. Their value as an octane booster with low vapor pressure needs to be established. The extent of conversion to alcohols is only fair. Some oligomerization to noncyclic hydrocarbons fuels occurs. This step has not been optimized. Sulfuric acid must be reconstituted for reuse. The economics for these oxygenate products, and the ethers below, may be the most important goal for the near term products, i.e., these should be much more valuable than the hexenes.

OPTION STEPS SIX (C): Hexenes + Alcohol(s) + (H⁺) → Hexyl ethers

Methyl, ethyl, propyl, and hexyl ethers have been made by a variety of means (Scheme II). The value of each as a fuel additive should be determined before expending further efforts toward optimizing a particular method of synthesis.

D. PREPARATION OF FOUR FUELS

Task 2 of Phase II of this NREL subcontract was to prepare four biomass derived fuels in quantity so that they may be further evaluated for fuel properties. Liters of fuel, a mixture of C₆, C₁₂, and C₁₈, were prepared. Some materials were sacrificed to find a suitable method of removing the last traces of iodine from the mixture. An extra polishing step (Step 4) was necessary to remove all traces of iodine before distillation. Analyses by Galbraith Labs of the easily distilled fuels after such treatment gave less than detectable level (2 ppm) for 3 different samples of hexenes. Some hexenes were also lost due to the high volatility of the alcohol/hexenes blend. Cold condensers are now also used along with tap water condensers.

While it was originally thought that pure 2-hexene would result, it is now clear that mixtures of several hexenes are in fact produced. To the extent that somewhat short reaction times for Step 2 are used, more dihalohexanes are produced. This leads in turn to more hexadienes in the "hexenes" fraction. If sterically hindered base is used on a separate fraction of iodohexanes, then more 1-hexene is produced. This has not been optimized.

Initial reactions of hexenes or of hexyl iodide to produce ethers were not very successful. Considerable exploration was necessary to find a new method of synthesis (literature methods using hexyl chloride did not work with the iodide). This was also overcome. We now can synthesize the dihexyl ethers by acid catalyzed dimerization of the alcohol(s). However, the dihexyl ethers are not thermally stable near the normal boiling point; the pot contents polymerize to a gel. Thus, a smaller quantity is presently available. Since these secondary ethers should not be stored dry, a small amount of 2-hexanol is included as stabilizer.

Phillips Petroleum Co. in Bartlesville has a method for analyzing small samples for octane numbers.⁷ It is a computer controlled method and is very accurate. While only about 20 mL is needed per run, several runs must be made with each fuel and on each engine, Research and Motor. Therefore, a total of about 150 mL of each fuel is required. A copy of the abstract of the original presentation of the method is attached. Also included for your information is a draft of an agreement for Phillips to do these samples. NREL should seek the same type of agreement. Prices range from \$75 to \$150/sample depending upon the availability of the fuel to be tested. The quantities of fuels supplied is more than enough for these tests. However, there is no such technique for diesels in the US, only in France. While Southwest Research Institute as well as several other commercial labs usually require about one liter to do the diesel fuel test for cetane number, Dixie Services (Houston, TX) indicated that they could closely bracket a blend of about 200 mL of our test fuel with a known reference fuel and thus gain the data we need. This may be a close approximation and might be properly termed a blending cetane number." Perhaps other labs can do the same type of test. If the projected near term

use of these products is in fact for blending purposes, then a "blending cetane number" is appropriate.

Unfortunately, since these are all novel fuels, except for the hexenes fraction, some methods of analyses that are highly customized for petroleum derived fuels may not work. For example, the NIR technique for fuel properties estimation requires calibration with similar fuels. ^1H 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,⁸ 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 sp^2 carbons, may suffice as an equivalent for the aromatic content of typical jet fuels.

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 C_{18} fuel which consists solely of branched and cyclic compounds should fit within this "specification domain." NMR data required to support these predictive property correlations are in progress.

So, besides RVP and flash point, octane numbers should be established for the actual hexenes blend as well as the C_{12} blend of isomers:

Vol. shipped	RON	MON	CN
440 mL	hexenes	hexenes	
500 mL	C_{12} fuel	C_{12} fuel	
400 mL			C_{18} fuel
73 mL			C_{24} fuel
70 mL			dihexyl ethers
	(hexanols)	(hexanols)	

Perhaps then, other methods such as NMR which uses very small samples can predict other fuel properties, such as Cetane Number for the larger molecule fuels. 2-Hexanol is commercially available and thus was not specified as a deliverable in this subcontract. In any case, a mixture of alcohols are produced, not just 2-hexanol. Likewise, as it turns out, a

mixture of ethers are produced, not simply bis-(2-hexyl)ether as the contract was originally written. The hexyl alcohols should have excellent fuel blending properties. We intend to do the tests for the hexyl alcohols. The C₂₄ fuel was not specified as a deliverable; again it was not known exactly how much of these would be available.

Some data is now available for the novel hydrocarbon fuels. The API gravity and relative specific gravity, both @ 60 °F, for the C₁₂ and C₁₈ fuels are 37.1 (0.841) and 28 (0.89), respectively.

E. SUMMARY AND 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 actually 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 four major economic concerns of the Robinson 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.

Each will be addressed.

1. 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 complicated (more difficult). Difficulty is relative to perspective. By using more steps (complexity) in this process it is actually less difficult to achieve a high quality liquid fuel because less severe conditions are employed for each step, extremely high yields result, 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. The liquid fuel products are easily handled by conventional distillation, transportation, storage, and sales. 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, two economic models must be considered: one using steam exploded cellulose and one using raw biomass as feedstocks. 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 all the hemicellulose stream? If there is, then the C_6 and C_6 oligomers will not be crossed with any C_5 components in the products, i.e., not any C_{11} , C_{16} , or C_{17} '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: what are the most valuable products that can be easily marketed? When there are 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 (steps) of the process even at this early stage.

2. Feedstock Cost Contribution:

The acquisition of values of the products and the cost database of a variety of feedstocks has just begun. In particular, this economic analysis is part of the tasks in the Advanced Energy Projects grant. What really exists is a very complex economics picture which 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 feedstocks. 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. An 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 2 of the process separates lignin from the raw biomass simultaneously with the reaction of holocellulose to polyols. Comminution of the starting biomass to a 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 offsets 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 gal 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:

<u>Feedstock & Price Rate</u>	<u>Cost per gal of Hexene</u>
from cornstarch <i>via</i> glucose @ \$98/t:	\$0.534/gal
from lignocellulosic biomass: @ \$40/t	\$0.218/gal
from lignocellulosic biomass: @ \$25/t	\$0.136/gal
from lignocellulosic biomass: @ \$10/t	\$0.054/gal

3. Reduction Costs:

To convert one mole of 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 production would cost less. Hexene not only requires more reduction but requires an extra step. The halocarbons (i.e., 10%) are converted in Step 3 to hexene. This in turn requires 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 eliminated during the course of this reduction reaction, it is instantaneously reduced to HI while H₃PO₃ is consumed (oxidized to H₃PO₄). The H₃PO₄ can be reduced by a variety of means to regenerate the original solution of acids required for use in Step 2. Thus the real costs of 6 equivalents of reduction required for the conversion of glucose equivalent into a hydrocarbon fuel is the cost of the reduction of 6 equivalents of H₃PO₄ back to H₃PO₃. The main goal of the DOE-BES-ARP grant we now have is to establish this cost. While this exact means and cost for this reduction must be held proprietary at this time, the cost might be *estimated* by simply using the cost of 6 equivalents of hydrogen.

Currently the cheapest means of producing hydrogen comes from reforming of fossil methane. A fairly large methane reforming plant (10 MM SCFD) can produce hydrogen at \$2.85 per thousand SCF or \$0.54/lb or \$0.0023948/mol H₂. Thus, the cost of H₂ required is \$0.0143688/mole of hexene, and times 30.492277 mol/gal gives a total reduction cost of \$0.438137/gal of hexene.

Combining the feedstock cost and the cost of reduction the overall costs of hexene are:

<u>Source & Price Rate</u>	<u>Feedstock</u>	<u>+</u>	<u>Reduction</u>	<u>=</u>	<u>Total</u>
glucose @ \$98/t:	\$0.534	+	\$0.438	=	\$0.972/gal
lignocell. biomass @ \$40/t:	\$0.218	+	\$0.438	=	\$0.656/gal
lignocell. biomass @ \$25/t:	\$0.136	+	\$0.438	=	\$0.574/gal
lignocell. biomass @ \$10/t:	\$0.054	+	\$0.438	=	\$0.492/gal

These costs for hexene show the impact of the feedstock contribution to the range of prices. MSW waste with tipping fees might reduce the cost of hexene to the cost of reduction or less. As can be seen, the cost of reduction to hexene is generally greater than the cost of the most practical feedstocks.

If one considers the cost of the preferred major products, namely the C₁₂ and C₁₈ hydrocarbons, then the reduction costs are less. The C₁₂'s reduction cost is 5.5/6 (91.67 %) and the C₁₈'s are 5.33/6 (88.83 %) that of hexene:

<u>Source & Price Rate</u>	<u>Feedstock + Reduction = Total</u>
From cornstarch/glu, C ₁₂ 's cost:	\$0.534 + \$0.4015 = \$0.936/gal (C ₁₈ is \$0.924)
From biomass, \$40/t, C ₁₂ 's cost:	\$0.218 + \$0.4015 = \$0.620/gal (C ₁₈ is \$0.607)
From biomass, \$25/t, C ₁₂ 's cost:	\$0.136 + \$0.4015 = \$0.538/gal (C ₁₈ is \$0.525)
From biomass, \$10/t, C ₁₂ 's cost:	\$0.054 + \$0.4015 = \$0.455/gal (C ₁₈ is \$0.443)

Some biomass feedstocks would thus allow a more competitive picture and even though the estimated cost of reduction is lower for these fuels it still becomes the major issue. Whatever the actual cost that will be established during this grant, these fuels will always be available from renewable resources while fossil fuels are in limited supply. It is our opinion that cost estimates within the range shown (\$0.44-0.66) should warrant further investigation to establish what the other incremental costs might be, particularly with regard to reagent regeneration for several steps of this process.

4) The Recycle Efficiency of HI and Other Reagents

A high ratio of HI allows for reaction to the more desirable C₁₂ fuel as shown in Table 1. Now it is typical to use a 9 mole ratio; a 40-57% yield of C₁₂ is achieved. Almost all of the HI is simply regenerated *in situ*. A quote from Deepwater Iodide (OK) for 57% HI in drums was only \$6.75/lb. Thus the cost of HI is \$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 it 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) How well is the iodine removed from the fuel so that when it is burned there is no corrosion or pollution due to HI formation? and 2) How does the efficiency of iodine recycle impact the replenishment costs of HI? The same data will answer both questions. As presented above, all iodine is recovered either *in situ* in Step 2, as NaI in Step 3, and as ppm of ZnI₂ in Step 4. Clearly, this goal has been accomplished.

There is a cost associated with the bipolar membrane regeneration of NaOH and HI from the NaI 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 than indicated earlier because of this added cost. However, this will not affect the cost of the other hydrocarbons. Aquatech (Allied Chemical) bipolar membrane units are commercially used for regeneration of acid and base. Payback for such Aquatech 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. Regeneration of the NaI solution is presently under study.

The lignin part of feedstock may be available as a value added product. The cost of lignin is at 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 these hexenes probably should be converted into more value added compounds, i.e., hexane solvent or oxygenates for fuel additives.

The versatility of this process to also be able to synthesize a value added product is attractive. The economics to the optional products requires further reduction or reaction of hexene. Pure hexane has more value as a solvent than as a fuel. It may be appropriate to compare the current petroleum based hexane spot price of \$0.85/gal with the estimated price range for hexane from this biomass reduction process. The incremental cost for the additional reduction together with adjustment for density difference results in a \$0.0695/gal hexane cost. Thus, hexane would cost:

<u>Source & Price Rate</u>	<u>Feedstock</u>	<u>+</u>	<u>Reduction</u>	<u>=</u>	<u>Total</u>
From cornstarch/glu @\$98/t:	\$0.97	+	\$0.07	=	\$1.04/gal
From lignocell. biomass @ \$40/t:	\$0.66	+	\$0.07	=	\$0.73/gal
From lignocell. biomass @ \$25/t:	\$0.57	+	\$0.07	=	\$0.64/gal
From lignocell. biomass @ \$10/t:	\$0.49	+	\$0.07	=	\$0.56/gal

Again this does not include the cost of recycling NaI, which will increase the cost. It does show that there is now a method to provide hexane from renewable resources. Other optional products such as the hexanols may be estimated by using a similar incremental reaction cost.

The C₁₂ 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. This group might be suitable as a narrow boiling point range, high value gasoline. But since these values are also similar to the values of kerosene, particularly those of jet fuel, then they gain considerable value when considered for this use. The C₁₈ isomer mixture fits right into the diesel fuel specifications. The C₂₄ and higher oligomers can be used as fuel oil.

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., methyl 2-hexyl ether, ethyl 2-hexyl ether, and dihexyl ethers. Such value added products may also need to be evaluated so that their properties may be compared with oxygenates marketed today for fuel additive purposes.

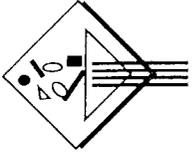
Economic projections of oxygenate products *via* this route may be much more favorable at this time rather than attempting to just make hydrocarbons to compete directly with fossil fuels. On the other hand if some of these hydrocarbons have highly valuable fuel properties (e.g., octane number) then they might also be used for blending purposes. Presently, we are exploring other fuel products and means to cut the reduction costs. Clearly, we have just

begun to explore not only a lot of chemistry but also several processing choices that will impact the economics of a variety of products possible from renewable resources and this novel *chemical reduction 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. Even if the real costs are twice as much, it might still be economical. Establishment of accurate economics will take some time. Total costs depend upon the exact steps, reagents, products, and precisely how the reagents are recycled. It is possible that the high quality, high value products available *via* this process may indeed be economically attractive in the near future, perhaps as fuel additives, even without a change in the margin of fossil fuels. These projections are viewed as being competitive to alternative biofuels considering all the technical, political, and social advantages of this process. Thanks to support from several sources, we are continuing to develop this process.

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StakeTech
STAKE TECHNOLOGY LTD.

September 30, 1994

Prof. M. Robinson
Chemistry Department
University of Texas
Odessa, Texas 79762
U.S.A.

Dear Prof. Robinson:

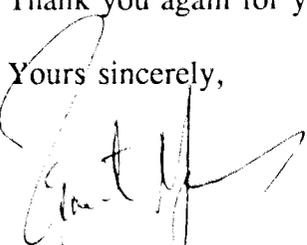
As per your request, please find enclosed the capital and operating cost estimates for a 400,000 dry Tonnes-per-year steam-explosion and delignification process for the conversion of biomass to lignin-free carbohydrates for liquid fuel application. The process as envisioned would include raw material handling, steam-explosion, water-extraction to remove hemicellulose, alkaline-extraction to remove lignin, and peroxide bleaching to further delignify the cellulose for your downstream conversion process. The end-products would be a lignin-free cellulose for your processing, a hemicellulose-rich water-extract (also a substrate for your conversion process) and a lignin-rich alkaline-extract for co-gen application. A major capital and operating cost is due to the requirement for bleaching, using the environmentally friendly but expensive peroxide bleaching process. The extent that your process could tolerate lignin contamination would be important in the overall process design and economics.

The cost estimates do not include any downstream conversion of the cellulose and hemicellulose carbohydrates to your hydrocarbons, since we do not have any information to permit such evaluation. We would appreciate if you could provide us with your capital and operating cost estimates so that we could evaluate the economic feasibility of the integrated plant jointly with you.

Please review the cost estimates provided at your convenience. Should you require further clarification, please do not hesitate to contact us.

Thank you again for your interest in our technology.

Yours sincerely,



Ernest Yu, Ph.D.
Vice-President, Technology

encl.

**UNIVERSITY OF TEXAS WASTE TO FUEL TECHNOLOGY
CONVERSION OF LIGNIN-FREE CELLULOSICS TO LIQUID FUELS**

Preliminary Capital Cost Estimates

Basis of Estimates:

All Costs in US Dollars

8000 hours per Year of Operation
10 Lines of StakeTech System at 5 ODT/Hour/Line
1200 Dry Tonnes of Raw Material per Day
900 Dry Tonnes of Carbohydrate Polymers per Day

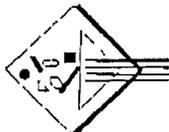
TOTAL CAPITAL COST SUMMARY

DESCRIPTION	CODE	TOTAL INSTALLED COST
Raw Material Handling	Unit 10	1,305,180
StakeTech Processing	Unit 20	27,109,648
Blow Bin	Unit 30	1,267,335
Hemicellulose Recovery	Unit 40	2,957,449
Lignin Recovery	Unit 50	3,404,819
Peroxide Bleaching	Unit 60	22,017,527

TOTAL		<u>58,061,960</u>

TOTAL OPERATING COST SUMMARY

DESCRIPTION	COST PER YEAR	COST/ODT RAW MATERIAL	COST/ODT PRODUCT
Raw Material	12,000,000	30.00	60.00
Utilities	2,367,543	5.92	11.84
Chemicals	17,926,863	44.82	89.64
Labor	2,060,000	5.15	10.30
	-----	-----	-----
TOTAL	<u>34,354,406</u>	<u>85.89</u>	<u>171.78</u>



STAKETECH
Stake Technology Ltd.

FACSIMILE TRANSMISSION

FROM: Ernest Yu

DATE: October 16, 1995

TO: DR. M. ROBINSON	COMPANY: UNIV. OF TEXAS, ODESSA
------------------------	------------------------------------

FAX #: (915) 552-2236

NO. OF PAGES: 2

SUBJECT: STAKETECH PROCESS ECONOMICS

Dear Dr. Robinson:

It was a pleasure talking to you over the phone again.

As per your request, we have re-calculated the economics of your proposed plant without the peroxide bleaching facilities. A summary of the economics of our SBC process is appended.

Please review the revised economics at your earliest convenience. Should you require further clarification, please do not hesitate to contact us. We would also appreciate if you could keep us updated with your project progress. If there are relevant publications in the open literature, please send us a copy whenever possible.

Yours sincerely,

A handwritten signature in black ink, appearing to read 'Ernest Yu'.

Ernest Yu, Ph.D.
Vice-President, Technology

encl.

UNIVERSITY OF TEXAS WASTE TO FUEL TECHNOLOGY

Conversion of Lignin-Free Cellulose to Liquid Fuels

Basis of estimates

400,000 ODT/yr

- Process includes raw material handling, steam-explosion; hemicellulose separation, and lignin separation
- 10 lines of StakeTech equipment @ *5 ODT/Day/Hr/line*
- 8000 operating hours per year (333 d)(24 Hr/d)
- 1200 dry Tonnes of raw material processed per day
- 900 dry Tonnes of carbohydrate polymers produced per day *75%*

metric ton!

Capital cost estimates

Total installed equipment costs - US \$ 37,400,000

Operating cost estimates

	Cost Per Year (US \$)	Cost/T Dry Product (US \$)
Raw material	9,013,533	45.11
Utilities	2,439,242	12.20
Chemicals	1,949,308	9.76
Labor	1,548,872	7.75
Total	14,951,137	74.82

if 50% Cellulose only

<i>Cost raw ODT</i>	<i>22.53</i>
<i>Cost 400K ODT/yr</i>	<i>6.10</i>
	<i>4.87</i>
	<i>3.87</i>
	<i>37.37</i>
<i>Cost of Biomassless</i>	<i>22.53</i>
	<i>14.84/metric ton</i>
	<i>or \$13.48/2000#</i>

STEAM EXPLOSION

Feb. 1995 Dr. J. Michael Robinson

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