

## CHEMICAL CONVERSION OF BIOMASS POLYSACCHARIDES TO LIQUID HYDROCARBON FUELS AND CHEMICALS

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### INTRODUCTION

Biomass has been traditionally converted to liquid fuels by either 1) fermentation or 2) pyrolysis methods. Modern improvements to these classical processes are many in number but do not essentially change the type of product resulting from these two vastly different sets of reaction conditions. While ethanol production by fermentation has become more efficient, it is still limited to a 67% yield due to the loss of one-third (1/3) of the available carbon as carbon dioxide gas. Pyrolytic reactions also lose carbon as gases and char but may achieve about 80% carbon conversion.<sup>1</sup> While most pyrochemical processes usually require nearly dry feedstock, the Shell Hydrothermal Upgrading (HTU) process requires a 3:1 ratio of water to biomass.<sup>2</sup> However, HTU produces only 50% biocrude which still contains 10-15% oxygen. Obviously, there remains a need for a variety of fuels from many sources, especially conventional liquid fuels for transportation purposes. To resolve this fuel problem and to use a renewable resource, a strategy was selected to prepare valuable liquid hydrocarbons from biomass by a new *chemical* process.

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. We envisioned the use of selective reduction reactions to 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 feedstock would be possible. Overall, a six-carbon sugar polymer like cellulose would afford a single pure 6-carbon hydrocarbon product such as hexene or hexane. This is precisely what we have developed, a novel *chemical* process.<sup>3</sup>

### RESULTS AND DISCUSSION

Our use of the term *chemical* implies mild conditions, i.e., boiling aqueous solutions at atmospheric pressure and with chemical catalyst systems rather than enzymes. This chemical process consists of multiple reactions, the first two of which occur in water. **Scheme I** comprises a brief summary of the main reaction steps that achieve the strategic objectives of the organic portion of the process. For simplicity in this abstract, Scheme I only shows the reaction path of a 6-carbon carbohydrate as in cellulose or starch.

**Step 1** is a reductive depolymerization of carbohydrate biopolymers. Cellulose (or starch) is simultaneously hydrolyzed in dilute acid and catalytically hydrogenated to glucitol (commonly named sorbitol) in near quantitative yields.<sup>4</sup> Hemicellulose is similarly converted into 5-carbon polyols (e.g., xylitol), sorbitol, and some gluconic acids. Lignin, if present, is simply removed by filtration or centrifugation after the reaction. While the acid is mild, the highly selective ruthenium catalyst is only active at about the temperature shown. Thus, Step 1 uniquely provides the polyols required for the next reaction and simultaneously provides a facile separation of lignin.<sup>5</sup> However, the ruthenium is easily deactivated by ambient oxygen in these batch laboratory reactions and thus does not recycle well for subsequent reactions. Collaboration is being sought to study various alloys that might be more suitable for this important biomass fractionation reaction. Alternatively, starch obtained from commercial (com) processes gives a pure 6-carbon source and commercial sorbitol is thus also directly available commercially using stable nickel catalysts.

**Step 2** of the process is the key reaction: the *chemical* conversion of polyhydric alcohols to liquid hydrocarbons by reduction with hydriodic acid. The major part of the reduction occurs in this step: five hydroxyl groups of sorbitol undergo reduction. Our strategy to overcome the physical problems of insoluble solids forming during this step was to use homogeneous chemical agents that concomitantly reduce I<sub>2</sub> to regenerate HI.<sup>6</sup> If the I<sub>2</sub> reacts quickly, it does not interfere with the polyol reduction reaction. Such use met with the unexpected results of simultaneous alkene formation and oligomerization. Considerable effort has been extended toward identifying the various oligomerization products and the variables that control their formation.

Thus in Step 2, polyhydric alcohols such as sorbitol are reduced essentially quantitatively to a mixture of halocarbon and hydrocarbon compounds by reaction with hydriodic acid (HI) and a phosphorous type reducing agent, either phosphorous acid ( $H_3PO_3$ ) or hypophosphorous acid ( $H_3PO_2$ ). The reaction occurs in boiling aqueous solution at atmospheric pressure for about 1-2 hour. Reaction conditions can be varied to give on one extreme about 99% 2-iodohexane and on the other extreme about 86% hydrocarbons with the remainder being halocarbons. The immiscible products are simply removed as a separate phase from the water solution. So Step 2 provides a highly reduced  $C_6$  compound and descending amounts of  $C_{12}$ ,  $C_{18}$ , and  $C_{24}$  hydrocarbons. These groups represent fuels in the range of gasoline, kerosene, diesel, and fuel oil, respectively. Each hydrocarbon group is a mixture of alkene and cycloalkane isomers. The higher homologues typically contain at least one ring. An example structure for the  $C_{12}H_{22}$  isomers (1,2,4-trimethyl-3-propylcyclohexene, MW = 166) is shown in Scheme I. Sizable amounts of substituted decalins (two rings) also are present. The mixture of isomers in each group depresses the melting point and helps the fuel remain liquid.

In contrast, we found that Step 2 products such as these do not form from glucose; it must first be reduced to sorbitol. Nor do such products form on treatment of wood directly with HI.<sup>7</sup> In fact, certain Canadian authors found that  $H_3PO_2$  greatly "suppresses the yield of oil products." Products obtained from glucose reactions in this manner are complex mixtures of high molecular weight oils and tars containing significant amounts of oxygen and iodine. We are presently revisiting these glucose reactions with new techniques for the production of small, valuable chemicals rather than fuels.

**Step 3** might be considered a cleanup reaction in that all of the remaining halocarbons in mixtures from Step 2 are subsequently converted to alkenes by an elimination reaction with caustic (NaOH or KOH) in boiling alcohol. Vast differences in boiling points of hexene (68 °C) from the other higher mass hydrocarbons, 200 °C and 300 °C, allow facile separation by distillation of the final mixture. The elimination of HI (Step 3) by KOH produces KI as insoluble by-product. KI is then recycled to KOH and HI (1-3 M solutions) by electrochemical means using an Aqualytics bipolar cellstack.<sup>8</sup> This electrochemical regeneration have been studied on a pilot scale in our labs and determined very efficient. Details will be presented.

Hydrocarbon fractions distilled immediately after Step 3 contained traces of iodine (15-250 ppm). However, further lowering of the iodine content is desired for two reasons: (1) potential corrosion due to the HI produced upon combustion and (2) potentially expensive iodine resource impact costs. Therefore one additional polishing reaction, **Step 4**, was added. The hydrocarbons are simply refluxed with powdered zinc for 0.5 hour and all traces of iodine are removed. There are several optional steps to produce chemicals and solvents from hexene, one of which the catalytic hydrogenation of hexene to furnish hexane, an important large volume industrial solvent for seed oil extractions and polymer reactions.

Physical values, H/C ratio, and octane numbers are shown for these fuels and compared to conventional liquid fuels. 2-Hexene, for example, has an Octane No. of 87, density of 0.75, and a H/C ratio of 2, all ideal for gasoline except that for other reasons alkenes are not desired in a gasoline fuel. The  $C_{12}$  hydrocarbons have several desirable properties (less volatile, highly branched, cyclic, partially unsaturated, and a H/C ratio of 1.83). This group of isomers is deemed most suitable as a narrow boiling point range jet turbine fuel. Indeed, this  $C_{12}$  mixture has a high density of 0.84 and a bp range of about 190-210 °C, similar to the values of kerosene, but structurally too branched to make a standard (linear alkane) diesel fuel. The  $C_{18}$  and  $C_{24}$  isomer mixtures fit into a fuel oil range unless cracked in a conventional refinery manner into smaller hydrocarbons. These hydrocarbon products have high thermal values (43 MJ/kg) relative to ethanol (26.8 MJ/kg) or pyrolysis oils (Shell HTU ~ 36 MJ/kg) resulting from traditional methods of biomass conversions.

Reactions of hemicellulose required two additional models: xylose and gluconic acid. Xylose reactions yield pentene and oligomer hydrocarbons in a similar manner as shown in Scheme 1 by first making xylitol. Mixtures of xylitol and sorbitol give the expected cross oligomers with the exception of little  $C_{10}$ . However, gluconic acid is not reduced to a polyol but is directly reacted with the reducing HI to afford lactones such as 4-ethylbutyrolactone as major products (75%) along with some iodohexanoic acids. The value of these stable lactones as potential oxygenate fuel additives is under study. Hexanols and other oxygenates such as TAME and THME are also available from biomass via this chemical process.

## 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 of obtaining high valued liquids from biomass. 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. These oligomeric hydrocarbons also do not require base treatment and subsequent reagent regeneration costs as do the haloalkanes. Step 2 is highly tunable, which allows a choice of products. Each simple reaction step is driven to essentially quantitative yield resulting in the same high yield for the entire process.

While we may only use hydrogen in Step 1, and in optional steps, it is convenient at this time to estimate the total costs of reduction based on a typical price for hydrogen. Using a hydrogen cost of \$0.40/lb and a cost range of \$10 to \$40/ton for biomass (dry weight basis) containing 75% holocellulose, then total feedstock and reduction costs might be estimated as \$0.37 to \$0.54 per gallon for hexene. Similarly, the C<sub>12</sub> and C<sub>18</sub> isomers range from \$0.34 to \$0.51/gal. However, there are other costs associated with this multiple step process that will definitely contribute to overall process economics. Establishment of accurate economics is a continuing process and will be discussed. Safe distillation and recovery of concentrated HI with saleable by-product phosphoric acid has been achieved. However, methods of coupled reductions that complement HI other than the use of phosphorous acid(s) have also been discovered. Industrial support is therefore being solicited to complete these studies and file several more patents. Total costs depend upon the exact steps, reagents, products, and precisely by which method of regeneration of HI from incipient I<sub>2</sub> is employed. It is likely that the high quality, high value products available *via* this process are today more economically attractive for their chemical (solvent) value, fuel additive (oxygenate) value, and as advanced jet fuels.

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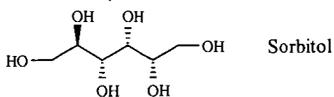
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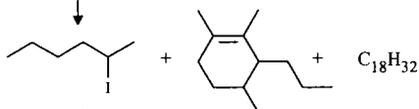
# Biomass to Hexene :

**Biomass:** Cellulose + Hemicellulose + Lignin

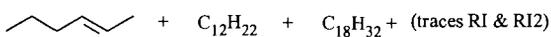
**Step 1** 94%  $\downarrow$   $H^+/H_2O$ , Ru/ $H_2$  (600 psi), 1 hr 165°



**Step 2** 100%  $\downarrow$  HI/ $H_3PO_3$ , 117°, 2 hr



**Step 3** 100%  $\downarrow$  NaOH/ROH heat 1 hr



**Step 4**  $\downarrow$  Zn/heat

