Novel Technology for Economic Replacing Fossil Oil with Biomass

Catalytic Simultaneous Hydrolysis of Lignocelluloses

December 18, 2011

Primary Sponsor:

Sun Pharmaceuticals, Inc., San Diego, CA

Contact Person:

Zuolin Zhu, Ph.D.

Chief Technology Officer

13718 Sorboone Court, San Diego, CA, USA.

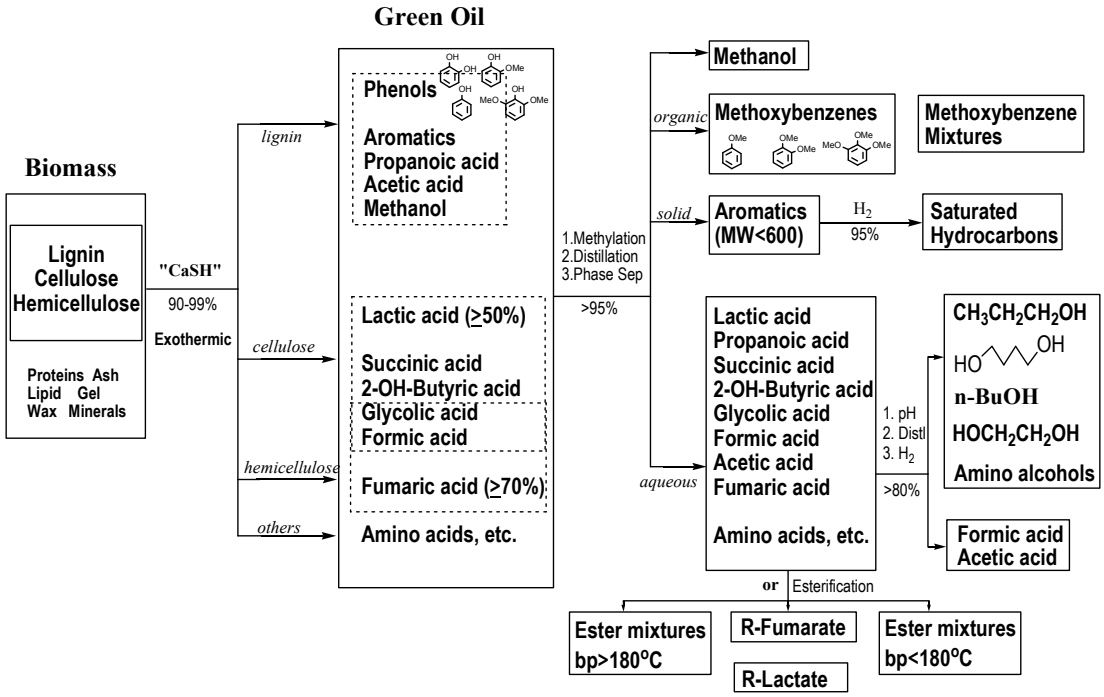
Phone: (858) 673-8068 (USA), 86-137-0561-3787(China)

Email: zuolinzhu@yahoo.com

Novel Technology for Economic Replacing Fossil Oil with Biomass

Catalytic Simultaneous Hydrolysis of Lignocelluloses

In the year of 2011, construction of a pilot plant with the capacity of 1000 dry ton biomass per year is completed in China Fuel (Huaibei), the joint venture of Sun Pharmaceuticals, Inc., San Diego, CA., USA. The flow chart is shown below:



The invention is eligible for the small business award. The award will emphasize and protect the share of the technology by U.S.A.

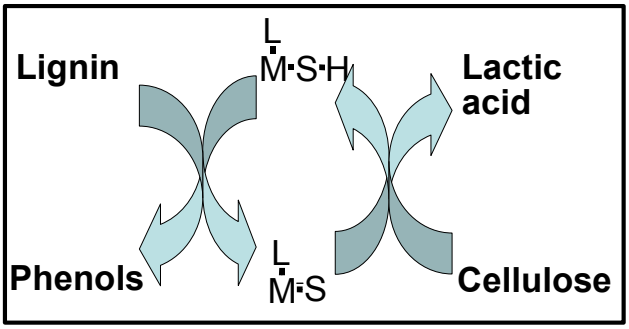
Focus Area 1, 2, and 3 all fit this novel technology.

All the intellectual work has been done by the employees of Sun Pharmaceuticals, such as the design of the catalytic systems, process and equipments. Sun Pharmaceuticals, Inc. is a high-tech company registered at San Diego, CA, USA. The company owns 30% of the technology right now.

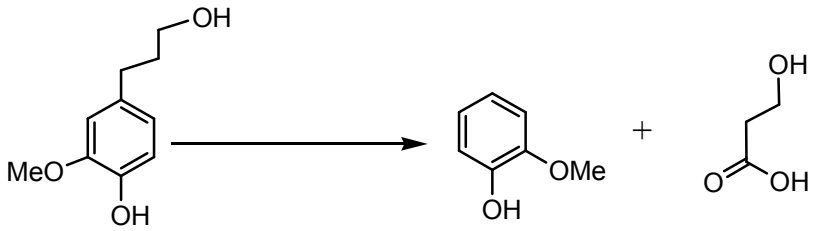
Catalytic Simultaneous Hydrolysis (CaSH) is better than what we can expect. A version of this technology was predicted by U. S. Department of Energy (DOE) may be decades away (*Top Value Added Chemicals from Biomass*, *Volume II*). For CaSH technology, no need to separate organic components of biomass and the reaction is light **exothermic**. All organic polymers of biomass are selectively converted into small organic molecules. For example, cellulose is converted into lactic acid (>50%), hemicellulose into fumaric acid (>70% pentoses), and lignin into four phenols (phenol, guaiacol, catechol, and 2,6-dimethoxyphenol), methanol, propanoic acid, and aromatic oligomers (MW<600). Isolation process is shown in the flow chart.

The Chemistry

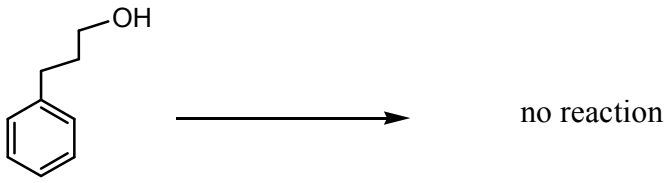
Oxidation of carbohydrates (cellulose, hemicellulose and starch) into organic acids by concentrated hydrogen peroxide or nitric acid, and hydrogenolysis of lignin into aromatics and phenols are known in literatures. This "CaSH" technology is the first redox catalytic hydrolysis of carbohydrates and lignin. No strong oxidants such as concentrated hydrogen peroxide or nitric acid and reductants such as hydrogen gas or hydrogen-donors are used.



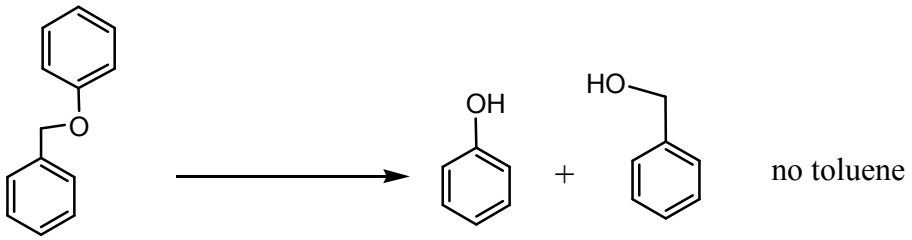
Investigation using model chemicals explained why only four main phenolic products are obtained, why the "CaSH" is hydrolysis, and why oxygen content of the aromatics from lignin is much lower than lignin itself.



(1)



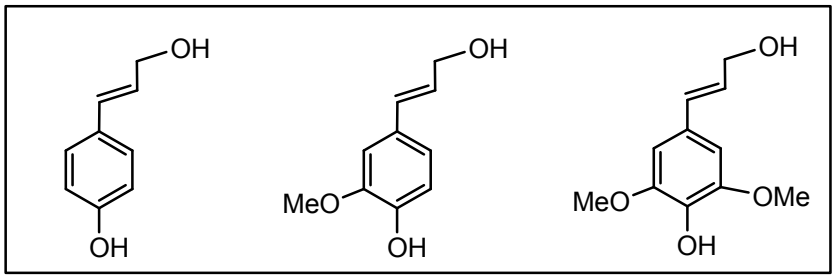
(2)



(3)

Reaction (3) confirms this is hydrolysis. Thermalysis will produce toluene and benzaldehyde.

Reaction (1) shows that de-alkylation occurred for lignin monomers with oxygen connected to phenyl ring. So, we only see simple phenolic products because there are only three monolignols were proposed as the building blocks of lignin.



Catechol may be formed from the hydrolysis of guaiacol.

The Process

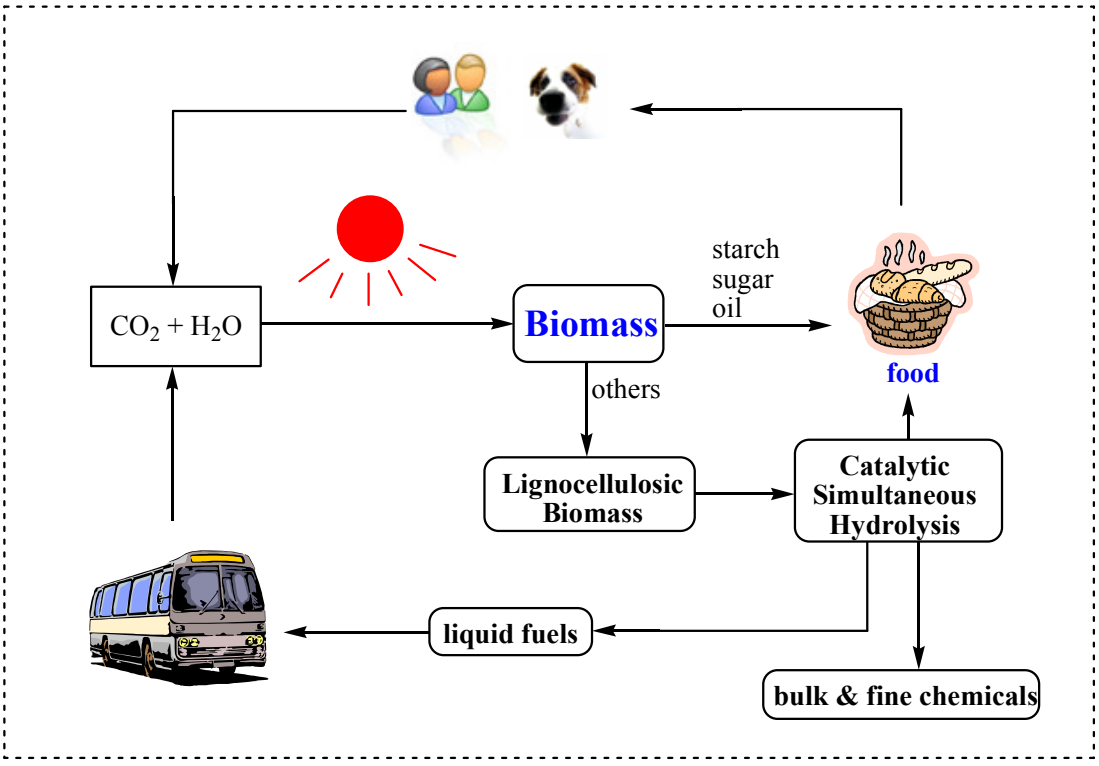
1. Methylation of phenolic compounds is carried out in aqueous solution.
2. Azeotropic distillation of methanol and methoxybenzenes obtain an aqueous solution of methanol and methoxybenzenes. Methoxybenzenes form an organic phase at bottom.
3. Aromatics from lignin are a mixture of many oligomers of single phenyl-ring with molecular weight less than 600. Conditions for the hydrogenation of these aromatics are much mild. Saturated hydrocarbons are high quality liquid fuels.
4. Distillation of formic acid and acetic acid from other organic acids is easy. Hydrogenation of organic acids simplifies the separation. Four main alcohols are obtained: n-propanol, n-butanol, ethylene glycol, and 1,4-butanediol. Compared with other organic acids, amino acids are neglectable. Alcohols such as n-propanol and n-butanol are better liquid fuels than ethanol.
5. Esterification of organic acids is another method for isolating organic acid. After the distillation of pure lactate and fumarate, mixture of esters is distilled into two portions. Portion one has boiling point less than 180°C, is good solvent for paints and inks. Potion two has boiling point higher than 180°C, it is a biodiesel-like product.

Importance of the technology

The “CaSH” technology produces all kinds of products that made from fossil oil today. Saturated hydrocarbons, mono-hydroxyl alcohols, and esters are all good liquid fuels. Phenols, methoxybenzenes, alcohols, and organic acids are bulk & fine organic chemicals. Usage of fossil oil is the major problem today. Extreme weather events and environmental degradation due to green-house gases and severe pollution endanger the life of human beings.

Comparison with other technologies

1. “CaSH” technology is better in source reduction. There is no pretreatment and separation steps for CaSH process. The amount of hazardous substance and pollutant is reduced significantly.
2. “CaSH” technology is greener than other technologies. For saturated hydrocarbon liquid fuel, hydrolysis of lignin followed by hydrogenation of the aromatics obtained has fewer reaction steps and milder reaction conditions. For methoxybenzenes and alcohol products such as n-propanol and 1,4-butanediol, CaSH technology has shorter process and uses greener starting materials.
3. “CaSH” technology is a light exothermic reaction, so the energy consumption is the lowest one for transferring polymeric organic materials such as cellulose and lignin into small organic molecules.
4. The highest level conservation of organic carbons of biomass. There is no gasification and black tar formation during hydrolysis. The isolation yield of CaSH technology is closer to 70%. Cost of good is comparable with petro-chem.



With “CaSH” technology, we will be able to extract carbon dioxide from air, because some of the chemical products will be converted into polymers for furniture, clothing, and buildings.

The most important contribution of the “CaSH” technology is the opportunity for replacing fossil oil with lignocellulosic biomass.

Additional Information

About China Fuel (Huaibei) Bioenergy Technology Development Co., Ltd.:

China Fuel (Huaibei) was founded in 2006, is the joint venture composed of Huaibei Mining Group (45 percent), Sun Pharmaceuticals, Inc. (30 percent), and Anhui Guohua Investment Group (25 percent).

Huaibei Mining Group invests in cash and is one of top 500 companies in China, a State-owned giant company.

Anhui Guohua Investment Group invests in cash and is one of top 10 private companies in Anhui Province, China.

Sun Pharmaceuticals, Inc. invests in brainpower and is a high-tech company, owned by U. S. citizens, registered in San Diego, California, USA.

Employees of Sun Pharmaceuticals such as Zuolin Zhu, Meg M. Sun, and Kangfu Gu work in United States and China during 2010 and 2011.

All the patents were filed jointly by China Fuel (Huaibei) and Sun Pharmaceuticals, they are all PCT applications that covers United States. For example,

1. A Novel biomass pretreatment technology that operates at room temperature and atmospheric pressure (PCT/CN2006/001129);
2. A kilo-scale pilot process that converts all carbohydrates of lignocellulosic biomass into saturated hydrocarbons (PCT/CN2007/001118);
3. Co-gasification of coal and biomass for ethanol synthesis (PCT/CN2007/001117);
4. The first biomimic catalytic system of cellulases (PCT/CN2007/071114);
5. A method for preparing esters from lignin (PCT/CN2009/074087);
6. A biomass liquefaction method without gasification and black-tar or charcoal formation (PCT/CN2008/074087);
7. A process for making grain-like food from lignocellulosic biomass (PCT/CN2009/074926);
8. Catalytic simultaneous hydrolysis of all organic polymers of lignocelluloses (PCT/CN2010/071254).