

UNIQUE FRACTIONATION OF BIOMASS TO POLYOLS PROVIDES INEXPENSIVE FEEDSTOCK FOR LIQUID FUELS PROCESS

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INTRODUCTION

Previous work in this laboratory established a unique process that converts C₃ and C₆ polyols (straight-chain hydrocarbons with a hydroxyl group on each carbon) to hydrocarbons using hydroiodic acid and phosphoric acids.¹ Polyols, such as sorbitol and xylitol, are commercially available from highly purified glucose and xylose but are expensive. To use less costly and renewable biomass resources as feedstock for this process, the biomass must first be fractionated (e.g. by steam explosion²) for cellulose and/or hemicellulose recovery; these polysaccharides can then be hydrolyzed and reduced to polyols. We are investigating a one-step Russian method³ to directly convert raw "biomass-to-polyols" (BTP) to determine more definitive optimum reaction conditions and the economics of this method for comparison to using steam-exploded cellulose. In the Russian method, biomass is subjected to simultaneous dilute acid hydrolysis and catalytic hydrogenation at ~170 °C and ~50 atm H₂ (cold), thus trapping the incipient aldoses as their corresponding, but less reactive, polyols (alditols).

At this point, the main limitation to the effectiveness of the Russian method is the recycle of the catalyst, as using ruthenium/carbon (Ru/C) once-through is costly. In this process, the solid phase by-product lignin remains separate from the solution of polyols as the latter is formed from cellulose/hemicelluloses. The solid, with the catalyst, are simply filtered from solution. A major milestone in our investigation is separation of the lignin from the catalyst either by (1) base-extracting the lignin or (2) reacting it further at higher temperature and pressure in base. As the Russian paper suggests, clean catalyst can be recovered at 280-320 °C and ~50-70 atm H₂ (cold).³

As lignite has structural features similar to cellulose and lignin, we anticipated these reaction conditions could also convert a high percentage of coal into smaller moieties. Coal has been converted to liquids using many different solvents, temperatures, catalysts, and gas atmospheres.⁴⁻⁶ However, few researchers have done acid or base hydrolysis/hydrogenation, particularly at such low severity conditions. Base extraction is used to remove humic acids, typically about 10-20 % of lignite.⁷ Some of the original coal liquefaction reactions were done at low temperature by Berthelot where he heated coal with hydroiodic acid in a sealed glass tube to 250°C.⁸ The bituminous coal was converted into a semi-liquid material with an oil content of 60 %. However, other research suggests that this conversion to oil would have contained a high iodide content.⁹ In more recent work, lignite had high hexane-soluble yield using sodium aluminate and molybdenum/nickel catalysts at ~360°C.¹⁰ Ruthenium catalysts have also been used successfully in coal liquefaction reactions at 400 °C and 50 atm of H₂, with a total conversion of Australian Yallourn brown coal of 96.5 % to THF-solubles/gas and an oil yield of 57.8 %.¹¹

We describe in this paper the results for the BTP conversion at our typical reaction conditions, the cleaning of the ruthenium catalyst and how well the clean catalyst performed. We also include some preliminary experiments on a Texas coal at each of the reaction conditions of our BTP, possibly in stages, to see if indeed lignite can be converted under such low severity reaction conditions.

EXPERIMENTAL

Materials

The sawdust used was an oak hardwood. The catalyst was purchased from Aldrich Chem. Co., 5 % ruthenium on carbon (5% Ru/C). Phosphoric acid, sodium hydroxide, and methylene chloride are reagent grade. Lignite coal was obtained from COPL at Pennsylvania State University, sample DECS-1, with an ultimate analysis (dry) of %C - 62.5, %H - 4.8, %N - 1.2, %S - 1.0, %O - 14.7, % ash - 15.8.

Reaction Conditions

The reactions are done in a 3 L stirred autoclave that is heated by electric coils on the outside and cooled by water-cooled coils inside the reactor. The heater is temperature-controlled by computer. The reaction conditions for the BTP process are 180 °C, 2h, 50 atm H₂ (cold). The acid is a 0.8 % solution of phosphoric acid, and enough Ru/C is added for a 0.5% metal loading (~200g sawdust to 20g of 5% Ru/C catalyst). After reaction, the solid material is filtered from the liquid product by vacuum filtration and rinsing with water. The remaining solid is not dried. For the coal reaction, only 50 g (dry) coal and 5g of catalyst are used, the reaction was done twice using 0.8 % solution of phosphoric acid and sulfuric acid each, and the remaining solid after filtration is extracted with methylene chloride by ultrasonication for 10 min and filtering the remaining solid.

For the sawdust reactions, initial experiments were done to determine if the lignin/catalyst could be run again without separation, but deactivation already occurred. Two methods were tried to remove the lignin from catalyst. The first involved base extraction of the catalyst to remove the lignin at atmospheric conditions. Using a 5 % solution of NaOH, the catalyst/base mixture was heated to 100 °C for 2-6 h, then filtered and rinsed repeatedly with water to remove the base.² The second method, described in the Russian literature³ was to mix the catalyst with a 1.5 % solution of NaOH in the stirred autoclave to a temperature of 235-250 °C, 2 h, 44 atm H₂ (cold), then filtered and rinsed repeatedly with water.

The reaction conditions for a second lignite reaction are 235 °C, 2 h, 44 atm H₂ (cold) while in a 1.5 % solution of NaOH, which is then filtered and rinsed repeatedly with water. Only 50 g (dry) coal and 5g of catalyst are used, and the remaining solid after filtration is extracted with methylene chloride by ultrasonication for 10 min and filtering the remaining solid. The results of these experiments and the process are explained in the next section.

RESULTS AND DISCUSSION

Figures 1-3 contain schematics of the processes used for these experiments. Figure 1 is a schematic of the entire process, each box representing a key step in our process and each circle representing a small step in our process that must be done in order to make our process economical. As described in previous publications,¹ the first step of our process is to convert either raw biomass or steam exploded biomass to polyols, followed by a second step to reduce the polyols to hydrocarbons using HI/H₃PO₃, and then finally to eliminate iodine from the hydrocarbons by using NaOH to produce hexene. The focus of this paper is Step 1, the BTP method, which is shown in the white box and highlighted in Figures 2 and 3.

BTP Method

As discussed in the introduction, the BTP method is used to convert the raw biomass to polyols using 0.7 % phosphoric acid, Ru/C catalyst at 180 °C, 50 atm H₂ (cold) for 2 h. Several different reaction conditions were tried as the Russian literature explained a range of reaction conditions,³ but we found with these parameters the greatest yield of polyols, about 70 % of the wood, and about 30% of the remaining wood is lignin, as expected. These results are reproducible. However, in the process of separating the polyols from the lignin and catalyst, the lignin and catalyst are solids that are not easily separated, and without the separation of the lignin and catalyst, the catalyst cannot be recycled as it becomes deactivated. Without being able to recycle the catalyst and the loss of potentially sellable product lignin, the process is not very economical. So a major milestone for using this method is to separate lignin from the Ru/C catalyst.

Separation of Lignin and Catalyst

Two methods to accomplish this separation have been tried. The first method was to extract the lignin using hot sodium hydroxide; this is a well-known method to extract lignin from plants. This facile method has significant potential to remove most if not all of the lignin and has much less severe conditions than the alternative method. After six hours, about 75 % of the lignin is extracted. The yield of polyols in subsequent BTP reactions using the cleaned catalyst was reduced to 58 % upon the first recycle reaction and 51% upon the second BTP recycle reaction indicating some deactivation of the catalyst.

The second method is from the Russian literature.³ It is claimed that clean catalyst is obtained after reaction of the catalyst/lignin at 280-320 °C, 50-70 atm H₂, and 1.5 % NaOH solution, the product being phenolic compounds. At this time, mechanical problems have kept us from completing these reactions. Another reactor has been acquired to complete this study.

Coal Reactions

As discussed in the introduction, we felt both of these mild reaction conditions could significantly alter the structure of lower rank coal, so we have some preliminary results from these reactions. When reacting the coal at the 180 °C reaction condition in acid, we converted ~40 % of the coal to methylene chloride-solubles with little of the H₂ consumed during the process. When reacting the coal in base at 250 °C (the temperature did reach 250 °C for about 20 min, but fell to about 235 °C over a period of 80 min) and an initial H₂ pressure of 44 atm, we converted ~20 % of the coal to water-solubles; however, as these are initial experiments, we plan to continue to vary these reaction conditions. The pressure profile for this reaction was unusual in comparison to the reactions at lower temperature and could indicate the reaction ran at supercritical conditions.

For low temperature reactions using a hydrogenation catalyst (reactions < 320 °C), usually conversions are quite low, typically < 20 % of the coal reacts.^{6, 10, 12} Most researchers believe the controlling mechanism of coal liquefaction is the depolymerization of the coal which does not significantly occur until 350 °C.⁶ Exceptions to these data are acid-catalyzed reactions, such as Berthelot using HI⁸ and other researchers using ZnCl₂ and SnCl₂,⁶ as these catalysts are known to crack C-C bonds.

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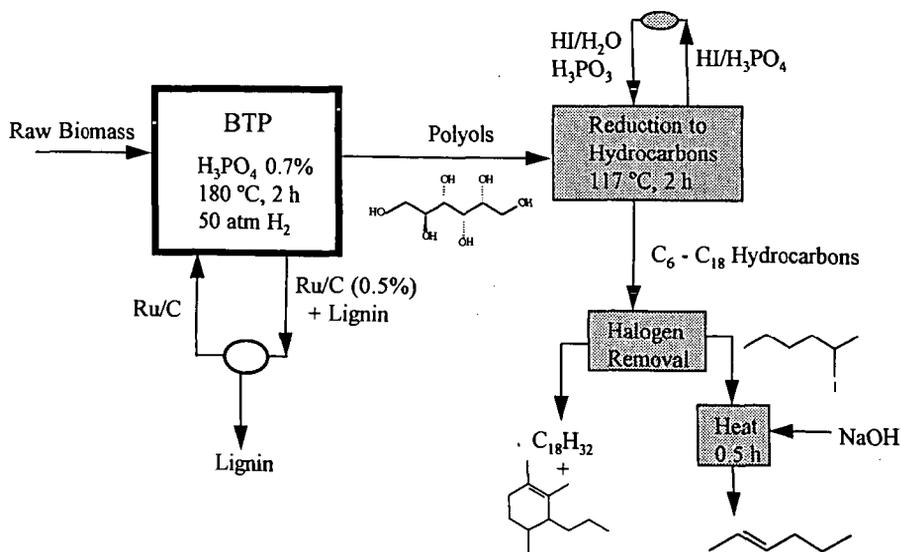


Figure 1: Schematic of Overall Biomass-to-Hydrocarbon Process

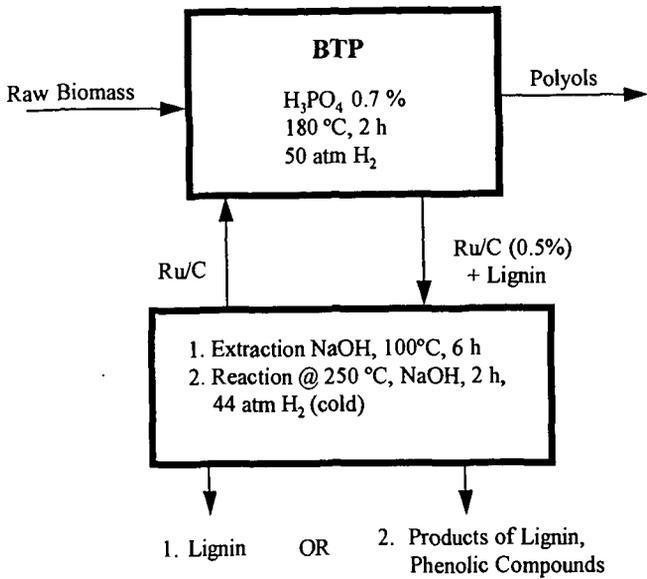


Figure 2: Schematic of BTP Process and Possible Processes to Separate Lignin and Ru/C for Recycle

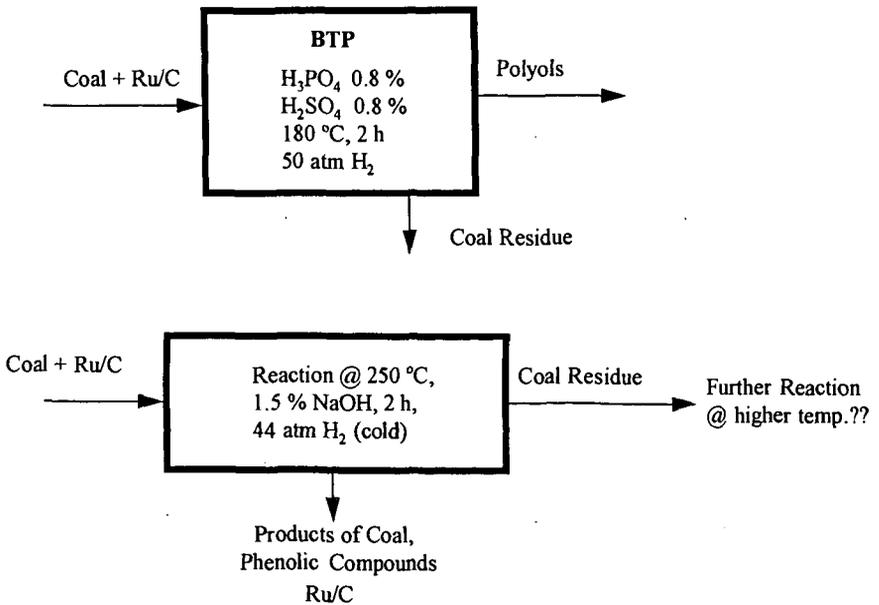


Figure 3: Schematic of BTP Process and Lignin Reaction Process Applied to Coal