

## Biomass waste – a source of raw materials and new energy source

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**Abstract:** Agricultural crop residues, such as straw, corn stover and wood wastes such as leftovers from timber cutting, broken furniture, sawdust, residues from paper mills etc. contain appreciable quantities of cellulose, hemicelluloses and lignin. Much effort has been devoted to convert these types of biomass into useful industrial and commercially viable products.

During liquefaction, lignocellulosic components are depolymerised to low molecular mass compounds with high reactivity and high hydroxyl group content. We have used a high energy ultrasound as an energy source to speed up the liquefaction process in our research. The liquefied biomass was used as a feedstock in synthesis of polyesters, polyurethane foams and adhesives. Adhesives for the wood particle boards with incorporated liquefied lignocellulosic materials emit less formaldehyde and products have the same or even better mechanical and physical properties.

A special attention was given to the utilization of the liquefied lignocellulosic materials as a new energy source with high heating value. It was found that the combustion efficiency of lignocellulosic liquid fuel is comparable to the combustion efficiency of Diesel fuel although it has much higher content of cyclic hydrocarbons. The emissions are within the range of the European emission regulations.

The utilization of liquefied lignocellulosic materials can at least partially reduce the crude oil consumption, thus increasing the use of the renewable resources in large extent.

**Keywords:** biomass liquefaction, polyester synthesis, adhesives, fuel

### 1. Introduction

Biomass based materials and wood in particular are among the most abundant renewable resources. Much effort has been devoted to convert these types of biomass into useful industrial and commercially viable products. One of the possible routes to achieving this is through **liquefaction** where wood or lignocellulosic materials, such as waste paper, starch, etc. reacts with phenol or multifunctional alcohols to yield low molecular mass, liquid products that can be used for polymer synthesis [1,2,3,].

In our research native hardwood and softwood as well as paper and different wood based waste materials were liquefied with different glycols and with a minor addition of p-toluene sulphonic acid as catalyst.

However, a novel approach to a very efficient energy input during the thermochemically conversion of lignocellulosic biomass into liquefied depolymerized products is the use of ultrasound power. Sonochemistry is nowadays an excellent tool in chemical, physical and biological processes. The irradiation with ultrasound can be regarded as a special type of energy input into the system. The range from 20 kHz to 1MHz is used in chemistry while higher frequencies are used in medical and diagnostic applications. The high frequency mechanical vibrations are transferred into the medium by titanium made horn, in different sizes and shapes. Ultrasound is transmitted through a medium via pressure waves and the main advantage is directly related to the physical effect of acoustic cavitation. Acoustic waves

can break the cohesion of a liquid and create micro cavities. The cavity is actually a micro bubble which corresponds to the sound wave by growing till becoming unstable. At that point bubbles collapse violently creating drastic conditions inside the medium for a very short time: temperatures of 2000-5000K and pressures up to 1800 atm inside the collapsing cavity. Consequently, under such extreme conditions volatile molecules vaporize and form free radicals as was proved in extensive studies of the sonification of water. Radicals cause fragmentation of large molecules, stripping off the ligands and oxidation. Shaw and Lee [6] exposed the effluent from pulp and paper kraft mill to power ultrasound and efficiently reduced the chemical oxygen demand (COD) and effluent turbidity. Shock waves, generated at the collapse of cavities induce mechanical effects, such as splitting large molecules to smaller fragments, particle size reduction, surface cleaning and intensive mixing and heating. The later are used for the formation of stable emulsions in liquid-liquid systems.

Sonochemical methods are used also in carbohydrate chemistry [7]. Hydrolysis and cleavage of di- and polysaccharides were quantitatively proved with starch, dextran, cellulose derivatives and other polysaccharides. In our research we have utilized high energy ultrasound for depolymerization and liquefaction of different lignocellulosic materials. It was found, that the reaction yield was in all experiments almost 100% and the reaction time grossly reduced.

Liquefied wood can be considered to be a polyhydric alcohol. After the liquefaction process, the presence of hydroxyl group-containing species in the wood components can be used as polyols for several different purposes. The hydroxyl value of the liquefied wood has been determined to be between 500 and 1000 mg of KOH/g. This high number means that the products can be used as the hydroxyl component in complex polyester synthesis [4]. Some benefits could be expected from such systems. These include the incorporation of the biomass components into the polymeric compositions and consequently, the provision of a certain degree of biodegradability. Esterification of a proportion of the hydroxyl groups reduces the reactivity of the liquid wood, a feature that is sometimes desired in polyurethane synthesis.

It was found during initial experiments that a mixture of liquefied wood with melamine-formaldehyde or melamine-urea-formaldehyde resin can react at elevated temperatures forming a solid crosslinked product that was suitable for the use in wood furniture industry. Such an adhesive has lower formaldehyde content than the standard melamine-formaldehyde or melamine-urea formaldehyde adhesives [5]. In the condensation – elimination reaction, the methylol groups of the melamine-formaldehyde resins precursors react with the hydroxyl groups on the liquefied wood, eliminating water or methanol. The acid catalyst which is present in the liquefied wood additionally speeds up the reaction.

In our research we have utilized high energy ultrasound for depolymerisation and liquefaction of different lignocellulosic materials, wood wastes in particular. A town with 350.000 inhabitants generate 5.700 tons of different wood waste materials per year, mainly broken furniture and packaging materials. Besides that, 2.300 tons of forest residues are deposited, mainly tree branches, bark and larger pieces of timber. The aim of this study was to find a highly efficient way to transform this biomass waste into valuable chemicals and as a new energy source. It was found, that the reaction yield in all experiments was almost 100% and the reaction time grossly reduced.

The first objective of this study was to synthesize a liquefied wood that contained high hydroxyl group content, with a good yield in the liquefaction reaction. The second goal was to achieve the utilization of liquefied wood in the synthesis of polyester-polyols. These polyols were successfully utilized in polyurethane foam production. The third goal was to establish

the criteria for creating a melamin-formaldehyde or a melamine-urea-formaldehyde resin precursor that would react at elevated temperature with liquefied wood and could be used as an adhesive. The fourth objective was to utilize the liquefied wood as an energy source with high heating value. Most of liquefied products have a heating value higher than 22 KJ/kg, that is in the range of pure ethanol and higher than brown coal. Initial tests have indicated that these products could also be used as a motor fuel. Since the production of such liquid fuel utilizes a huge variety of lignocellulosic wastes and takes place under very mild reaction conditions, an overall energy output is high. Several possible applications in energy production were identified and explored by our group.

The utilization of liquefied lignocellulosic materials can at least partially reduce the crude oil consumption, thus increasing the use of the renewable resources in large extent.

## 2. Materials And Methods

The most common wood waste materials such as medium density fibreboard (MDF), veneered particleboard, particleboard, oriented strand board (OSB), plywood and wheat straw were milled on ROTSCH SM-2000 mill. All meals (flours) including spruce (*Picea spp.*) sawdust were sieved through a 2 mm screens and dried at room temperature to constant water content.

All chemicals were of synthesis grade (Merck) and were used without further purification.

### 2.1. Experimental setup

The liquefaction was carried out in a 1000mL three-neck glass reactor, equipped with the mechanical stirrer and condenser.

The ultrasonic device was UP400S processor, produced by Hielscher Ultrasonics GmbH, Warthestrasse 21, 14513 Teltow, Germany. The high frequency (24 kHz) power output can be regulated by adjustment of amplitude from 20% to 100% of the nominal power of 400W. The high frequency output is transferred through titanium cylindrical horn, introduced into the reactor through the side neck and submerged 20mm into the reaction mixture. The horn had diameter of 22 mm, with the calculated power output (at the maximum amplitude)  $105\text{Wcm}^{-2}$ .

The experimental setup is shown in Figure 1.

### 2.2. Biomass (wood waste) liquefaction

The reactor was charged with 140g of biomass and 700g of glycol. 21g of p-toluenesulfonic acid was added. The liquefaction of different wood waste materials was governed in diethylene glycol: glycerol = 1:4 mixtures.

The mixture was heated for maximum of 2 hours at 180 °C while being constantly stirred.

The ultrasound was switched on when the temperature of the reaction mixture reached 160°C. The energy input was controlled by the amplitude of the ultrasound. Ultrasound of amplitude from 20% to 100% was used for waste wood liquefaction.

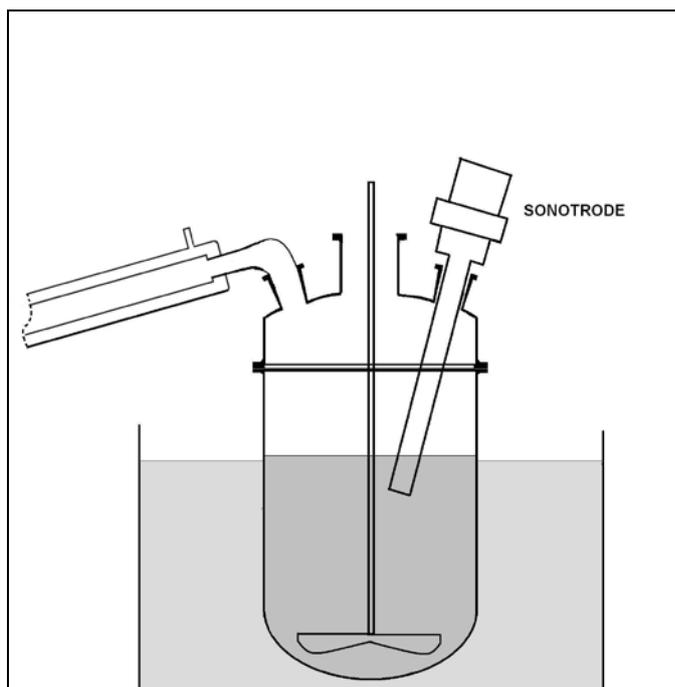


Fig. 1: Glass reactor with external heater, mixer and ultrasound sonotrode

### 2.3. Polyester polyols from the liquefied wood (LW)

Three different formulations with two different dibasic organic acids were used in order to study the differences in the physical and the chemical properties of the final products. 300 g of liquefied wood were used in combination with 60 g of adipic acid; the resulting polyester was identified as P1. With 60 g of phthalic acid anhydride, the product was identified as P2. With 30 g of adipic acid and 30 g of phthalic acid anhydride, the resulting polyester was identified as P3.

The liquefied wood was introduced into the four-necked 1000 cm<sup>3</sup> glass reactor, equipped with a water condenser and mechanical stirrer. The reactor was placed in an electric jacket heater. Adipic acid and/or phthalic acid anhydride were added when the liquefied wood reached 180°C. Dibutyl tin oxide (0.2% w/w) was added as the sterification/transesterification catalyst. The mixture was heated gradually up to 200°C, under stirring and was held at this temperature. Water was continuously distilled from the reaction system. A slight stream of nitrogen was introduced into the reactor for easier transport of water vapor into a condenser. A sample was withdrawn periodically from the reaction system and its acid value was determined. The total reaction time was between 160 minutes and 180 minutes. After completion of the reaction, when the acid value was reduced to less than 30 mgKOH/g, the reaction mixture was cooled to ambient temperature.

#### 1.1. Product characterization

Hydroxyl values were determined by standard ASTM Standard D4274-05 (2005) method. The extent of liquefaction was evaluated by determining the residue after the washing out the sample with dioxane and water (4:1 v/v). The residue was dried in an oven at 105°C to constant weight. The conversion yield was calculated as the weight percentage based on the starting wood material.

### 3. Results and Discussion

#### 3.1. The efficiency of the ultrasound

Initial experiments were dedicated to determining the influence of the ultrasound to the speed of the liquefaction reaction. The increase of the ultrasound amplitude reduces liquefaction time needed to achieve the same liquefaction residue amounts. The efficiency of the ultrasound is illustrated in Figure 2, where the liquefaction process without the use of the ultrasound needs 120 minutes to achieve the total liquefaction while with the ultrasound at the minimal amplitude of 20% only 80 minutes. Accordingly, the use of the ultrasound with 60% amplitude completes liquefaction in 60 minutes that represents only half of the time which is consumed in order to achieve the same liquefaction extent without ultrasound.

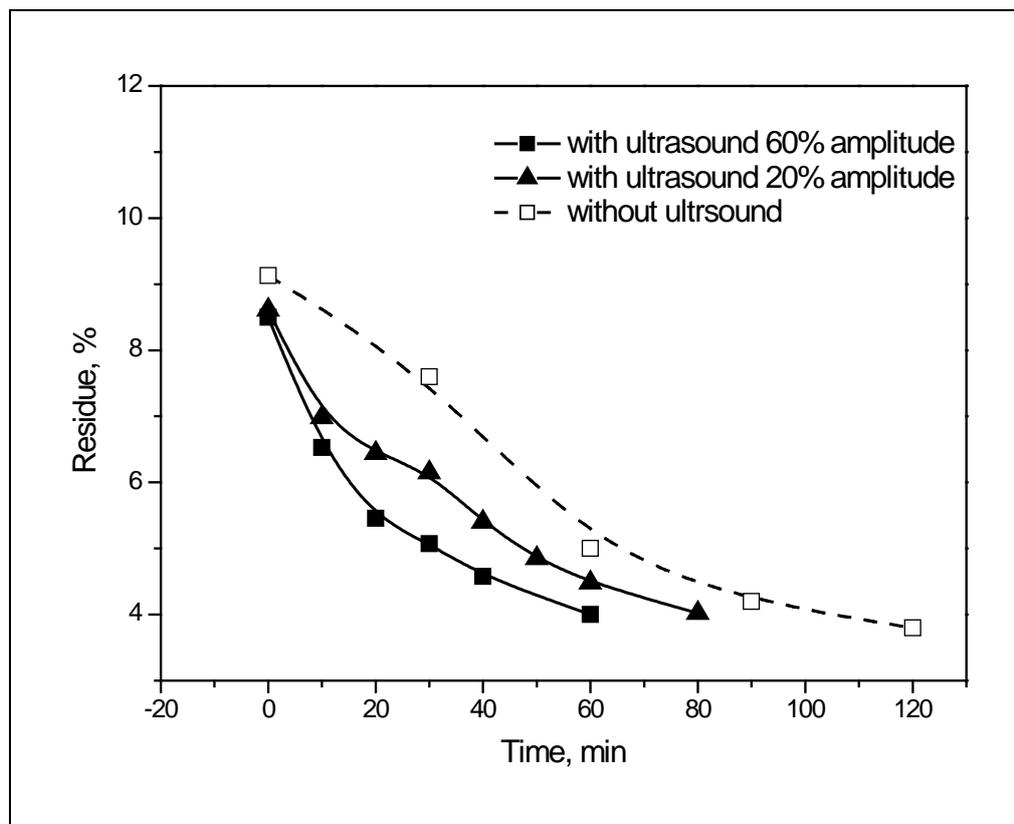


Fig. 2: The decrease of the wood residue in % during the liquefaction with ultrasound 60% amplitude (squares), 20% amplitude (triangles) and without ultrasound (empty squares). (Values at 0 min represent residue % of the samples taken after the reaction mixture achieved 160 °C and in case of ultrasonically assisted liquefaction - when the ultrasound was switched on.)

The powerful energy input through the cavitation effect is demonstrated in the reduction of the biomass particles size and through the depolymerization of the large biopolymers. The size reduction is visible by naked eye since after initial few minutes the reaction mixture becomes homogeneous dispersion. The process continues till all the biomass is completely dissolved and a dark brown liquid is formed with particles sizes less than 1µm.

### 3.2. Polyester polyols from liquefied wood

Liquefied wood was used as a component in polyester synthesis due to the large number of hydroxyl groups that are available in the liquefied wood. The liquefied wood was used as a substitute for part of the polyhydroxy alcohols that are standard raw material in polyester formulation. Polyester polyols were prepared by using adipic acid and/or phthalic acid anhydride in a high temperature polycondensation/esterification reaction. The polyesters were prepared under the standard high temperature polycondensation conditions, confirming the use of the liquefied wood as a raw material in polyester synthesis. The products were characterized using FTIR, GPC/SEC and viscosity measurements showing similar properties to those possessed by equivalent commercial polyesters. The characteristic data are presented in Table 1.

Table 1: Characteristic data of polyesters and the initial liquefied wood

	Mn(Av.) g/mol	MW(Av.) g/mol	PDI	OH value mgKOH/g	Viscosity kPa.s	% of wood (w/w)
LW	4790	19400	4.0	1043	2.8	28
P-1	10300	39900	3.9	798	1.9	22
P-2	4590	60000	13.1	378	1.9	23
P-3	7980	79500	10.0	437	2.2	23

A rise of the average molar mass was achieved together with a reduction of the hydroxyl group content. Such a modification of the polyester reactivity and complexity is favorable for further utilization in polyurethane synthesis. The final OH values of the polyesters were in the range of saturated polyesters that are used in polyurethane production. The viscosity is grossly dependent on the type of the glycol used for the liquefaction and on the wood glycol ratio. The use of wood in these experiments replaced up to 23% of polyhydroxy alcohols in polyester formulations. This amount varies according to product requirements and can be increased significantly.

### 3.3. Liquefied Wood As A New Particle Board Adhesive System

The OH groups in the liquefied wood, including those of the remaining unreacted glycols were available for the condensation reactions with different melamine-formaldehyde and melamine-urea-formaldehyde resin precursors. By measuring the mechanical properties of selected particle boards and by measuring the formaldehyde release, it was found, that a 50% addition of the liquefied wood met the European standard quality demands for particle boards. Formaldehyde release was lower than 8mg/100g in all experiments due to the positive influence of the liquefied wood components. It can be concluded that the products of the liquefied lignin with their aromatic character behaved as a formaldehyde scavenger. Lower formaldehyde emissions from particle boards due to the use of the liquefied wood, are extremely important in the provision of better quality of life. The properties of particle boards made with the mixture of the liquefied spruce wood and the melamine-urea-formaldehyde resin precursor Meldur H97 and melamine-formaldehyde resin precursor MS-1 were within the European standard EN 312 (2003), type P2 limitations..

On the basis of the presented values one can conclude that liquefied woods can be used as a substitute for synthetic resin precursors in adhesives that are used for particle board production.

### **3.4. Liquefied biomass as a fuel**

A special attention was given to the utilization of the liquefied lignocellulosic materials as a new energy source with high heating value. Most of liquefied products have a heating value higher than 22 KJ/kg, that is in the range of pure ethanol and higher than brown coal. Initial tests have indicated that these products could also be used as a motor fuel. Since the production of such liquid fuel utilizes a huge variety of lignocellulosic wastes and takes place under very mild reaction conditions, an overall energy output is high. The viscosity of the liquefied biomass depends on the biomass content in the formulation and can be between 149 kPa.s to 2 kPa.s. However, if it is applied at higher temperatures, the viscosity is reduced to 100 Pa.s and can be directly introduced into the burner. The sulphur content is less than 0.3%. The carbon monoxide, nitrogen oxides and solid particles emission were within the range of the European emission regulations for heavy duty diesel engines.

Preliminary test were carried out in a prototype gas turbine, where efficiency, power output, exhaust emissions as well as wear and durability of components were examined. These results were compared to the results obtained during the tests with Diesel fuel. Due to high viscosity of the lignocellulosic liquid fuel, a new fuel injection system was designed and manufactured to allow injection of heated and pressurized fuel.

It was found that the combustion efficiency of lignocellulosic liquid fuel is comparable to the combustion efficiency of Diesel fuel although it has much higher content of cyclic hydrocarbons. It was also proven that utilization of lignocellulosic liquid fuel in the prototype gas turbine complies with current emission regulations for electric power generation. Differences in exhaust emissions while utilizing lignocellulosic liquid fuel and Diesel fuel were analyzed and interpreted. It was found that total hydrocarbon emissions are higher than those of Diesel fuel; however the difference diminishes for high air-fuel ratios, high combustion chamber air inlet temperature, and high fuel temperatures. All effects enhance evaporation of fuel with high viscosity thereby additionally enabling higher conversion rate of cyclic hydrocarbons. It was also found that NO<sub>x</sub> emission increased slightly at the same enthalpy of exhaust gasses while using lignocellulosic liquid fuel, which could be attributed to high oxygen content of the fuel. Influence of utilizing lignocellulosic liquid fuel on wear and durability of components of the gas turbine and its fuel injection system is currently examined.

## **4. Conclusions**

Different lignocellulosic materials were liquefied with yields higher than 95% and with additional use of the ultrasound the reaction times could be reduced for more than 50%.

Polyesters were synthesized using liquefied wood and other lignocellulosic materials as a replacement for a certain amount of polyhydric alcohols – produced from crude oil. The chemical and physical properties of such polyesters are favorable for their use in polyurethane synthesis. The use of wood in these experiments replaced up to 23% of polyhydroxy alcohols in polyester formulations.

Liquefied lignocellulosic materials were also used as adhesives for particle boards production – with reduced formaldehyde emission and excellent mechanical properties. By measuring the

mechanical properties of selected particle boards and by measuring the formaldehyde release, it was found, that a 50% addition of the liquefied wood met the European standard quality demands for particle boards. It can be concluded that the products of the liquefied lignin with their aromatic character behaved as a formaldehyde scavenger. Lower formaldehyde emissions from particle boards due to the use of the liquefied wood, are extremely important in the provision of better quality of life.

The liquefied biomass has high heating value. The residual particles have low average diameter and the liquefied biomass has low viscosity. These are the properties, favorable to its utilization as the liquid fuel in traditional oil burners and in diesel engines. The emissions are within the range of the European emission regulations. Successfully completed initial test thus pave the way for utilization of a new renewable fuel in gas turbines, which are known for their high efficiency, high power density, high reliability, technology availability and affordability. Overall energy conversion efficiency will be increased by utilizing co- or tri-generation power plants. The key achievement arises from the fact that the fuel is produced from mainly unused renewable source and from the fact that its use has very low carbon footprint.

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