

Microwave Heating in Wood Liquefaction

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ABSTRACT: Microwave radiation was used as the sole heating source to achieve liquefaction of Central European hardwoods, with glycols and organic acid anhydrides, using phosphoric acid as the acid catalyst. Pulsed microwaves of 300–700 W power were applied for 5–20 min. The efficiency of liquefaction increased with higher microwave power, longer radiation time, and higher phosphoric acid addition. With minor amounts of added acid it was possible to

achieve complete liquefaction in 20 min. The method was tested for different hardwood types, with a series of glycols and anhydrides, and was found to be generally applicable. © 2006 Wiley Periodicals, Inc. *J Appl Polym Sci* 101: 1051–1056, 2006

Key words: renewable resources; polyester; biopolymers; wood; liquefaction

INTRODUCTION

Wood is among the most abundant and widely accessible renewable resources available to man. Apart from its traditional uses, it is also an attractive source of chemical feedstocks, particularly those normally obtained from nonrenewable sources. Although various components of wood are exploited commercially, wood is generally not used as a feedstock in its entirety. The main reasons for this are the varied structural and chemical properties of its main polymeric components: cellulose, lignin, and hemicelluloses, which are difficult to process together under the same conditions.

Wood liquefaction is one of the several chemical processes in which wood is derivatized or degraded without a costly separation and purification prior to the reaction in which wood is converted into a multifunctional liquid.¹ The process is normally carried out at elevated temperatures with the use of reagents and catalysts that have sufficient reactivity toward wood components. Most of the reported research has been done on the use of phenol^{2–4} and various polyols^{5,6} as the liquefaction reagents, most commonly in conjunction with the use of strong acids as catalysts. Products of phenol liquefaction were further used in the production of phenol-formaldehyde and novolac-type resins,^{2,7} and attempts at using liquid wood as the polyol component in polyurethane foam formulations

have also been reported.⁸ Liquefaction using dibasic esters with subsequent use of the products for polyurethane resins has been recently reported.⁹ In our studies we explored the use of glycols in combination with organic acid anhydrides as the reagents to achieve liquefaction.⁶ These reagents were chosen due to their reactivity as an acid and a solvolysis agent (glycol), and to obtain a partial polyester basis suitable for further use in the synthesis of saturated and unsaturated polyesters and alkyds.

Liquefaction comprises a complex set of reactions taking place on the polymeric components of wood. They include derivatizations such as esterification or etherification of free hydroxyl groups in cellulose or lignin as well as reactions that break the polymer chain of cellulose. The complexity of the reactions taking place is considerable because of the large number of minor wood components ranging from gums and resins to minerals and salts. In addition, liquefaction is affected by physical constraints on wood reactivity such as the high crystallinity of cellulose. The tight packing of cellulose in the crystalline domains makes the reaction kinetics of otherwise reactive functional groups dependent on the diffusion of reagents into the tightly packed system. To overcome this limitation and speed up the liquefaction, increasingly harsh catalysts and reaction conditions, mainly mineral acids and high temperatures, have been employed. Detailed elucidation of the reaction pathways was not the focus of our work, although several reports of such studies have been published.^{5,10}

In our previous studies we were successful in applying microwaves to achieve rapid and efficient polyester (polyethyleneterephthalate) and polyamide (polycaprolactam) derivatization and depolymerization.^{11–13} With an appropriate choice of reagents that

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absorb microwaves, a rapid heating throughout the entire reactor volume can be achieved. This generally has the effect of speeding up reactions compared to reactions using conventional heating. The cause for this effect is still not fully understood, but it is most commonly ascribed to micro-local overheating due to radiation inhomogeneities or to the effect of preferential rotational excitation in the system.¹⁴ In particular, microwaves have been found to give good results in reactions that require high temperatures and pressures; however, effects such as increased selectivities have also been reported. The only application of microwaves to wood degradation is a recent description of microwave heated wood pyrolysis.¹⁵

In this study, we examined the potential of using microwaves as the source of thermal energy in liquefaction of Central-European hardwoods, using glycols and dibasic organic acids.

EXPERIMENTAL

Wood used in the experiments was debarked, untreated, room temperature dried sawdust (0.1–1.0 mm particle size) of poplar (*Populus ssp.*), alder (*Alnus ssp.*), linden (*Tilia ssp.*), and beech (*Fagus sylvatica*). The wood residue left after commercial tannin extraction from chestnut wood (*Castanea sativa* Mill.) was also used. During the extraction process the material was milled, extracted with water, and dried. This material was in the form of room temperature dried fibrous material. The woods and wood waste used were selected on the basis of their abundance and low value in traditional wood uses, which makes them typical fuel materials. Apart from the chestnut residue, the wood types used can be characterized as woods inappropriate for outdoor use. Conifer wood was not considered in this study because of its substantially higher resin content. The majority of experiments were performed on poplar wood, which was taken as a standard.

The glycols used in the reactions were propylene glycol (PG), ethylene glycol (EG), and diethylene glycol (DEG). The acid anhydrides used were maleic acid anhydride (MA), phthalic acid anhydride (PA), and trimellitic acid anhydride (1,2,4-Benzenetricarboxylic acid anhydride, TMA). The glycols and acids chosen are typical raw materials in polyester and polyester polyol production. Ortho phosphoric acid was used as the acidic catalyst. Our previous studies indicated that phosphoric acid contributes to excellent microwave absorption¹³ and that it is therefore better suited to these conditions than sulfuric acid¹⁶ or hydrochloric acid⁹ most commonly used in high temperature experiments by other authors.

The liquefactions were carried out in a Milestone MEGA 1200 laboratory microwave oven equipped with a temperature sensor that can be inserted directly

into the sealed 100 mL PTFE reaction vessels. Samples were irradiated from 5 to 20 min with 300–700 W pulsed microwave radiation. A typical reaction mixture consisted of 2 g wood, 10 g glycol, 1 g acid anhydride, and 0.2 g mineral acid. All chemicals used were of analytical grade.

After irradiation, the samples were cooled to room temperature, diluted with acetone, and filtered to separate the liquid from the solid particles. The solids were washed with acetone and dried to constant weight in an oven at 90°C, after which they were weighed. The mass of wood remaining after the reaction was taken as our main indication of reaction efficiency. The acetone was removed from the liquid product in a rotatory evaporator. Samples of the remaining liquid wood were analyzed by size exclusion chromatography (SEC) after neutralization by addition of excess magnesium oxide and filtering.

SEC measurements were performed at 25°C on a Perkin–Elmer liquid chromatograph equipped with an LC-30 differential refractometer (DRI). Separations were carried out using a PLgel 5 μ m Mixed-E column (300 mm length and 7.5 mm ID) with a precolumn (Polymer Laboratories). The column was calibrated with polystyrene standards of low polydispersities. Tetrahydrofuran (THF, Fluka) was used as the eluent with a nominal flow rate of 1.0 mL min⁻¹. The samples were dissolved at room temperature in THF at a concentration of 1.0%. Fourier transform infrared (FTIR) spectra of selected samples were obtained using a Perkin-Elmer 1725 \times spectrometer by applying a thin film of the sample to a NaCl plate.

RESULTS AND DISCUSSION

The first series of experiments was designed to obtain information on the effect of (a) microwave irradiation time, (b) microwave irradiation power and (c) the amount of phosphoric acid used as a catalyst, on the liquefaction reaction. While these three conditions were varied, the reaction mixture composition was otherwise kept constant at 2 g poplar wood flour, 10 g propylene glycol, and 1 g maleic acid anhydride.

Heating the reaction mixture with radiation between 300 and 700 W power for 5–20 min allowed a rapid heating with sufficient final temperatures to achieve liquefaction. The temperature profiles of heating a reaction mixture with 0.2 g phosphoric acid at three different microwave irradiation powers is shown in Figure 1. The profiles show a rapid heating within the first 5 min of irradiation and a gradual leveling off at the upper temperatures. The leveling off temperatures are highly dependent on irradiation power. At 700 W microwave power the temperature approached the 280–300°C range—the upper operating limit for the PTFE reaction vessels used, and so higher power radiation was not applied. The product

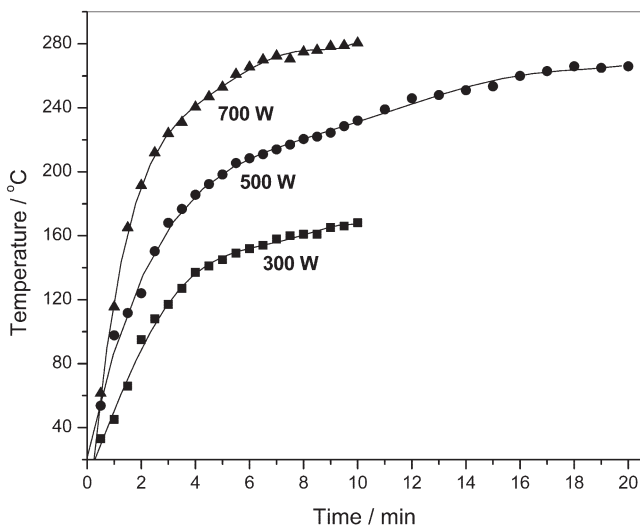


Figure 1 *In situ* temperature profiles in reaction vessel under microwave irradiation at different irradiation powers.

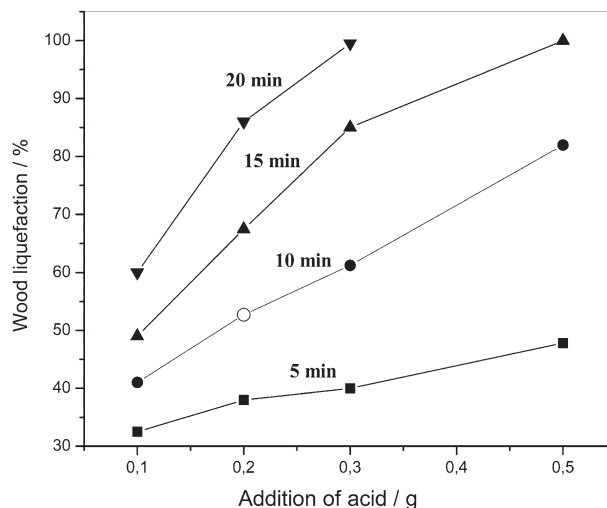


Figure 2 Wood liquefaction under microwave irradiation at constant radiation power of 500 W and different irradiation times and acid (catalyst) additions. The empty point on the 10 min curve was used as the reference point for later experiments.

of the reaction was a dark viscous liquid with varying amounts of solid wood remains. In reactions with low efficiencies, the wood particles retained a fibrous structure, whereas in more efficient reactions there was no solid remaining. The efficiency of liquefaction was determined gravimetrically by weighing the dry solid remaining after the reaction. A list of conditions used and resulting mass percent conversions are shown in Table I.

The results show that reaction yields improved with longer irradiation time, more powerful irradiation, and higher amounts of added phosphoric acid as the acidic catalyst. These results are all in line with expectations, as well as with the previously determined temperature profiles. According to the heating profiles, it was expected that the liquefaction would be very slow at the beginning of heating when the temperature of the reaction mixture is still low. The reactions should reach maximum rates only after the steady state maximum temperature is approached. There is a clear effect of irradiation power, which can

be associated with the higher maximum temperature or other effects of microwaves. Increasing additions of phosphoric acid also promoted liquefaction. The effect of the catalyst can in part be attributed to its chemical role as the protonating agent in the acid catalyzed esterification and transesterification mechanisms, as well as other reaction routes. In addition, the effect is in agreement, with phosphoric acid being a good absorbing agent for microwaves, which may further assist the heating process and the attained temperatures. The combined effect of irradiation time and acid addition at 500 W power is shown in Figure 2. The results show that complete wood liquefaction can be reached with a very modest acid addition in reaction times as short as 20 min. This compares favorably to our previous experiments using conventional external heating on reaction mixtures with the same components which gave conversions between 38 and 56%, with heating up to 11 h at 190°C.⁶ The results are also

TABLE I
Efficiency of Liquefaction of Poplar Wood Flour in % Conversion Under Different Conditions of Microwave Irradiation

Acid addition (g)	Efficiency of liquefaction (% conversion)					
	500W				300 W	700 W
	5 min	10 min	15 min	20 min	10 min	10 min
0	—	—	—	—	—	56
0.1	32	41	49	60	—	70
0.2	38	53	68	86	35	86
0.3	40	61	—	99	41	—
0.5	48	82	100	—	42	—
0.7	54	—	—	—	—	—

Reaction mixture: 2 g wood, 10 g PG, 1 g MA.

encouraging in comparison with liquefactions using phenol at 170 and 250°C that gave yields between 29–69% and 37–99%, respectively,¹⁰ as well as with a particularly successful liquefaction using polyethylene glycol and glycerol, with sulfuric acid as catalyst at 150°C, in which 95% of the wood was liquefied.¹⁷ It should also be noted that unlike in some other liquefactions⁵ no recondensation of the products was observed in our experiments, which could be attributed to the use of simple glycols.

In several cases, the liquid wood was analyzed by SEC. Two typical chromatograms are shown in Figure 3. Both chromatograms contain a strong peak at high elution times (low molar mass), representing the unreacted glycol, which was present in excess in the reaction mixture. The peaks at shorter elution times represent the oligomeric species of wood degradation products coupled with the diol and organic acid. The chromatograms differ in the extent of wood components present, since they were obtained from product reactions in which (a) 60 and (b) 100% wood was liquefied. The difference is visible in the relative amounts of oligomeric products versus glycol. A detailed identification of the various species represented in the chromatograms was not performed; however, the chromatograms are virtually the same as those obtained for liquid wood synthesized using conventional heating.⁶

Figure 4 shows an FTIR spectrum of a typical liquefaction product after excess glycol was evaporated. The spectrum was obtained from a sample in which 100% of the wood was liquefied (same sample that gave chromatogram b in Fig. 3). The spectrum is dominated by a sharp ester C=O stretching peak at 1728

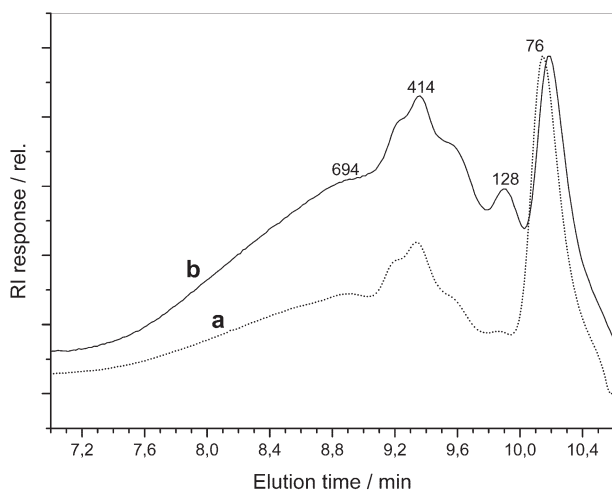


Figure 3 Size exclusion chromatographs of liquefaction products (reaction mixture: 2 g poplar wood flour, 10 g PG, 1 g MA, 500 W, 20 min) using different amounts of phosphoric acid additions: (a) 0.1 g, 60% wood conversion and (b) 0.3 g, 99.5% wood conversion. Relative molar masses are indicated on chromatogram b.

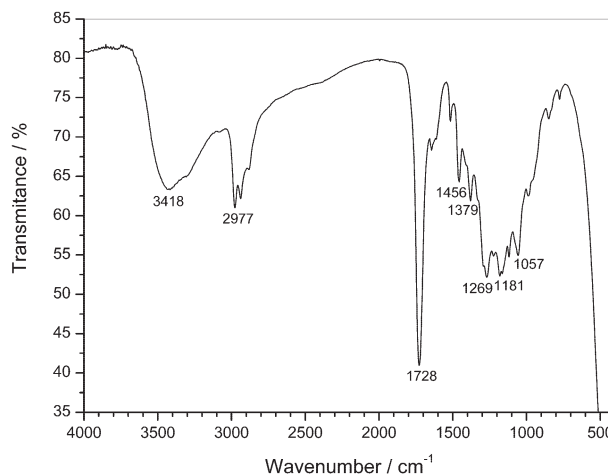


Figure 4 FTIR spectrum of liquid wood from an experiment in which wood was quantitatively liquefied (same sample as shown in chromatograph b, Fig. 3).

cm^{-1} , as well as a CO—O—R stretch at 1269 cm^{-1} , and an ether asymmetric stretch at 1057 cm^{-1} , which could be attributed to cellulose linkages. The spectrum is in agreement with a maleate ester, which could have been formed with either the glycol or wood components. In a slightly different liquefaction setup without anhydrides, Kobayashi et al.⁵ reported a specific peak at 1720 cm^{-1} from liquefied cellulose as indicative of levulinic acid and they also found peaks due to aromatic structures in lignin at 1500 and 1600 cm^{-1} . The latter peaks cannot be assigned in our spectra. A virtually identical spectrum was obtained for a product from a 60% wood liquefaction.

An interesting difference was, however, observed between the shown spectra and those obtained from an identical system where liquefaction was achieved at 190°C with conventional external heating.⁶ In the later case, all product spectra showed a prominent peak at 1645 cm^{-1} attributable to the double bond conjugated to the ester group in maleates, whereas this peak was almost absent in products obtained with microwave heating. This difference indicates that the maleic acid double bond reacted under microwave heating conditions, thus yielding virtually saturated polyesters. This result could be important for the further use of the material. It can be concluded, however, that FTIR spectra and SEC chromatograms together show that the wood degradation products reacted with glycol or acid anhydride to yield low molar mass polyesters.

Because of its importance for further use of the obtained liquid wood, we determined the hydroxyl numbers in a number of liquid wood samples. These were found to lie in the range 500–600 mg KOH/g sample. In comparison to the values for the pure glycols (~1200), which were used in excess, the obtained values indicate that part of the glycol was consumed

by reacting with acid anhydrides and in limited glycol oligomerization.

On the basis of the above results, we selected irradiation with 500 W power for 10 min and an addition of 0.2 g phosphoric acid as the optimal conditions for further experiments in which we examined the behavior of various wood types, different organic acids, different glycols, as well as the effect of the amount of maleic acid anhydride added on the reaction yields.

Using the selected conditions, the liquefaction experiments were repeated with beech, linden, alder, and extracted chestnut wood. The conversion rates were 62, 57, 55, and 47%, respectively, and can be compared with the 53% previously obtained for poplar. The differences between different wood types are rather small but they reflect the known wood characteristics well: beech and linden are very soft woods with little resistance to outdoor conditions, while chestnut has good outdoor durability. In addition, the chestnut wood had higher cellulose content due to the prior tannin extraction.

The use of maleic anhydride was further studied by varying the amounts used to establish its effect on the conversion efficiency and the optimal addition. By using 0, 0.5, 1 (standard addition used), 1.5, and 2 g, liquefactions of 40, 45, 53, 54, and 53% (poplar wood) were achieved. These results indicate that MA contributes to the liquefaction efficiency, although the effect levels off at higher concentrations. This result is in agreement with the findings of Mosier et al., who showed that dilute maleic acid anhydride causes the hydrolysis of cellobiose and microcrystalline cellulose as efficiently as dilute sulfuric acid.^{18,19} The next step was to vary the type of anhydride used. Maleic anhydride was substituted by PA or TMA. PA is important in making the polyester compatible with styrene while TMA is used to improve chain rigidity and resin viscosity. Liquefaction of poplar wood using PA and TMA gave conversions of 42 and 50%, which is only slightly lower than that with MA (53%). While this result does not open new routes to improving yields, it does indicate that different anhydrides could be used to obtain various product properties.

The propylene glycol component was varied to include trimethylol propane (TMP) and neopentyl glycol (NPG), both of which are widely used in resin and coatings formulations. TMP contains three hydroxyl groups, and so it can contribute to the formation of three-dimensional structures. In terms of product properties, it contributes to water resistance and higher rigidity. NPG is a difunctional reagent that contributes to thermal stability and resistance to aqueous saponifying chemicals.²⁰ Liquefaction conversions were 47 and 95% for NPG and TMP, respectively. Compared to the 53% conversion with PG, the result for NPG is only slightly lower, indicating that the two reagents could be mixed to modify product properties.

Using TMP, however, substantially improved the liquefaction efficiency. The use of TMP was further explored by using TMP with no acid added and a 1:1 mixture of TMP and PG, which gave 49 and 61% conversion, respectively. The superior results obtained with TMP are most likely due to the three sterically unhindered primary hydroxy groups in TMP available for the reaction.

Finally, we performed several experiments in which we eliminated phosphoric acid from the reaction mixture. The absence of a strong acid was expected to reduce the liquefaction efficiency because of lower acidity of the mixture and a lower maximum temperature reached; however, for further use of the liquefaction products, it would eliminate the need for neutralization and subsequent filtering. To compensate for the less aggressive chemical conditions, we chose a slightly higher irradiation power. Using poplar wood under 600 W/12 min, 600 W/15 min, and 650 W/10 min microwave irradiation, we achieved 49, 51, and 47% conversion, respectively. Although the choice of conditions could be further optimized to suit the experimental setup, these results show that relatively high liquefaction rates can be achieved even without the use of mineral acids.

CONCLUSIONS

The performed experiments have shown that wood liquefaction can be efficiently carried out using microwave radiation as the sole heating source. This method allows a rapid heating of the reaction mixture to temperatures above 250°C, which contributes to the acceleration of the liquefaction process. For example, when using simple glycols and organic acid anhydrides with an addition of phosphoric acid as the catalyst, complete liquefaction was achieved in 20 min. Higher yields of wood liquefaction are achieved by higher radiation power, longer irradiation time, and higher concentrations of phosphoric acid. The obtained liquid wood had a complex composition of low molecular mass species, whose chemistry was not studied in detail. Variation of liquefaction reactants showed that this process can accommodate a wide variety of reagents (glycols and anhydrides) commonly used in resin and coatings formulations, without reducing efficiency. In principle, this leaves considerable freedom in designing the chemical structures of liquid wood components that may best suit their final use. In addition, the results of using different types of wood indicate that these liquefaction conditions apply to a number of hardwoods. We believe that the described method of microwave heating holds particular promise for use in fast laboratory development experiments.

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