

# Wood Liquefaction Using Dibasic Organic Acids and Glycols<sup>†</sup>

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Received 26-05-2005

<sup>†</sup> Dedicated to the memory of Prof. Dr. Tatjana Malavašič

## Abstract

Liquefaction of Central European hardwoods was performed using a number of different glycols in combination with dibasic organic acids and a minor addition of ortho-phosphoric acid as a catalyst. The reaction carried out at 190 °C resulted in liquefaction of 15–56% of the original wood. The best effects were achieved using propylene glycol as the solvolytic reagent and maleic anhydride as the acidic reagent. The unsolubilized solid remains were investigated using scanning electron microscopy. The liquefaction product examined by size exclusion chromatography and infrared spectroscopy was composed of low molar mass oligomeric polyesters.

**Key words:** renewable resources, liquid wood, wood dissolution, waste wood, polyester

## Introduction

Wood is one of the most abundant and accessible renewable resources available to man. With a growing emphasis on sustainable development, new methods involving alternative wood uses are being explored. A particularly interesting application is to use wood as a feedstock from which to produce plastics that could replace a part of the conventional fossil oil based plastics.<sup>1,2,3</sup> The global use of plastics has experienced decades of consistent growth and is showing no signs of easing up, especially as developing countries are poised to increase their per capita consumption. The growth in plastics consumption is in principle limited by finite oil reserves, however plastic waste and its incompatibility with nature is often a more visible and in some cases dangerous problem. The solution to both problems can be sought by increasing the use of renewable resources employed for plastic production and by emphasizing properties of plastics such as biodegradation that would ensure that plastics remain in the natural carbon cycle.

Wood is a complex mixture of natural polymeric materials of which cellulose, hemicelluloses – both polysaccharides, and lignin, a natural polyphenolic material, represent the largest parts. In addition, wood contains resins and other components such as minerals which are present in smaller amounts and

differ substantially between species. In general, wood components are impractical to separate although the production of cellulose in the paper industry or tannins for the leather industry are examples of well established processes. Wood components can also be found as industrial waste after such extractions. A major limitation to the use of wood as a chemical feedstock is the structural and chemical variety of its components and the difficulties with their solubility in various solvents. Solubility is an important issue especially in the case of cellulose, which forms highly ordered fibrils in which the polar macromolecules attach strongly through hydrogen bonds. These tightly packed structures prevent the intrusion of solvents and reagents, thus making cellulose a particularly difficult material to transform chemically.

One approach to using wood components is to chemically derivatize the wood components and thus increase their solubility in selected solvents.<sup>4,5</sup> The solubilized macromolecules are then used in preparing useful polymeric materials. Another approach is to partially degrade the macromolecules to smaller soluble oligomers which are then used as feedstock for further uses. Very often both methods overlap slightly in that a limited degree of degradation takes place during the derivatization and/or solubilization process. Such is indeed the case in wood liquefaction in which wood is reacted with a phenolic or polyhydric reagent

under elevated temperatures and in the presence of catalysts to yield a liquid product mixture known as liquid wood. The most developed application of this approach is the liquefaction of wood with phenol, the product of which is ultimately used in the production of phenol-formaldehyde resins.<sup>6,7</sup> The high concentration of hydroxyl groups in wood components makes liquid wood a good potential starting feedstock for use as polyols in polyester and polyurethane production. Polyhydric alcohols such as ethylene glycol, polyethylene glycol (PEG) and glycerol were also investigated as a potential liquefaction reagent.<sup>8,9,10</sup> It was established that using PEG initial liquefaction was followed by re-condensation of liquefaction products which resulted in an increase of insoluble residues. Re-condensation was observed only when both cellulose and lignin were present in the reaction mixture, and it was successfully prevented by the addition of low molecular weight glycols, e.g. 10–30% glycerol.<sup>9</sup>

In this work, we explored the use of chestnut wood remains after tannin extraction and other typical Central European hardwoods in liquefaction using glycols and dibasic organic acids. The reagents were chosen in order to obtain liquid wood suitable for polyester and polyurethane production.<sup>11,12,13</sup>

## Experimental

The type of 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.*), and linden (*Tilia ssp.*). Industrial waste in the form of remains from chestnut wood (*Castanea sativa Mill.*) following tannin extraction was also used. During the tannin extraction process the wood was milled, the tannins were extracted using water, and the remaining material dried. This material was in the form of room temperature dried, fine, 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.

The glycols used in the reactions were propylene glycol (PG), ethylene glycol (EG), and diethylene glycol (DEG). The dibasic acids used were maleic acid anhydride (MA), phthalic acid anhydride (PA), and trimellitic acid anhydride (1,2,4-Benzenetricarboxylic acid anhydride, TMA). The glycols and acid anhydrides chosen are typical components used as raw materials in polyester and polyester polyol production. Orthophosphoric acid and sulphuric acid were used as the acidic catalyst. A typical reaction mixture contained 3 g of wood, 20 mL of glycol, 2 g of the selected acid anhydride, and 0.5 g of mineral acid. PG, MA, and PA were of technical grade, which were obtained from

Color d.d. a paint and resin producer and are used in their resins production, whereas all other chemicals were of analytical grade.

The reaction apparatus used was a 100 mL round bottom flask with an attached condenser, equipped with mechanical stirring and external heating. The reaction temperature was set at 190 °C and was maintained within a  $\pm 5$  °C range. The reaction time was 3 to 11 hours after the reaction temperature was reached. After the desired reaction time the excess glycol was distilled off, holding the reaction mixture at the same temperature for 30 to 45 min. The thick reaction mixture was then partly cooled, diluted with acetone, and filtered to remove the unsolubilized particles. These were then rinsed with acetone and distilled water and dried in an oven at 105 °C until a constant mass was reached. The acetone was removed from the solution on a rotatory evaporator at approx. 50 °C after which the remaining solution, i.e. liquid wood, was ready for further analyses. The extent of wood liquefaction (yield of liquid products) was used as the primary parameter for reaction evaluation. Liquefaction experiments in which phenol was used as a reagent were carried out at the boiling point of phenol, 182 °C. Reagent mixtures and reaction conditions used in experiments are given in Table 1.

In several cases, the wood particles remaining after the degradation were observed by scanning electron microscopy (SEM). Micrographs were obtained using a JEOL JSM-T220 microscope. The samples were prepared by deposition of a thin gold film, sputtered using a Balzers SCD 050 deposition system.

The soluble reaction products were analyzed by size exclusion chromatography (SEC) performed at 25 °C on a Perkin-Elmer liquid chromatograph equipped with an LC-30 differential refractometer. Separations were carried out using a PLgel 5  $\mu$ m Mixed-E column (300 mm length and 7.5 mm ID) with a pre-column (Polymer Laboratories, Ltd). 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<sup>-1</sup>. The samples were dissolved at room temperature in THF to achieve a concentration of 1.0%. Fourier transform infrared (FTIR) spectra of selected samples were obtained using a Perkin-Elmer 1725 X spectrometer by applying a thin film of the sample to a NaCl plate.

## Results and Discussion

The main group of liquefaction experiments was focused on the use of the extracted chestnut wood residue in combination with a range of conditions and reagents. The reaction mixtures used and product yields are summarized in Table 1.

**Table 1.** Reagents and conditions employed in extracted chestnut wood liquefaction and reaction yields.

| Sample | Reagents                      |                 |               | Reaction conditions                |           |          |                  |
|--------|-------------------------------|-----------------|---------------|------------------------------------|-----------|----------|------------------|
|        | Wood (g)                      | Glycol (mL)     | Org. acid (g) | Min. acid (g)                      | Temp (°C) | Time (h) | Liquefaction (%) |
| 1      | 3                             | PG 20           | MA 2          | –                                  | 190       | 4        | 31.6             |
| 2      | 3                             | DEG 20          | MA 2          | –                                  | 190       | 3        | 15.6             |
| 3      | 3                             | DEG 20          | MA 2          | –                                  | 240       | 3        | 22.3             |
| 4      | 3                             | EG 20           | MA 2          | –                                  | 190       | 3        | 22.2             |
| 5      | 3                             | PG 20           | MA 2          | –                                  | 190       | 11       | 41.7             |
| 6      | 3                             | PG 20           | MA 6          | –                                  | 190       | 4        | 29.3             |
| 7      | 3                             | PG 20           | MA 2 TMA 2    | –                                  | 190       | 3        | 28.3             |
| 8      | 3 <sub>NaOH<sup>a</sup></sub> | PG 20           | MA 2          | –                                  | 190       | 3        | 40.0             |
| 9      | 3 <sub>NaOH<sup>a</sup></sub> | PG 20           | MA 2 PA 2     | –                                  | 190       | 3        | 22.3             |
| 10     | 3                             | PG 20           | MA2           | H <sub>3</sub> PO <sub>4</sub> 0.5 | 190       | 3        | 46.3             |
| 11     | 3                             | EG 20           | MA 2          | H <sub>3</sub> PO <sub>4</sub> 0.5 | 190       | 3        | 46.3             |
| 12     | 3                             | EG 20           | MA 2          | H <sub>2</sub> SO <sub>4</sub> 0.5 | 190       | 3        | 22.7             |
| 13     | 3                             | PG 20           | TMA 2         | H <sub>3</sub> PO <sub>4</sub> 0.5 | 190       | 7        | 41.0             |
| 14     | 3                             | PG 20           | PA 2          | H <sub>3</sub> PO <sub>4</sub> 0.5 | 190       | 7        | 43.0             |
| 15     | 3 <sub>NaOH<sup>a</sup></sub> | PG 20           | MA 2          | H <sub>3</sub> PO <sub>4</sub> 0.5 | 190       | 7        | 43.3             |
| 16     | 3                             | PG 20           | MA 2          | H <sub>3</sub> PO <sub>4</sub> 0.5 | 190       | 7        | 55.7             |
| 17     | 3                             | Phenol 12       | –             | H <sub>3</sub> PO <sub>4</sub> 0.5 | 182       | 4        | 38.0             |
| 18     | 3                             | Phenol 10 PG 10 | MA 2          | H <sub>3</sub> PO <sub>4</sub> 0.5 | 182       | 4        | 56.3             |

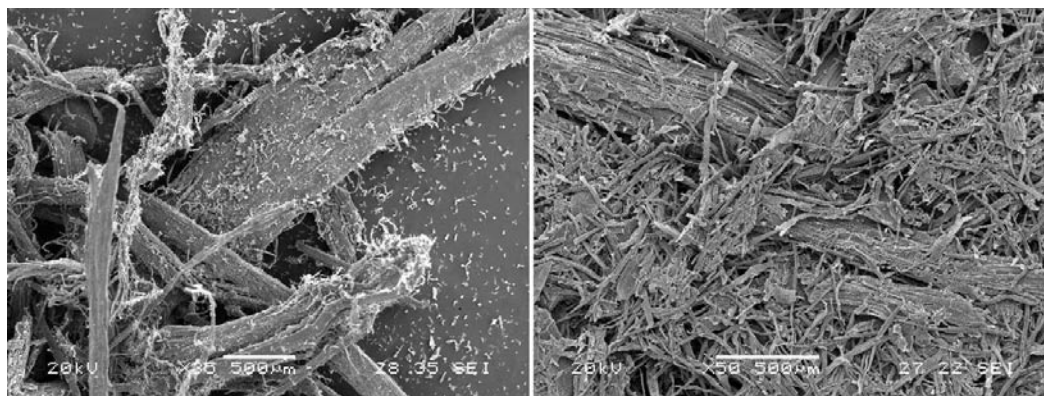
<sup>a</sup> Chestnut wood extract soaked in aqueous NaOH solution for 24 hours prior to liquefaction.

Liquefaction rates achieved were between 15 and 56% of the original wood, indicating that the selected reagents did promote liquefaction and that the conditions were not excessively harsh. These results have lead to a number of important conclusions. The yield showed a positive correlation to reaction temperature. For example, raising the reaction temperature from 190 to 240 °C increased the yield from 15.6 to 22.3%. In general, the reaction proceeded very poorly with temperatures below 160 °C. The choice of glycol had a small effect on the yield, with PG giving a slightly better result than EG and DEG. This suggests that a mixture of glycols can be used to obtain the desired product properties. As expected, the introduction of a mineral acid improved the yields due to acid catalysis of etherification and esterification reactions. Under the mild conditions we employed, orthophosphoric acid was more efficient than sulfuric acid, which is in agreement with our previous experience using orthophosphoric acid in solvolysis reactions of polyesters.<sup>14</sup> Lengthening of the reaction time improved the yield, however, relatively little improvement was achieved when extending the reaction time beyond 7 hours. In a number of experiments we used extracted wood that was soaked overnight in a 10% aqueous solution of NaOH (Samples 8, 9, and 15). By this we hoped to swell and thus loosen the otherwise tight cellulose structure, thereby making it more accessible to the liquefaction reagents. The yields with this pre-treated wood were only marginally better than without any treatment. We attribute this to the fact that the pretreatment dissolved a portion of the hemicellulose, which left a higher content of cellulose

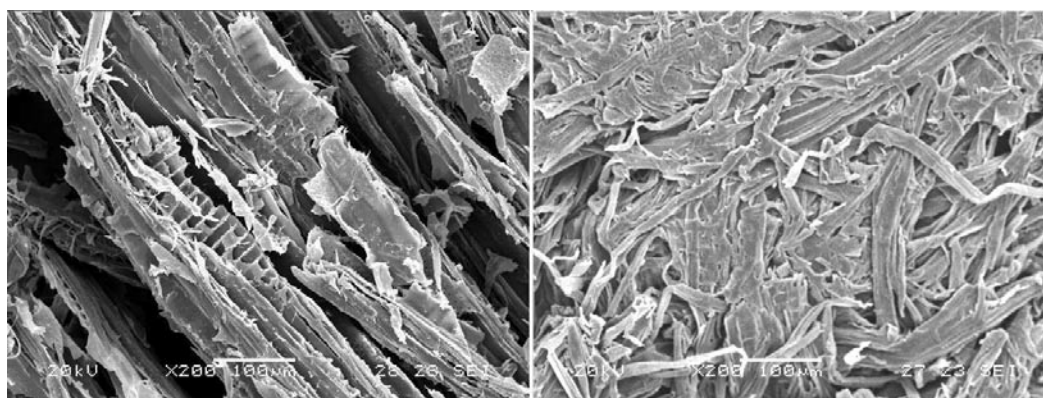
that was consequently more difficult to liquify. The amount of added reagents was also studied. Glycols were used in excess to allow proper stirring of the reaction mixture, so that their effect was considered to be maximal. The addition of MA, however, was varied and caused an increase in reaction yield up to an addition of 2 g. Higher additions did not cause any appreciable increase in yield. Both PA as well as TMA appeared to be less efficient than MA, although the results show that both anhydrides could be used when further use would require the presence of aromatic moieties (PA) or when a more viscous branched structure made possible by the trifunctional TMA would be needed.

Based on the above results we concluded the reagent composition and conditions of Sample 16 in Table 1 to be optimal for an acceptable liquefaction yield. For verification purposes we performed the same liquefaction on a 20 times larger scale (60 g of wood) and obtained a virtually identical yield (56.3%). The same method was further applied to linden, alder, and poplar sawdust which gave yields of 55.7, 58.7, and 63.7%, respectively. This confirmed our initial concern over chestnut as a relatively resistant wood and supported our presumption that the extraction process removed tannin and thereby most likely raised the relative content of cellulose in the extracted wood.

Two liquefactions involving phenol as the liquefaction reagent (Samples 17 and 18) were carried out in order to relate our current results to the liquefaction in phenol experiments which have been reported in the literature. The obtained yields indicate the PG/MA combination to be of comparable efficiency



**Figure 1.** Micrograph of chestnut wood prior to the liquefaction reaction (left) and the chestnut wood residue after the reaction (right, Sample 16 in Table 1).



**Figure 2.** Micrograph of poplar wood prior to the liquefaction reaction (left) and the poplar wood residue after the reaction (right).

to using phenol alone and that an addition of phenol to PG and MA can raise the reaction yield. The use of phenol was not studied further.

In several cases we analyzed the wood particles that remained after liquefaction using SEM and compared them to the starting material in order to gain more information about the process. Figure 1 shows the SEM micrographs of extracted chestnut wood prior to the reaction and of the residue after the reaction.

The micrographs reveal a substantial difference in wood particle composition and size. The starting material (left) consisted of a mix of small particles, torn fibers, and intact wood parts, while the remains left after the liquefaction (right) show a homogeneous entanglement of larger fibers of uniform size. This confirmed our expectations that during the reaction the smallest particles and damaged (e.g. broken) fibers would undergo dissolution first, leaving behind only the most resistant undamaged cellulose fibers.

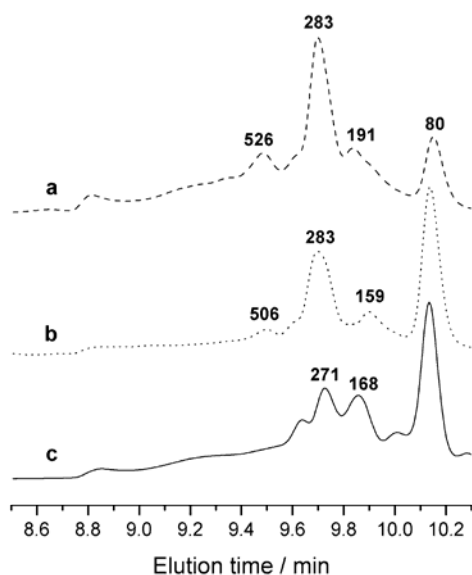
SEM micrographs can also help illustrate the observed difference in the liquefaction efficiency between the more resistant chestnut wood and the soft poplar wood. Figure 2 shows the micrographs of

the untreated poplar wood and the residue after the reaction. The starting material clearly shows damaged wood structures, which are fully absent in the residue after the reaction and have been replaced by large fibers of uniform size. This indicates that broken fibers and small particles of the wood cells were completely dissolved during the reaction and that only the most resistant pulp fibres remain in the residue. As indicated by the drastic change in the material, the degree of liquefaction in poplar was substantially higher than with extracted chestnut wood.

The liquefaction products were analyzed by SEC to evaluate their composition and molar mass distributions. Analysis of the product mixture showed that a complex mixture of degradation products was formed, with a difficult-to-resolve molar mass distribution centered in the oligomeric range. Typical chromatograms obtained from chestnut wood liquefaction are shown in Figure 3. They reveal a relatively large peak at longer elution times (low molar mass), corresponding to the excess propylene glycol remaining after incomplete distillation. The multi-peak cluster with a tail at shorter elution times (higher molar mass) represents the liquefied

wood products. These are oligomeric in nature with better resolved lower oligomers with separate shoulders and less resolved higher oligomers which are also less concentrated. Samples used to obtain chromatograms a) and b) in Figure 3 differ in terms of liquefaction time: 11 and 4 hours, respectively (Samples 5 and 1 in Table 1). The higher liquefaction conversion in chromatogram b) can be seen by the higher content of oligomeric species relative to the glycol peak. Other wood types gave a slightly different distribution of liquefaction products, as can be seen from chromatogram c) obtained from poplar wood using orthophosphoric acid.

The species represented by the peaks in the chromatograms were not identified as that was not the focus of this investigation. However, reactions of cellulose and glucose with diethylene glycol yielded products with relative masses 389, 241, and 170 for the former, and 418 and 203 for the latter. These product molar masses are very close to those observed in our liquid wood samples indicating that the degradation proceeds to the level of derivatized mono-, di-, and oligosaccharides. In the case of wood, the situation is immensely more complex due to the presence of hemicelluloses, lignin, and other components, so simple conclusions and identification cannot be claimed.

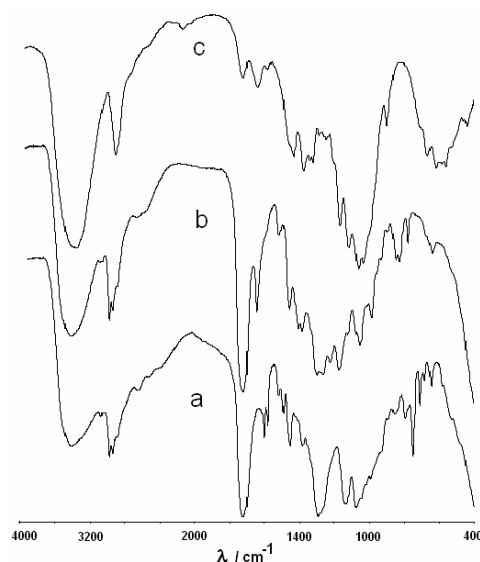


**Figure 3.** Size exclusion chromatograms of liquefaction products using propylene glycol and maleic acid anhydride at 190 °C for a) 11 and b) 4 hours. Chromatogram c) represents liquid wood obtained from poplar wood using orthophosphoric acid as a catalyst. Relative molar masses are indicated above the respective peaks.

The liquefaction products were also analyzed by FTIR. Figure 4 shows the spectra of liquefaction products obtained with MA and PA (Samples 1 and 14 in Table 1, respectively). Both spectra are dominated by a strong absorption at 1723  $\text{cm}^{-1}$  due to ester C=O

stretching, as well as a CO-O-R stretching peak at approx. 1270  $\text{cm}^{-1}$ . Peaks indicative of double bonds conjugated to the ester group can be found at 1645  $\text{cm}^{-1}$  in maleates or at 1600 and 1581 as are characteristic of conjugated aromatic double bonds in phthalate esters. Spectrum c) in Figure 4 was obtained from cellulose to help identify remaining cellulose moieties. A comparison of the spectra shows that both samples of liquid wood show a peak at approximately 1060  $\text{cm}^{-1}$ , which dominates the spectrum of cellulose, as well as a number of other peaks found in cellulose (1431, 1372, 1166  $\text{cm}^{-1}$ ). These peaks indicate the presence of cellulose degradation products in liquid wood, as could be expected.

Combining the evidence gathered by SEC and FTIR, it can be concluded that the liquefaction process yielded low molecular mass oligomeric polyesters with integrated degradation products from the natural polymers found in wood. The efficiency of our liquefactions using glycols and dibasic organic acids with or without an acid catalyst was comparable to those reported for other systems. For example, liquefactions in phenol using a range of alkali and salt catalysts at 170 and 250 °C gave conversions between 29–69% and 37–99%, respectively.<sup>8</sup> The use of PEG and glycol with sulfuric acid as catalyst at 150 °C was more efficient with liquefactions of approx. 95% wood.<sup>9</sup> Our liquefaction system showed no tendency toward re-condensation of liquefaction products which is in agreement with indications that low molecular weight glycols prevent the undesired reaction.<sup>10</sup> In addition, the products of our work were liquids as opposed to solid products obtained from phenol liquefactions<sup>8</sup> which is important for further uses of the material.



**Figure 4.** FTIR spectra of liquid wood synthesized using a) phthalic anhydride and b) maleic anhydride. Spectrum c) was recorded on pure cellulose.

## Conclusions

The presented work shows that efficient hardwood liquefaction with yields beyond 50% can be achieved using organic dibasic acids in combination with glycols and orthophosphoric acid as a catalyst. The best results were achieved by using maleic acid anhydride, propylene glycol, and orthophosphoric acid at 190 °C for 7 hours. Depending on the further uses of the liquefaction products it is possible to include other glycols and organic acids to give the desired properties. Electron microscopy revealed that the wood remains after liquefaction mainly contained uniform fibers, thus indicating that cellulose is the wood portion most resistant to liquefaction under these conditions. The liquefaction products were a complex mixture of low molar mass oligomeric polyester species. Based on the functional groups of native wood components and the esters created due to inclusion of glycols and organic acids during the liquefaction process, the products should be a useful feedstock for further synthesis into various polymers such as polyesters and polyurethanes.

## Dedication

The authors wish to dedicate this contribution to the memory of Prof. Tatjana Malavašič in appreciation for her professional contribution to the development of polymer science in Slovenia, as well as her personal influence on generations of students and coworkers.

## Acknowledgements

The authors wish to gratefully acknowledge the support for the presented work received from the Ministry of Higher Education, Science, and Technology

of the Republic of Slovenia within Program 074145, the technical support of Color d.d., Medvode, and the dedicated work contributed by Mr. Matej Fale.

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## Povzetek

Utekočinjanje lesa Srednjeevropskih listavcev smo opravili z vrsto glikolov v kombinaciji z dibaznimi organskimi kisljinami in manjšim dodatkom ortofosforne kisline kot katalizatorja. Reakcija, ki je potekala pri 190 °C je povzročila utekočinjenje 15–56% začetnega lesa. Najboljši izkoristek je bil dosežen z uporabo propilen glikola kot solvolitskega reagenta ter maleinskega anhidrida kot kislinskega reagenta. Neutekočinjene ostanke lesa po reakciji smo proučili z elektronsko mikroskopijo. Analiza utekočenjenega lesa z gelsko prepustnostno kromatografijo in infrardečo spektroskopijo je pokazala, da so produkti reakcije nizkomolekularni oligomerni poliestri.