A process for preparing phenolic formaldehyde resole resins and adhesive compositions in which portions of the phenol normally contained in said resins are replaced by a phenol/neutral fractions extract obtained from fractionating fast-pyrolysis oils.

18 Claims, 4 Drawing Sheets
WHOLE OIL

- EtOAc/FILTER
  - Char: 3%

EtOAc Ins: 23%

EtOAc Sol: 87%

- Water
  - Water-soluble 39%

- NaHCO₃ acids: 7%

- Evaporate P/N: 31%

FIG. 1
FIG. 2

COMPARISON WOOD FAILURE
CASCOPHEN AND RESOLES WITH P/N

SHR E S S S T R E N G T H, PSI
1000
800
600
400
200
0
Cascophen  P/N + P  P/N + P
dry  cold soak

FIG. 3

COMPARISON WOOD FAILURE
CASCOPHEN AND RESOLES WITH P/N

WO O D F A I L U R E, %
60
50
40
30
20
10
0
Cascophen  P/N + P  P/N + P
dry  cold soak
FIG. 4

TEMP., °C

2nd (2.0 g) NaOH addn.

TIME, hrs.
FIG. 5

TEMP., °C

TIME, hrs.

2nd ADDITION OF PARAFORMALDEHYDE AND PHENOL
PROCESS FOR PREPARING PHENOLIC FORMALDEHYDE RESOLE RESIN PRODUCTS DERIVED FROM FRACTIONATED FAST-PYROLYSIS OILS

CONTRACTUAL ORIGIN OF THE INVENTION

The U.S. Government has rights in this invention under Contract No. DE-AC02-83CH10093 between the U.S. Department of Energy and the Solar Energy Research Institute, a Division of the Midwest Research Institute.

The present invention is a continuation-in-part application of original U.S. application Ser. No. 07/169,506, filed Mar. 17, 1988, now U.S. Pat. No. 4,942,269, issued July 17, 1990. The original application is incorporated herein by reference in its entirety.

BACKGROUND OF THE INVENTION

1. Field of the Invention

The invention relates to the production of phenolic type resole resins from biomass materials and, more particularly, to the treatment of fast-pyrolysis oils derived from lignocellulosic materials to make phenolic type resole resins. Specifically, the present invention relates to taking phenol/neutral fractions and rendering them suitable for the production of phenolic type resole resins, subsequent to obtaining said fractions from fast-pyrolysis oils derived from lignocellulosic materials.

2. Description of the Prior Art

Adhesive resins such as resoles are utilized in a wide variety of applications, inclusive of which is the bonding of wood layers to manufacture plywood, and adhesive resins such as novolaks are used in the formation of molded pieces and articles, and the like. However, certain disadvantages are attendant to existing techniques for manufacturing these different types of phenolic resins.

For example, phenol has been traditionally derived from petroleum-based products; however, the production of petroleum-based phenol is quite expensive, and efforts in the industry in recent years have been to at least partially substitute the phenol in such resins with inexpensive phenols derived from wood-based products or extracts. More specifically, phenols derived from bark, wood chips and the like have been looked upon as a potential substitute for petroleum-based phenol in such resins.

The pyrolysis of biomass, and in particular lignocellulosic materials, is known to produce a complex mixture of phenolic compounds. In nature, lignin acts as an adhesive to bind the cellulose fibers together. Therefore, lignin and lignin-derived material from wood would appear to be a natural starting point for the development of biomass-based adhesive resins. Sources for such phenolic materials include black liquor from kraft pulping and other pulping processes, where the lignin is present in a stream which is commonly burned to recover process heat and chemicals.

Unfortunately, these lignins are generally not very reactive after recovery for a variety of reasons, such as high molecular weight, chemical modification during recovery due to condensation reactions and the like, and lack of reproducibility of properties. Various types of pyrolysis processes have also been utilized, frequently yielding similar kinds of results; however, fast-pyrolysis, which proceeds at temperatures between about 450° C. to about 600° C. and has short vapor residence times in the order of seconds has not been used.

Fast-pyrolysis of biomass features the depolymerization of cellulose, lignin, and hemicellulosic polymers which produces an oil having a relatively low molecular weight and which has considerable chemical activity under proper conditions. Crude pyrolysis oil apparently undergoes a limited amount of repolymerization due to condensation. However, the thermal stability of fast-pyrolysis oils at room temperature is qualitatively quite good imparting a good shelf life for the oils, although at 100° C. the crude oils solidify overnight. Solidified pyrolysis oils are characterized by their low strength and brittleness. The potential of pyrolysis products for use in adhesive resins is not a new concept, as indicated above, but the efficient and cost-effective reduction of this to practice has been an elusive goal over many years.

The general approach of producing phenols from biomass has previously been to purify the phenolic fractions present in the pyrolysis oils by the use of solvents to partition the constituents by differences in solubility and reactivity. Different variations of solvents, reagents, and sequence of extractions have been developed in the past, and this has resulted in different partitioning coefficients for a couple of hundreds of chemical compounds known to be in pyrolysis oils, and therefore produced extracts having varying relative compositions. Another significant difference between various research efforts pertaining to this area in the past has been the type of pyrolysis process used to produce the oils used as feed in the extraction process. These include updraft gasification, entrained fast-pyrolysis, and fluidized bed fast-pyrolysis, all at atmospheric pressures, as well as slow, high pressure liquefaction processes. In addition, both hardwoods and softwoods have been used as feedstock in the past for the oil forming processes. These differences in extraction and pyrolysis processes, coupled with the differences in feedstock, yield different materials as products. Thus, the usefulness of a particular extract as an adhesive component is quite different, one from the other.

U.S. Pat. Nos. 4,209,647 and 4,223,465 disclose methods for recovering phenolic fractions from oil obtained from pyrolysis of lignocellulosic materials and the subsequent use of that fraction in making of phenol-formaldehyde resins. However, these processes use pyrolysis oils which are usually formed at ill-defined temperatures and which have undergone phase separation cracking and some condensation, and suffer from very low yields.

A number of other patents including U.S. Pat. Nos. 2,172,415, No. 2,203,217, No. 3,069,354, No. 3,309,356 and No. 4,508,886 as well as Japanese Patent No. 38-16895 all disclose a variety of processes for recovering phenolic fractions from oils derived from biomass materials and soil resources. These processes vary in the particular procedures and techniques utilized to ultimately separate the phenolic fractions as well as the procedures utilized to derive the oil from the biomass or other feed material. However, they all have a common thread linking them in that the ultimate end product is a phenolic fraction, which is desired to be as pure as possible. This phenolic fraction is then utilized to produce phenol-formaldehyde resins. The phenol substitutes usually were slower than phenol derived from petroleum-based products. The complex procedures
disclosed in these references to produce relatively pure phenolic fractions are not particularly economical. Thus, there is still a need for a process designed to produce pyrolysis oils from lignocellulosic materials and then extract a phenolic composition from such oils which is capable of functioning as efficiently as petroleum-based phenols in the formation of phenol-formaldehyde resins and which is less expensive to produce.

SUMMARY OF THE INVENTION

Accordingly, it is one object of the present invention to provide phenolic type resole resins, in which the phenol content is in part replaced by a phenol/neutral fractions (P/N) from fast pyrolysis oils derived from lignocellulosic materials.

Another object of the present invention is to provide inexpensive adhesive compositions comprising phenolic type resole resins, in which the phenol content is in part replaced by a phenol/neutral fractions (P/N) from fast pyrolysis oils derived from lignocellulosic materials.

To achieve the foregoing and other objects and in accordance with the purpose of the present invention, as embodied and broadly described herein, a process is disclosed for fractionating fast-pyrolysis oils to produce phenol-containing compositions suitable for manufacturing phenol-formaldehyde resins. The process includes admixing the oils obtained from the fast-pyrolysis process with an organic solvent having a solubility parameter of about 8.4–9.1 [cal/cm³]¹/² with polar components in the 1.8–3.0 range and hydrogen bonding components in about the 2 to 4.5 range to extract the phenol and neutral fractions from the oils. The organic solvent-soluble fraction containing the phenol and neutral fractions is separated from the mixture and admixed with water to extract water-soluble materials therefrom. The organic solvent-soluble fraction is then separated from the water fraction and admixed with an aqueous alkali metal bicarbonate solution to extract strong organic acids and highly polar compounds from the solvent fraction. The residual organic solvent-soluble fraction is separated, and the organic solvent is removed therefrom to produce the phenol and neutral fractions (P/N).

In general, preparation of the phenolic type of resole resins, which are phenol-formaldehyde resins formed under alkaline conditions, is accomplished by dissolving the P/N fractions and phenol with a strong alkaline material, adding formaldehyde and heat under constant stirring. After a moderate time of reaction, a second addition of a strong alkaline material such as sodium hydroxide may be added to obtain a resole resin.

In preparing the adhesive composition from the phenolic type of resole resins prepared according to the invention, up to about 75% of the phenol normally used in a phenol-formaldehyde resin is replaced with the P/N fraction, and the phenolic type of resole resins are used to glue plywood, etc. Resoles containing the phenol/neutral fractions of the invention show improved shear strength and improved wood failure percents when the resins are used as adhesives.

BRIEF DESCRIPTION OF THE DRAWINGS

The accompanying drawings which are incorporated in and form a part of the specification illustrate preferred embodiments of the present invention, and together with the description, serve to explain the principals of the invention. In the drawings:

FIG. 1 is a flow diagram illustrating the process of the present invention;
FIG. 2 is a graph illustrating shear stress strength of resin adhesives produced using the phenol and P/N end-products of the present invention compared to a commercial product, and
FIG. 3 is a graph illustrating wood failure test results of resole adhesive resins produced using the phenol and P/N end products of the process of the present invention compared to a commercial adhesive product.
FIG. 4 is a graph showing the time/temperature relationship for the preparation of resole resins according to one aspect of the invention.
FIG. 5 is a graph showing the time/temperature relationship for the preparation of resole resins according to another aspect of the invention.

DETAILED DESCRIPTION OF THE PREFERRED EMBODIMENT

During the course of studying the problem of producing inexpensive but effective phenolic compositions from biomass, it was discovered that certain polar organic solvent having at least a moderate solubility parameter, moderate degree of polarity, and good hydrogen bonding capabilities were capable of extracting both phenol and neutral fractions from fast-pyrolysis oils. Moreover, it was discovered that this extraction technique was equally effective for fast-pyrolysis oils of differing starting materials. Thus, it was discovered that the present invention may be utilized with pyrolysis oils derived from redwood, pine sawdust, bark, grasses, softwoods as well as certain hardwoods with very little differences in the final results. Apparently, the fast-pyrolysis process preserves the delicate products in monomeric and oligomeric states. A key factor in the process of the present invention is that the oils derived from the lignocellulosic materials must be done so utilizing a fast-pyrolysis. Fast-pyrolysis is generally known in the art, and such a technique has been specifically disclosed in an article entitled, "Production of Primary Pyrolysis Oils in a Vortex Reaction", American Chemical Society Division of Fuel Chemistry Preprints, Vol. 32, No. 2, pp. 21–28 (1987). Thus, details of such fast-pyrolysis techniques need not be specifically repeated and disclosed herein, and the contents of this Article are therefore specifically incorporated herein by reference. Oils from other fast-pyrolysis concepts are also good feedstocks. Such concepts are referenced in "Fast-Pyrolysis of Pretreated Wood and Cellulose", Ibidem, pp. 29–35 (1987), and "Preliminary Data for Scale up of a Biomass Vacuum Pyrolysis Reactor", Ibidem, pp. 12–20 (1987); "The Role of Temperature in the Fast-Pyrolysis of Cellulose and Wood", Industrial Engineering Chemistry Research", Vol. 27, pp. 8–15 (1988), and "Oil From Biomass by Entrained flow Pyrolysis", Biotechnology and Bioengineering Symposium, No. 14, pp. 15–20 (1984).

In general, the biomass solids in such fast-pyrolysis of biomass solids entrain the feedstock particulates tangentially at high velocities into a vortex reactor tube which has an internal surface design that guides the centrifuged solids into a tight helical pathway on the reactor wall. This results in a very high heat transfer to the wood or other feedstock particles which allows mild cleavage of the polymeric components of the feedstock. Consequently, high yields (greater than 55%) of dry woods and bark oils are generally obtained. If the feedstock is not fully pyrolyzed, the solids enter a recycle
loop located at the end of the vortex reactor. After attrition to a powder, char particles elute with the vapor stream and are isolated in a char cyclone. Alternative methods to produce primary pyrolysis oils thought to be similar to fast-pyrolysis include fast-pyrolysis in fluidized beds and in entrained flow reactors.

Utilizing the process of the present invention, the pyrolysis oils are fractionated in a unique way which produces a combined phenolics and neutral fraction of high phenolic hydroxyl and aldehyde content. In general, a polar organic solvent is added to the oils to separate the phenol and neutral fractions from said oils. The organic solvent-soluble fraction is then mixed with water to extract water-soluble materials, and then further washed with an aqueous alkali metal bicarbonate solution to extract strong organic acids and highly polar compounds. The residual organic solvent-soluble fraction containing the phenol and neutral fractions is then isolated, and the organic solvent is removed, preferably by evaporation, to produce a phenol-containing composition having the phenol and neutral fractions of the organic solvent removed. The yield of the phenolics and neutral fraction in the extract is about 30% of the fast-pyrolysis oil derived from sawdust and about 50% of the oil derived from bark.

In prior art phenol-producing processes, the processes ended only after the phenolic-containing compositions were generally reduced to purified phenolics only, with the neutral fractions also being removed. By neutral fractions, it is meant those compounds which are not solubilized by a strong base such as sodium hydroxide, and have molecular weights of approximately 100–800. Such neutral fractions include carboxylic compounds, furfural-type compounds and the like. It was apparently previously believed that such neutral fractions must also be extracted in order to provide a phenol composition which may be utilized as a substitute for petroleum-based phenols in the production of phenol-formaldehyde adhesive resins. It has been discovered, however, that by utilizing the process of the present invention, the resultant composition containing both phenol and neutral fractions function just as well as and in some aspects better than a relatively pure phenol composition in the production of phenol-formaldehyde resins because, since the compositions have aldehyde groups, much less formaldehyde is needed to make these formulations. Reduced formaldehyde levels lead to minimization of potential environmental problems. In addition, the economics are such that, it is substantially less expensive to manufacture the combined phenol and neutral fraction composition. Moreover, by utilizing the entire fraction which includes phenolic compounds and neutral compounds as feedstocks for resins, it was found that this prevented the pyrolysis-derived reactive phenolics from undergoing air oxidation under alkaline conditions, which is what prevails when one isolates and purifies the phenolics fraction alone. This latter air oxidation which can be a problem is a type of condition that prevails in many prior art techniques and is accomplished by extractions with aqueous sodium hydroxide solutions, and accompanied by the formation of insoluble tars and reduced yields of phenolics.

Investigations of the fractionation scheme of the present invention as generally described above utilizing pine fast-pyrolysis oils were carried out employing a number of different solvents to determine the preferred and optimum solvents and the requirements thereof. In general, the whole oil was first dissolved in the organic solvent preferably in an oil:solvent ratio of 0.5:1 to 1:3 by weight. The oil was initially filtered to separate char which is carried over from the pyrolysis reactor operations. Upon standing, the solvent/oil mixture then separates into two phases, the solvent-soluble phase and the solvent-insoluble phase.

One requirement for the organic solvent is that the solvent and water exhibit low mutual solubility. Preferably, acceptable solvents include those with solubilites that are not more than about 10 grams of solvent in 100 grams of water and about 5 grams of water in 100 grams solvent, in terms of mutual solubility. Thus, this solvent requirement eliminates all low-molecular-weight alcohols (methanol, ethanol, propanol) that are infinitely soluble in water, methylylketone, the carboxylic acids (formic, acetic and propionic) which are infinitely soluble in water, and methyl formate. The classes of solvents that would be acceptable only from a pure mutual solubility point of view include hydrocarbons (aliphatic, aromatic), higher alcohols (greater than 6 carbon atoms), higher ketones (greater than 5 carbon atoms), esters (greater than 2 carbon atoms), ethers, polychlorinated hydrocarbons, and higher nitriles (greater than 4 carbon atoms).

Another requirement for the organic solvent which further limits potential candidates is that the solvent must have a low boiling point or a low-boiling point azeotrope. The preferred boiling point is around 100° C., although this is somewhat relative. Yet another requirement for the organic solvent is that the solvent have some degree of polarity, preferably high polarity, as well as high hydrogen bonding capability in addition to a moderate-to-good solubility parameter. The solubility parameter is defined as a measure of all the intermolecular forces present in the solvent. The overall solubility parameter is composed of components due to dispersive forces, polar forces (caused by a high dipole moment in the molecule), and hydrogen bonding capability. These three-component Hansen parameters are determined in accordance with an article commencing on page 141 of the "CRC Handbook of Solubility Parameters and Other Cohesion Parameters" by Allan F.M. Barton, 1983. Solubility parameters, measures in [cal/cm³]¹/², range from 5–7 for hydrocarbons and nonpolar solvents, to 14.5 for methanol and 23.4 for water high-polar substances. Thus, low boiling point ethers, such as diethyl ether, are excluded from being preferred solvents since they have very low solubility parameters (7.4) and very low polar components (1.4). Hydrocarbons are also excluded as preferred solvents because of their very low polar components and overall low solubility parameters.

It has been found that the preferred group of solvents for use in the present invention include acetate and propionate esters, methyl alkyl ketones and ethyl alkyl ketones. More specific preferred organic solvents are listed below in Table I; the most preferred being ethyl acetate due to its availability, relatively low solubility in water, and high oil solubility. The most preferred range for solubility parameters includes 8.4–9.1 with polar components in the 1.8–3.0 range and hydrogen bonding components in the 2.4–5 range. Additional acceptable solvents are the isomers of those listed in Table I. Mixtures of esters are also acceptable as are mixtures of the higher ketones. Ternary solvent systems also are possible, primarily mixtures of esters and high molecular weight ethers such as disopropylether to reduce the
boiling point. However, the most preferred solvents for use with the present invention are ethyl acetate, as indicated above, as well as butyl acetate and methylisobutylketone.

### TABLE I

<table>
<thead>
<tr>
<th>Property</th>
<th>Ethyl Acetate</th>
<th>Propyl Acetate</th>
<th>Butyl Acetate</th>
<th>i-Butyl Acetate</th>
<th>i-Amyl Acetate</th>
<th>i-Propyl Acetate</th>
<th>Ethyl Acetone</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mol. Wt.</td>
<td>88.1</td>
<td>102.1</td>
<td>116.2</td>
<td>100.2</td>
<td>114.2</td>
<td>86.14</td>
<td>86.14</td>
</tr>
<tr>
<td>Boiling Point, °C.</td>
<td>77.1</td>
<td>101.5</td>
<td>126.1</td>
<td>116.5</td>
<td>144</td>
<td>92</td>
<td>102.0</td>
</tr>
<tr>
<td>(at 70 mmHg)</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Density, 20°C.</td>
<td>0.90</td>
<td>0.89</td>
<td>0.88</td>
<td>0.80</td>
<td>0.88</td>
<td>0.81</td>
<td>0.81</td>
</tr>
<tr>
<td>Heat Vaporization, kcal/mole (20°C)</td>
<td>8.4</td>
<td>9.3</td>
<td>10.4</td>
<td>10.00</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Solubility, wt %</td>
<td>7.71</td>
<td>8.20</td>
<td>8.58</td>
<td>8.50</td>
<td>7.73</td>
<td>8.06</td>
<td></td>
</tr>
<tr>
<td>in water</td>
<td>8.08</td>
<td>2.3</td>
<td>0.43</td>
<td>1.7</td>
<td>~0</td>
<td>~2</td>
<td>2.4</td>
</tr>
<tr>
<td>Water in Azeotrope</td>
<td>2.94</td>
<td>3.9</td>
<td>1.86</td>
<td>1.9</td>
<td>~0</td>
<td>~2</td>
<td>2.6</td>
</tr>
<tr>
<td>Water Wt %</td>
<td>9.47</td>
<td>14</td>
<td>28.7</td>
<td>24.3</td>
<td>44.0</td>
<td>24</td>
<td></td>
</tr>
<tr>
<td>boiling point, °C.</td>
<td>70.38</td>
<td>82.2</td>
<td>90.2</td>
<td>87.9</td>
<td>94.7</td>
<td>82.9</td>
<td></td>
</tr>
<tr>
<td>Dielectric constant</td>
<td>6.02</td>
<td>6.00</td>
<td>5.01</td>
<td>13.11</td>
<td>17.0</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Solubility param.</td>
<td>9.1</td>
<td>8.4</td>
<td>8.46</td>
<td>8.57</td>
<td>8.55</td>
<td>8.5</td>
<td>8.8</td>
</tr>
<tr>
<td>Total</td>
<td>7.44</td>
<td>6.6</td>
<td>7.67</td>
<td>7.49</td>
<td>7.80</td>
<td>~7.8</td>
<td></td>
</tr>
<tr>
<td>Polar comp.</td>
<td>2.6</td>
<td>2.0</td>
<td>1.8</td>
<td>3.0</td>
<td>2.8</td>
<td>~3.4</td>
<td></td>
</tr>
<tr>
<td>H-Bonding comp.</td>
<td>4.5</td>
<td>4.8</td>
<td>3.1</td>
<td>2.0</td>
<td>2.0</td>
<td>2.0</td>
<td></td>
</tr>
</tbody>
</table>

As indicated above, the preferred solvent is ethyl acetate, and the process of the present invention will hereinafter be described in terms of utilizing ethyl acetate as the solvent. However, it should be understood that any of the identified solvents may be utilized in the following described process. As previously indicated the whole oil is dissolved in the ethyl acetate at a pre-

using any known evaporation technique, including vacuum evaporation techniques. The dried phenol-neutral fraction typically contains 0.5–1% of water with traces of ethyl acetate. Table II illustrates typical yields for various pine sawdust fast-pyrolysis oils and fractions of oils obtained during different test runs as well as for Douglas fir bark fast-pyrolysis oils.

### TABLE II

<table>
<thead>
<tr>
<th>Yields for Various Pyrolysis Oils</th>
<th>wt % Yields of Pyrolysis Oils Based on Dry, Char-Free Oil</th>
<th>Water Soluble</th>
<th>Organic Acids</th>
<th>Phenol/Neutral</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pyrolysis Oil</td>
<td>E0A C Insol Sol Phenol/Neutral</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Pine sawdust</td>
<td>42.8  24.7  5.7</td>
<td>21.3*</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Pine sawdust</td>
<td>28.2  39*  6.1</td>
<td>26.7*</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Combined pine oil</td>
<td>22.8  28.9  6.7</td>
<td>25</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Pine sawdust</td>
<td>41e  27.2  6.3</td>
<td>26</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Douglas fir bark</td>
<td>0    12.1  15</td>
<td>Phenols: Neutrals:</td>
<td>Solids: 2.9 47.8</td>
<td>15.6</td>
</tr>
<tr>
<td>Douglas fir bark</td>
<td>0    ND*  19</td>
<td>Phenols: Neutrals:</td>
<td>Solids: 4.8 50.8</td>
<td>17</td>
</tr>
</tbody>
</table>

*Phenolics: 16.5; Neutrals: 9.5
*Water soluble by difference
*From two condensers
*E0A insoluble by difference
*Not Determined

ferred pH of about 2-4 and then filtered. Upon standing, the ethyl acetate/pyrolysis oils mixture separates into two phases. Chemical spectroscopic analysis revealed that the ethyl acetate-insoluble fraction contains carbohydrate and carbohydrate-derived products. The ethyl acetate-soluble fraction, containing the phenol/neutral fractions, is then separated and washed with water to remove the remaining water-soluble carbohydrate and carbohydrate-derived materials, preferably in a 1:6 to 1:1, water/oil weight ratio. The ethyl acetate-soluble fraction is then further extracted with an aqueous metal bicarbonate solution, preferably a 5% by weight aqueous solution of sodium bicarbonate. The pH of the bicarbonate extraction solution is preferably maintained at approximately 8-9.5, and a 6:1 to 0.5:1 bicarbonate solution-oil weight ratio is preferably utilized. The aqueous bicarbonate layer extracts the strong organic as indicated in Table II, the aqueous alkali metal bicarbonate solution utilized to extract strong organic acids and highly polar compounds further purifies the phenol/neutral fractions. While any suitable alkali metal bicarbonate solution may be utilized, the preferred solution is selected from sodium bicarbonate, potassium bicarbonate, lithium bicarbonate and ammonium bicarbonate, with sodium bicarbonate being the preferred and most optimal solution. From the aqueous bicarbonate solution, it is possible to isolate a fraction rich in organic acids as a by-product. In this instance, the aqueous layer can be neutralized, for example with 50% by weight of phosphoric acid (although other acids can be used) saturated with sodium chloride, and extracted with ethyl acetate. It is possible to then evaporate the solvents and isolate the remaining fractions as well.
The phenol/neutral fraction can be further fractionated into isolated phenolics and neutrals if desired. This can be accomplished by utilizing a 5% by weight solution of sodium hydroxide in a volume ratio of 5:1 of solution:extract. The aqueous layer is then acidified to a pH of about 2 utilizing a 50% solution of phosphoric acid (although other acids can be used). It is then saturated with sodium chloride and extracted with ethyl acetate. Evaporation of the solvent leads to the isolation of the phenolics fraction; evaporation of the initial ethyl acetate solution freed from phenolics leads to the neutrals fraction. It should be noted, however, that the present invention does not require this separation of the phenol from the neutral fractions, and it is in fact this aspect of the present invention which makes the present process so economical. In the past, as previously indicated, the phenolics have always been the desired end-product, and sodium hydroxide has typically been utilized in such process treatment. This is unnecessary with the process of the present invention, since it has been discovered that the combined phenolic and neutral fraction composition is sufficiently pure to function by itself in the formation of adhesive resins.

The process of the present invention can be operated in both batch mode as well as in a continuous mode. In the batch mode embodiment, the whole oils are extracted with ethyl acetate and then washed with water. Following the water wash, the composition is then washed with the aqueous sodium bicarbonate to eliminate the acidic components, which come from pyrolysis of the carbohydrate fraction and would be deleterious to the resins. In a continuous operation, the pyrolysis oils is preferably extracted simultaneously with water and ethyl acetate, and then the ethyl acetate’s soluble fraction is extracted countercurrently with the aqueous bicarbonate solution. The whole ethyl acetate fraction, which includes both phenolic and neutral compounds, is then utilized as a feedstock for resins after solvent evaporation.

**EXAMPLE I**

1.0 kg of fast-pyrolysis oil derived from pine sawdust was dissolved into 1 kg of ethyl acetate. After filtration of the solution, this solution then separated into two easily identified and separated phases. The ethyl acetate-soluble phase was then isolated, and 0.8 kg of water was added to this phase. The resulting water-soluble fraction was isolated and saved for further processing. 2 kg of 5% sodium bicarbonate solution was then added to the ethyl acetate-soluble fraction, and the aqueous phase therefrom was saved for further processing. This aqueous phase was the acids-soluble fraction. The resulting washed ethyl acetate-soluble solution, containing the phenol and neutral fractions, was then solvent evaporated to remove the ethyl acetate solvent. The yield of phenol/neutral was 31% by weight based on the dry oil.

The remaining ethyl acetate-insoluble fraction was solvent evaporated and yielded weight percent of the starting dry oil. The aqueous wash yield after solvent evaporation was 39 weight percent of the oil. The aqueous bicarbonate solution was neutralized with a 50% phosphoric acid solution, and after saturation with sodium chloride, the organic phase was extracted into ethyl acetate. After solvent evaporation, the acids fraction yield was approximately 7 weight percent. FIG. 1 illustrates this mass balance of the various fractions resulting from this Example I utilizing the process of the invention.

**EXAMPLE II**

9.5 kg of fast-pyrolysis oils derived from pine sawdust were dissolved into 10 kg of ethyl acetate. After filtration, this solution settled into two easily identified and separated phases. 1.8 kg of water was then added to the ethyl acetate-soluble phase, and this solution was then separated into two easily identified and separated phases. The resulting water-soluble fraction was saved for further processing, and the other ethyl acetate-soluble fraction was then admixed with 8.9 kg of a 5% sodium bicarbonate solution. The aqueous phase of this solution was then separated and saved for further processing, which was the acids-soluble fraction. The resulting washed ethyl acetate-soluble solution, containing the phenol/neutral fraction was separated, and the solvent was then evaporated. The yield of the phenol/neutral fraction was 30% by weight based on dry oil.

Using a procedure similar to that described above in Example I, the mass balance of the fractionation was determined as follows: the ethyl acetate insoluble fraction comprised 21 weight percent, the water-soluble fraction comprised 31 weight percent, and the organic acids comprise 7.2 weight percent.

**EXAMPLE III**

The fractionation of Douglas fir pyrolysis products which are solids at room temperature, was similar to that described for pine. 4.6 kg of Douglas fir fast-pyrolysis product were dissolved into 9.8 kg of ethyl acetate solution. No ethyl acetate insoluble fraction was observed. The whole solution was then extracted with 12 kg of a 5 weight percent aqueous sodium bicarbonate solution. The ethyl acetate-soluble solution contained 68 weight percent of phenolics and neutrals. The phenols and neutrals were then separated by extraction with 11 kg of a 5 weight percent aqueous solution of sodium hydroxide. From the ethyl acetate solution, 17 weight percent of neutrals were obtained. The alkaline aqueous solution containing the phenolics was acidified with 50% phosphoric acid (although other acids could have been used). This solution was then saturated with sodium chloride and extracted with ethyl acetate to yield 50.8 weight percent for the phenolics fraction upon solvent evaporation. In the extraction with aqueous bicarbonate solution, a precipitate was formed (5 weight percent) along with the soluble acids fraction of 19 weight percent. The data for the fractionated materials are provided in Table II above.

**EXAMPLE IV**

Fast-pyrolysis oil derived from pine sawdust also fractionated on a continuous basis. This continuous process utilized, but is not limited to, a 6-stage system of mixer tanks and settler tanks. The oil, ethyl acetate and water were mixed and allowed to settle, with the organic phase being sent on to multi-stage extraction with 5 weight percent aqueous sodium bicarbonate solution with each extraction stage having a separate settler tank. The bicarbonate extraction was run countercurrent to the flow of the organic phase. The aqueous fractions, that is the combined ethyl acetate insoluble and water-soluble fractions, the aqueous bicarbonate solution, and the organic phase were all collected and processed as described above. Conditions of the extraction included the following: oil flow, water flow, ethyl
acetate flow, and aqueous bicarbonate flow rates were 10, 6, 34 and 35 mL/min, respectively. It should be noted, however, that the countercurrent continuous extraction process is not limited to these flow rates. The yield of phenol/neutral fractions composition was about 20% based on the oil flow rate and phenol/neutral isolated fractions. A total of 20 kg of oil was fractionated in this way. Variations in flow rates and number of settler and mixer tanks, however, can yield different proportions of materials. Phase separation was readily accomplished within the settlers.

Analysis of the products for intermediate stages of extraction revealed that 1-3 stages of bicarbonate extraction may be used. Turning from the Examples given above, the fractionation scheme described above allowed the isolation of 21% to 31% of the stericine oils as a phenol/neutral fraction, or overall yields of 12-21% based on starting dry wood. This fraction consisted of approximately 73% phenolics, extractable from sodium hydroxide solution from an ethyl acetate solution, and 27% neutrals. The total yield of phenol/neutral fraction isolation is reproducible as shown by the runs in Table II above.

The typical oil contained 6.2% phenolic hydroxyl and 0.4% carboxylic acid contents by weight ranges. Ranges of 5.5-6.5% phenolic hydroxyl and 0.1-0.6% carboxylic acid contents are expected for the different starting feeds. The phenol/neutral fraction included about 6.6% phenolic hydroxyl content and no carboxylic acid content. Expected ranges for phenols/ neutrals are 6.0-12% depending on the feed. The acids fraction included about 9.2% phenolics and 0.9% carboxylic acid contents. Ranges for various feeds are 5-10% for phenolics and 0.5-3% carboxylic acid contents.

In characterizing the resultant phenol compositions, the apparent molecular weight distributions obtained from gel permeation chromatography on polystyrene- divinylbenzene copolymer gels (50 Angstrom) with tetrahydrofuran as solvent, indicated that the phenolics fraction had components ranging from the monomeric substituted phenols (around 150) to oligomers (up to several thousand in molecular weight). The acids and neutrals had the lowest molecular weight components. From molecular beam mass spectra of the phenol/neutral fractions, a number of phenolic compounds were detected: guaiacol (2-methoxymethylphenol) m/z 124; catechols m/z 110; isomers of substituted 2-methoxyphenols with alkyl groups such as methyl (m/z 138), vinyl (m/z 150), 3-hydroxypropyl-1-yl (m/z 180), allyl (m/z 164), hydroxyethyl (m/z 168), and ethyl (m/z 152), most likely in the p-position. In addition, carboxylate-derived compounds were present such as furfural alcohol and a number of other furfural derivatives.

From proton nuclear magnetic resonance spectrum of the phenol/neutral fraction, of the total intensity, the aromatic protons (6.5-10 ppm) constituted 52%, the aliphatic (1.5-3.5 ppm) about 20%, and the methoxy region and oxygenated and side-chain region (3.0-4.2 ppm) constituted 30%. This was in agreement with the description from the molecular beam mass spectra of mixtures of phenolics with substituted groups. The carbon-13 nuclear magnetic resonance spectra confirmed this data.

Bark derived phenols have a very high phenolic hydroxyl content (7.4-11.5%) depending on pyrolysis conditions (steam to nitrogen carrier gas) and therefore are very suitable for adhesive formulation replacing phenol at greater than a 50% level.

As previously indicated, a principal purpose of producing the phenol/neutral fractions is to provide a substitute for pure phenol in the production of resins and the like. Specifically, resoles, which are phenol-formaldehyde resins formed under alkaline conditions for gluing wood, were produced and compared to resoles utilizing standard formulations of commercially available phenol.

Of the various fractions of pyrolysis oil, only the phenol/neutral fractions gave a positive gel test under the above conditions. In preliminary gel testing of the phenol/neutrals extract, one gram of paraformaldehyde was arbitrarily added to 4 grams of the extract. The pH of the extract was adjusted by adding 0.2-1.0 mL of 50% by weight sodium hydroxide. There appeared to be a strong buffering of the pH by the extract at a pH 9.5. Cascopeh 313 was used for comparison. At 0.5 mL of added sodium hydroxide, the gel time of the phenol/neutral fraction was much shorter than that of the Cascopeh, with a gel time of only 29% that of Cascopeh at 124°C. At 112°C, it was 34%, while at 101°C it was 46% of Cascopeh. At the original pH of 3 of the phenol/neutral fractions, there was no gelting of the mixture even at 132°C with the same amount of added paraformaldehyde.

Resoles have also been made utilizing a 50% replacement of phenol with the phenol/neutral fractions produced by the process of the present invention. FIG. 2 discloses a comparison of shear stress strength between Cascopeh and resoles produced with the phenol/neutrals fraction of the present invention. Specimens were tested after a cold water soak (rightmost bar) and met test requirements. As can be seen from FIG. 2, the Cascopeh showed a shear stress strength in psi of approximately 700, while the resole with the phenol/neutral fraction produced from the present invention showed a strength of approximately 800 psi, significantly higher than Cascopeh. Moreover, the resole produced from the phenol/neutral fraction of the present invention illustrated a cold soak strength of approximately 600, which is considerably higher than the standard 500 which has generally been set for existing products such as the Cascopeh. The tests performed used the British standard 1904; Part 1:1964, and the testing of 10 specimens per evaluation. Thus, FIG. 2 illustrates the fact that the shear strength of resins produced by substituting 50% of the phenols therein with the phenol/neutral fraction produced from the present invention are in fact stronger than phenol-formaldehyde resins utilizing pure phenol.

It has been found that useful resins may be obtained by substituting from about 25 to about 75 weight percent of the phenol normally present in a resole resin with the P/N fraction of the invention. About 35 to 65% by weight is preferred. Most preferably, about 50% by weight is desired.

Referring to FIG. 3, wood failure tests are compared between the Cascopeh and resoles having the phenol/neutral fractions produced from the present invention. To interpret FIG. 3, it should be understood that it is preferred to have a wood failure, not a resin failure. Thus, if the wood fails, the resin is deemed to be good, and if the resin fails, it is deemed not to be good since the resin has actually separated. Thus, it is desirable to have a higher wood failure percent in order to show resin strength. Referring to FIG. 3, it should be clear...
that the Casco phen samples had a wood failure of approximately 38\%, while the resin produced by substituting 50\% of the phenolic portion with the phenol/neutral fraction from pyrolysos oils was well over 50\%, illustrating a significant difference in resin strength capability. Moreover, the cold soak test results illustrated that the resole having the phenol/neutral fraction produced from the present invention had a cold soak rating the same as a non-cold soak rating of the Casco phen. Thus, these tests further indicated that resole resins produced by substituting 50\% of the phenol with the phenol/neutral fraction produced from the present invention are considerably better in function and strength than standard commercially available products. The tests performed used the British Standard 1204: part 1:1964, and testing of 10 specimens per evaluation.

With respect to the economic benefits of the present invention, petroleum derived phenol costs about $0.34 (spot price) and $0.40 (list price) per pound. Prior to the present invention, the main competition has been the lignin-derived substitutes from commercial pulping processes. Kraft lignins have to be made chemically more reactive to replace phenol in phenol-formaldehyde resins with similar performance. These commercial products are sold as resin co-reactants, and their price range forms $0.33-$0.85 per pound depending on the reactivity needed (based on Kraft lignins). Less expensive products are available from the process of the present invention are co-reactants with the ability to replace about 50\% of the phenol in phenol-formaldehyde resins as described above. Indications are that for molding compounds and for plywood adhesive resins, 50\% phenol replacement would provide a very similar performance to the commercial phenolic adhesives, and in fact would give a better performance as illustrated and described above in FIGS. 2 and 3. However, there is a significant cost reduction factor in that the phenol/neutral composition of the present invention have an amortized cost projection at approximately $0.16 per pound compared to $0.34-$0.40 per pound for commercial phenol. If the lignocellulosic starting material is bark, this cost is even less because the yield of phenolics from the bark is higher than that of sawdust or pine. Plant sizes were 250 to 1000 tons of feedstock per day, 15\% return on capital, plant life of 20 years, and waste sawdust at $10.00 per dry ton.

As described above, the most developed application for the end products of the present invention is the replacement of 50\% and potentially more of phenol in phenol-formaldehyde resins for use as molding compounds, foundry, and shell moldings. Potential applications for the resulting product of the process of the present invention include the replacement of phenol in softwood and hardwood plywood resins, the insulation market, composite board adhesives, laminated beams, flooring and decking, industrial particle board, wet-formed hard boards, wet-formed insulation boards, structural panel board, and paper overlays. Alternative adhesive systems from the carbohydrate-rich fractions of the present invention could also be made.

In addition, another product that can be derived from the other fractions of the pyrolysos oils is an aromatic gasoline. Passage of vapors of these compounds over zeolite catalysts produces high octane gasoline, as more clearly discussed in "Low-pressure upgrading of Primary Pyrolysos Oils from Biomass and Organic Waste", in Energy from Biomass and Wastes, Elsevier Applied Science Publishers, London, pp. 801-830 (1986).

A final advantage to the present invention is that about one-third of the usual amount of formaldehyde employed in conventional phenolic adhesives is necessary in producing adhesives wherein 50\% of the phenol is substituted with phenol/neutral fractions provided by the present invention. Since there is significant environmental concern over formaldehyde emissions from resins, the products resulting from the process of the present invention therefore become very important from this context.

As can be seen from the above, a novel process for fractionating fast-pyrolysos oils to produce phenol-containing compositions having phenol/neutral fractions contained therein suitable for manufacturing phenol-formaldehyde resins are disclosed. The process is simple and economic, and can be used in either batch or continuous mode operations. The resulting phenol/neutral composition can be subsequently utilized to produce novolaks and resole resins of comparable or superior performance characteristics relative to standard phenol-formaldehyde resins yet the pyrolysis-derived phenolic feedstocks are projected to cost less than half the cost of petroleum-derived phenol. Moreover, these resulting resins have numerous different types of applications, and the cost benefits alone are significant.

**EXAMPLE V**

Phenol/neutral derived from a fast-pyrolysos oil obtained from Pine sawdust according to the process similar to that in Example IV. The P/N oil was dissolved in the phenol and the sodium hydroxide and formaldehyde were subsequently added. The formulation used is as follows:

- 9.4 g Pyrolysos Oil
- 10.6 g 88\% Phenol
- 1.8 g 50\% Sodium Hydroxide (first addition)
- 2.0 g 50\% Sodium Hydroxide (second addition)
- 32.4 g Formaldehyde 37\%

This formulation provides for a ratio of formaldehyde to phenolics of about 2:1 and this region of molar ratio is near the average for that of resins used by the industry in general.

After the pyrolysos oil, phenol, sodium hydroxide and formaldehyde were mixed and reacted as shown in FIG. 4 (i.e. after a moderate time of reaction, the second addition of sodium hydroxide was made and the reaction continued).

FIG. 4 gives the time/temperature relationship for the preparation of this resole resin.

To evaluate and compare this resin with a commercial resole resin in which none of the phenol was replaced with the P/N fractions, the stroke curve method was used. The resins were subjected to a given temperature and the time taken to reach a state of gellation was measured. The results were as follows:

<table>
<thead>
<tr>
<th>Stroke cure (dry rubber), seconds at</th>
<th>150° C.</th>
<th>165° C.</th>
</tr>
</thead>
<tbody>
<tr>
<td>(P/N) Resin Resole</td>
<td>27</td>
<td>80</td>
</tr>
<tr>
<td>Commercial Resin Resole</td>
<td>34</td>
<td>79</td>
</tr>
<tr>
<td>(Chembond PS 13)</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

The P/N resole resin was a homogenous fluid (by visual inspection) and was readily soluble in water at room temperature.
EXAMPLE VI

Phenol/neutral derived from a fast-pyrolysis oil obtained from Pine sawdust according to the process similar to that in Example IV were placed in a reaction container with water.

Sodium hydroxide and paraformaldehyde were added in accordance with the following formulation:

9.4 g Pyrolysis Oil (P/N)
19.4 g Water
3.6 g Sodium Hydroxide (50%)
6.2 g Paraformaldehyde (91%) (first addition)
7.0 g Paraformaldehyde (91%) (second addition)
10.6 g 88% Phenol

The pyrolysis oil, water, and sodium hydroxide were mixed at room temperature until dissolved. 6.2 g paraformaldehyde were added and the mass reacted as shown in FIG. 5. After about 1 hour and 25 minutes 7.0 g paraformaldehyde and 10.6 g phenol were added and the reaction continued. The time/temperature relationship of the reaction is shown in FIG. 5. This resin gave a stroke cure at 150°C of 44 seconds, and this is well within the range of commercially used resole resins. The viscosity of the resin was in the low to medium range and of such a nature that application with commercial equipment (roll, curtain coat or spray) would easily be practical.

The resole resins from Examples V and VI exhibited excellent dry knife characteristics per se; however, these resins may be modified by the use of thickeners and additives such as wheat flour, ground Alder bark and METHOCHEL (cellulose methyl ether).

Resole resins were prepared similar to Examples V and VI by adding METHOCHEL to control viscosity as follows:

EXAMPLE VIIa
Resole & Methocel

50.0 g Pyrolysis oil (P/N)
50.0 g 88% Phenol
13.8 g 50% NaOH
9.13 g 50% NaOH
9.15 g 50% NaOH
141.0 g 37% Formaldehyde (0.50 g Methocel dissolved in)

This formulation cured in 28-29 seconds at 150°C. Its viscosity was measured at 6,600 cps.

EXAMPLE VIIb
Resole & Methocel

127.5 g Pyrolysis oil (P/N)
125.0 g 88% Phenol
35.0 g 50% NaOH
18.0 g 50% NaOH
23.0 g 50% NaOH
352.5 g 37% Formaldehyde
1.25 g Methocel

The solution was at a temperature between 45° and 48°C. This resin was employed in the plywood adhesive formulation described below.

About one half of the formaldehyde was heated to 65°C. The METHOCHEL was added and mixed for 3-4 minutes, after which the rest of the formaldehyde was added.

In order to produce a useful resole resin and/or adhesive composition containing the P/N fraction from the fast-pyrolysis oil process according to the invention, it has been found that up to 75% of the phenol normally used in a phenol-formaldehyde resole resin can be replaced with the P/N fraction.

While any caustic may be used to catalyze the P/N fraction and phenol in preparing the resole resins, it is preferred to use sodium hydroxide, potassium hydroxide and calcium hydroxide. Most preferred, however, is sodium hydroxide.

EXAMPLE VIIIa

Plywood Resole Adhesive & Bark & Wheat Flour

118 g Water
30 g Modal (ground Alder bark)
14 g Wheat Flour
Mix 3 minutes
35 g Resin (P/N)
13 g 50% NaOH
Mix 3 minutes
3 g Soda ash
187 g Resin (P/N)
Brookfield #6 spindle: 5600 cps
20 rpm

EXAMPLE VIIIb

Plywood Resole Adhesive using Ca(OH)2 & Bark & Wheat Flour

140 G Water
8 g Calcium Hydroxide
24 g Modal (ground Alder bark)
20 g Wheat Flour
237 g Resin (P/N)
5 g Paraformaldehyde
Approximate resin solids: 27% (based on 50% resin)
Approximate total solids: 40%
Brookfield #6 spindle: 3550 cps
20 rpm

While the foregoing description and illustration of the invention has been shown in detail with reference to preferred embodiments, it is to be understood that the foregoing are exemplary only, and that many changes in the compositions can be made without departing from the spirit and scope of the invention, which is defined by the attached claims.

What is claimed is:
1. An improved process for preparing phenol-formaldehyde resole resins comprising, replacing a portion of the phenol normally used in making resole resins with a phenol-neutral fractions extract obtained by a process of fractionating fast-pyrolysis oils, wherein the neutral fractions have molecular weights of between about 100 to about 800, and the phenol-containing compositions/neutral fractions extract is soluble in an organic solvent having a solubility parameter of approximately 8.4-9.1 [cal/cm3]1/2 with polar components in the 1-8-3.0 range and hydrogen bonding components in the 2-4.5 range.
2. The process of claim 1 wherein said fast-pyrolysis oils are produced from lignocellulosic materials.
3. The process of claim 2 wherein said lignocellulosic materials are selected from the group consisting of softwoods, hardwoods, pine sawdust, bark, grasses and agricultural residues.
4. The process of claim 1 wherein said phenol/neutral fractions extract replaces up to about 75% by weight of the phenol in said phenol-formaldehyde resin resins.

5. The process of claim 1 wherein said phenol/neutral fractions extract replaces about 50% by weight of the phenol in said phenol-formaldehyde resin resins.

6. The process of claim 1 wherein said phenol/neutral fractions extract replaces about 25% by weight of the phenol in said phenol-formaldehyde resin resins.

7. A phenol-formaldehyde resin wherein a portion of the phenol normally contained in said resin is replaced by a phenol/neutral fractions extract obtained by a process of fractionating fast-pyrolysis oils; wherein the neutral fractions have molecular weights of between about 100 to about 800 and the phenol/neutral fractions extract is soluble in an organic solvent having a solubility parameter of approximately 8.4–9.1 [cal/cm³]¹/² with polar components in the 1.8-3.0 range and hydrogen bonding components in the 2-4.5 range.

8. A phenol-formaldehyde resin according to claim 7, wherein said fast-pyrolysis oils are produced from lignocellulosic materials.

9. A phenol-formaldehyde resin according to claim 8, wherein said lignocellulosic materials are selected from the group consisting of softwoods, hardwoods, pine sawdust, bark, grasses and agricultural residues.

10. A phenol-formaldehyde resin according to claim 7, wherein said phenol/neutral fractions extract is up to about 75% by weight replacement of the phenol normally contained in said resin.

11. A phenol-formaldehyde resin according to claim 7, wherein said phenol/neutral fractions extract is about 50% by weight replacement of the phenol normally contained in said resin.

12. A phenol-formaldehyde resole resin according to claim 7, wherein said phenol/neutral fractions extract is about 25% by weight replacement of the phenol normally contained in said resin.

13. An adhesive composition comprising a phenol-formaldehyde resole resin wherein a portion of the phenol normally contained in said resin is replaced by a phenol/neutral fractions extract obtained by a process of fractionating fast-pyrolysis oils; said phenol/neutral fractions extract having neutral fractions having molecular weights of between about 100 to about 800 and the phenol/neutral fractions extract is soluble in an organic solvent having a solubility parameter of approximately 8.4–9.1 [cal/cm³]¹/² with polar components in the 1.8-3.0 range and hydrogen bonding components in the 2-4.5 range.

14. The adhesive composition of claim 13, wherein said fast-pyrolysis oils are produced from lignocellulosic materials.

15. The adhesive composition of claim 14, wherein said lignocellulosic materials are selected from the group consisting of softwoods, hardwoods, pine sawdust, bark, grasses and agricultural residues.

16. The adhesive composition of claim 13, wherein said phenol/neutral fractions extract is up to about 75% by weight replacement of the phenol normally contained in said resin.

17. The adhesive composition of claim 13, wherein said phenol/neutral fractions extract is about 50% by weight replacement of the phenol normally contained in said resin.

18. The adhesive composition of claim 13, wherein said phenol/neutral fractions extract is about 25% by weight replacement of the phenol normally contained in said resin.