

## **Integrated Pyrolysis of Pine Needles and Cashewnut Shells: Optimizing Process Conditions for the Production of Renewable Fuel and Value-Added Chemical**

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Table TS1. Chemical Compositions of CNS at 500 °C

| <b>CASHEWNUT SHELL @ 500 °C</b> |                                            |                                                |                       |                 |
|---------------------------------|--------------------------------------------|------------------------------------------------|-----------------------|-----------------|
| <b>Functionality</b>            | <b>Chemical Name</b>                       | <b>Molecular formula</b>                       | <b>Retention Time</b> | <b>Area (%)</b> |
| <b>phenolics</b>                | Acetone                                    | C <sub>3</sub> H <sub>6</sub> O                | 1.794                 | 0.51            |
|                                 | Phenol                                     | C <sub>6</sub> H <sub>6</sub> O                | 9.534                 | 0.14            |
|                                 | Phenol, 3-methyl-                          | C <sub>7</sub> H <sub>8</sub> O                | 11.543                | 0.14            |
|                                 | Phenol, 2-methoxy-                         | C <sub>7</sub> H <sub>8</sub> O <sub>2</sub>   | 11.723                | 0.07            |
|                                 | Maltol                                     | C <sub>6</sub> H <sub>6</sub> O <sub>3</sub>   | 12.267                | 0.05            |
|                                 | Catechol                                   | C <sub>6</sub> H <sub>6</sub> O <sub>2</sub>   | 13.978                | 0.14            |
|                                 | 4-Vinylphenol                              | C <sub>8</sub> H <sub>8</sub> O                | 14.325                | 0.08            |
|                                 | 3-Tridecylphenol                           | C <sub>19</sub> H <sub>32</sub> O              | 29.032                | 0.29            |
|                                 | (Z)-3-(pentadec-8-en-1-yl) phenol          | C <sub>21</sub> H <sub>36</sub> O              | 29.96                 | 0.03            |
|                                 | 3-((4Z,7Z)-Heptadeca-4,7-dien-1-yl) phenol | C <sub>23</sub> H <sub>38</sub> O              | 31.304                | 69.46           |
|                                 | 3-((4Z,7Z)-Heptadeca-4,7-dien-1-yl) phenol | C <sub>23</sub> H <sub>38</sub> O              | 31.342                | 13.66           |
|                                 | Phenol, 3-(8-pentadecenyl)-, acetate, (Z)- | C <sub>23</sub> H <sub>36</sub> O <sub>2</sub> | 31.582                | 0.05            |
|                                 | Phenol, 3-(10Z)-10-nonadecen-1-yl-         | C <sub>25</sub> H <sub>42</sub> O              | 32.078                | 0.16            |
|                                 | 3-((4Z,7Z)-Heptadeca-4,7-dien-1-yl) phenol | C <sub>23</sub> H <sub>38</sub> O              | 32.873                | 0.34            |
|                                 | (Z)-3-(Heptadec-10-en-1-yl) phenol         | C <sub>23</sub> H <sub>40</sub> O              | 33.008                | 0.82            |
|                                 | 3-((4Z,7Z)-Heptadeca-4,7-dien-1-yl) phenol | C <sub>23</sub> H <sub>38</sub> O              | 33.056                | 0.21            |
|                                 | Mangol I                                   | C <sub>23</sub> H <sub>40</sub> O              | 34.001                | 2.68            |
|                                 |                                            |                                                |                       |                 |
| <b>ketones</b>                  | 2-Propanone, 1-hydroxy-                    | C <sub>3</sub> H <sub>6</sub> O <sub>2</sub>   | 2.883                 | 1.81            |
|                                 | 4-Penten-2-one, 3-methyl-                  | C <sub>6</sub> H <sub>10</sub> O               | 4.7                   | 0.04            |

|                                    |                                         |                                               |        |      |
|------------------------------------|-----------------------------------------|-----------------------------------------------|--------|------|
|                                    | 2-Propanone, 1-hydroxy-                 | C <sub>3</sub> H <sub>6</sub> O <sub>2</sub>  | 5.091  | 0.28 |
|                                    | 2-Propanone, 1-(acetyloxy)-             | C <sub>5</sub> H <sub>8</sub> O <sub>3</sub>  | 6.878  | 0.22 |
|                                    | Cyclopentanone                          | C <sub>5</sub> H <sub>8</sub> O               | 7.878  | 0.2  |
|                                    | Cyclopentanone, 3-methyl-               | C <sub>6</sub> H <sub>10</sub> O              | 8.291  | 0.46 |
|                                    | 1,2-Cyclopentanedione, 3-methyl-        | C <sub>6</sub> H <sub>8</sub> O <sub>2</sub>  | 10.511 | 0.21 |
|                                    | 2-Cyclopenten-1-one, 2,3-dimethyl-      | C <sub>7</sub> H <sub>10</sub> O              | 10.673 | 0.05 |
|                                    | 2-Cyclopenten-1-one, 3-ethyl-2-hydroxy- | C <sub>7</sub> H <sub>10</sub> O <sub>2</sub> | 12.371 | 0.06 |
|                                    |                                         |                                               |        |      |
| <b>Acids</b>                       | Acetic acid                             | C <sub>2</sub> H <sub>4</sub> O <sub>2</sub>  | 2.548  | 0.51 |
|                                    |                                         |                                               |        |      |
| <b>Aromatic -<br/>Hydrocarbons</b> | 1H-Pyrrole, 1-methyl-                   | C <sub>5</sub> H <sub>7</sub> N               | 3.986  | 0.11 |
|                                    | Pyrrole                                 | C <sub>4</sub> H <sub>5</sub> N               | 4.305  | 0.08 |
|                                    | 1,8,11,14-Heptadecatetraene, (Z,Z,Z)-   | C <sub>17</sub> H <sub>30</sub>               | 31.739 | 0.33 |
|                                    | 1,8,11,14-Heptadecatetraene, (Z,Z,Z)-   | C <sub>17</sub> H <sub>30</sub>               | 31.873 | 0.09 |
|                                    | 1,8,11,14-Heptadecatetraene, (Z,Z,Z)-   | C <sub>17</sub> H <sub>30</sub>               | 32.95  | 0.16 |
|                                    | Cardoltriene                            | C <sub>21</sub> H <sub>32</sub> O             | 33.962 | 6.08 |

Table TS2. Chemical Compositions of PN at 500 °C

| <b>PINE NEEDLES @ 500 °C</b> |                         |                                               |                       |                 |
|------------------------------|-------------------------|-----------------------------------------------|-----------------------|-----------------|
| <b>Functionality</b>         | <b>Chemical Name</b>    | <b>Molecular formula</b>                      | <b>Retention Time</b> | <b>Area (%)</b> |
| <b>phenolics</b>             | Phenol, 2-methoxy-      | C <sub>7</sub> H <sub>8</sub> O <sub>2</sub>  | 11.743                | 5.53            |
|                              | 2-Methoxy-4-vinylphenol | C <sub>9</sub> H <sub>10</sub> O <sub>2</sub> | 15.981                | 4.58            |
|                              | Creosol                 | C <sub>8</sub> H <sub>10</sub> O <sub>2</sub> | 13.77                 | 3.9             |

|                |                                                 |                                                |        |       |
|----------------|-------------------------------------------------|------------------------------------------------|--------|-------|
|                | Phenol, 2-methoxy-4-(1-propenyl)-               | C <sub>10</sub> H <sub>12</sub> O <sub>2</sub> | 18.247 | 3.08  |
|                | (Z)-3-(pentadec-8-en-1-yl) phenol               | C <sub>21</sub> H <sub>34</sub> O              | 30.975 | 2.64  |
|                | Phenol                                          | C <sub>6</sub> H <sub>6</sub> O                | 9.525  | 2.61  |
|                | p-Cresol                                        | C <sub>7</sub> H <sub>8</sub> O                | 11.538 | 2.44  |
|                | (E)-4-(3-Hydroxyprop-1-en-1-yl)-2-methoxyphenol | C <sub>10</sub> H <sub>12</sub> O <sub>3</sub> | 22.538 | 1.22  |
|                | 3-((4Z,7Z)-Heptadeca-4,7-dien-1-yl) phenol      | C <sub>23</sub> H <sub>38</sub> O              | 31.022 | 1.16  |
|                | Phenol, 2-methoxy-3-(2-propenyl)-               | C <sub>10</sub> H <sub>12</sub> O <sub>2</sub> | 16.666 | 1.07  |
|                | Phenol, 4-ethyl-2-methoxy-                      | C <sub>9</sub> H <sub>12</sub> O <sub>2</sub>  | 15.31  | 1.02  |
|                | Phenol, 2-methyl-                               | C <sub>7</sub> H <sub>8</sub> O                | 11.09  | 0.79  |
|                | Phenol, 2,4-dimethyl-                           | C <sub>8</sub> H <sub>10</sub> O               | 12.977 | 0.56  |
|                | Phenol, 2-methoxy-4-(1-propenyl)-               | C <sub>10</sub> H <sub>12</sub> O <sub>2</sub> | 17.524 | 0.46  |
|                | Apocynin                                        | C <sub>9</sub> H <sub>10</sub> O <sub>3</sub>  | 18.818 | 0.4   |
|                | Phenol, 4-(2-propenyl)-                         | C <sub>9</sub> H <sub>10</sub> O               | 16.49  | 0.37  |
|                | Vanillin                                        | C <sub>8</sub> H <sub>8</sub> O <sub>3</sub>   | 17.446 | 0.37  |
|                |                                                 |                                                |        |       |
| <b>ketones</b> | 2-Propanone, 1-hydroxy-                         | C <sub>3</sub> H <sub>6</sub> O <sub>2</sub>   | 2.848  | 8.97  |
|                | 4-Penten-2-one, 3-methyl-                       | C <sub>6</sub> H <sub>10</sub> O               | 6.838  | 2.12  |
|                | 1,2-Cyclopentanedione, 3-methyl-                | C <sub>6</sub> H <sub>8</sub> O <sub>2</sub>   | 10.532 | 2.06  |
|                | 1-Hydroxy-2-butanone                            | C <sub>4</sub> H <sub>8</sub> O <sub>2</sub>   | 4.607  | 1.55  |
|                | 2-Propanone, 1-(4-hydroxy-3-methoxyphenyl)-     | C <sub>10</sub> H <sub>12</sub> O <sub>3</sub> | 19.44  | 1.23  |
|                | 1,4-Dioxaspiro[2.4] heptan-5-one, 6-methyl-     | C <sub>7</sub> H <sub>10</sub> O <sub>3</sub>  | 13.159 | 0.72  |
|                | Stigmast-4-en-3-one                             | C <sub>29</sub> H <sub>48</sub> O              | 40.304 | 0.63  |
|                | 2-Cyclopenten-1-one, 3-ethyl-2-hydroxy-         | C <sub>7</sub> H <sub>10</sub> O <sub>2</sub>  | 12.378 | 0.42  |
|                | 2-Pentadecanone, 6,10,14-trimethyl-             | C <sub>18</sub> H <sub>36</sub> O              | 23.796 | 0.3   |
|                |                                                 |                                                |        |       |
| <b>Acids</b>   | Acetic acid                                     | C <sub>2</sub> H <sub>4</sub> O <sub>2</sub>   | 2.563  | 11.11 |
|                | Formic acid                                     | CH <sub>2</sub> O <sub>2</sub>                 | 1.887  | 0.5   |
|                | n-Hexadecanoic acid                             | C <sub>16</sub> H <sub>32</sub> O <sub>2</sub> | 25.349 | 1.82  |

|                                    |                                            |                                                |        |      |
|------------------------------------|--------------------------------------------|------------------------------------------------|--------|------|
|                                    | cis-13-Octadecenoic acid                   | C <sub>18</sub> H <sub>34</sub> O <sub>2</sub> | 25.262 | 1.31 |
|                                    | Tetradecanoic acid                         | C <sub>14</sub> H <sub>28</sub> O <sub>2</sub> | 22.756 | 0.6  |
|                                    | Dodecanoic acid                            | C <sub>12</sub> H <sub>24</sub> O <sub>2</sub> | 19.982 | 0.58 |
|                                    |                                            |                                                |        |      |
| <b>Aromatic -<br/>Hydrocarbons</b> | (E)-3,3'-Dimethoxy-4,4'-dihydroxystilbene  | C <sub>16</sub> H <sub>16</sub> O <sub>4</sub> | 32.721 | 1.81 |
|                                    | 1,3,5-Cycloheptatriene                     | C <sub>7</sub> H <sub>8</sub>                  | 4.55   | 1.05 |
|                                    | Caryophyllene                              | C <sub>15</sub> H <sub>24</sub>                | 17.863 | 0.86 |
|                                    | 1-Undecene                                 | C <sub>11</sub> H <sub>22</sub>                | 11.806 | 0.58 |
|                                    | Neophytadiene                              | C <sub>20</sub> H <sub>38</sub>                | 23.717 | 0.23 |
|                                    | Butane                                     | C <sub>4</sub> H <sub>10</sub>                 | 1.75   | 6.44 |
|                                    | Oxacyclotetradecane-2,11-dione, 13-methyl- | C <sub>15</sub> H <sub>26</sub> O <sub>3</sub> | 25.068 | 1.2  |
|                                    | Cyclopropane, 1,1-dimethyl-2-methylene-    | C <sub>6</sub> H <sub>10</sub>                 | 4.261  | 0.69 |