Preliminary investigation on concentrating of acetol from wood vinegar

Ze Wang, Weigang Lin, Wenli Song*, Jianzhong Yao

State Key Laboratory of Multi-Phase Complex System, Institute of Process Engineering, Chinese Academy of Sciences, Beijing 100190, China

A R T I C L E   I N F O

Article history:
Received 23 February 2009
Accepted 30 September 2009
Available online 6 November 2009

Keywords:
Wood vinegar
Pyrolysis liquid
Acetol
Concentrating

A B S T R A C T

Acetol, as one of the components in biomass pyrolysis liquid, is a high value added compound for medicine synthesis. Benefit may be obtained if acetol can be extracted from the pyrolysis liquid, while the instability of acetol makes the concentrating difficult. In this paper, the concentrating of acetol from wood vinegar is preliminarily investigated, and the conditions of distillation, solvent extraction, and Na₂CO₃ effect on the concentrating result are discussed. Herein the content of acetol can be concentrated from below 4% in the raw wood vinegar to above 60%, and the number of main components reduce from over 20 to 5, while the yield of acetol is still rather low. It was found that in the organic solution distillation process, acetol can be easily concentrated from 1% to above 40%, while a further distillation of the concentrated acetol system was rather hard. The conversion of acetol in the distillation process was probably an important cause to the low yield of acetol, and a lower distillation temperature was advantageous for the concentrating of acetol.

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1. Introduction

With declining petroleum resources, and more environmental concerns on fossil fuels, it is imperative to develop sustainable fuels and chemicals from renewable resources [1–4]. As one of the important renewable resources, biomass can be converted to liquid products by thermochemical approach for pyrolysis-oil and chemicals [2–7]. Pyrolysis-oil may be used as a transport fuel after upgrading treatment [8–12] or by emulsion with diesel [13]. Chemicals like methanol, acetic acid can be obtained from the pyrolysis liquid a long time ago [3]. Recently, hydrothermal approach was applied in treating the biomass to produce chemicals like liquid alkanes [2,6,14,15] or the unique compound like 2-(4-hydroxy-benzyl)-4-methyl-phenol [16]. The bio-refinery is getting upgrading treatment [8–12] or by emulsion with diesel [13]. The second, acetol can be prepared by the reaction between bromoacetone and sodium formate or acetate, followed by hydrolysis of the ester with methyl alcohol. The second, acetol can be prepared by the treatment of glycerol or propylene glycol at 200–300°C with a dehydrogenating catalyst. While the two methods are both in high cost due to the expensive bromoaetone or catalyst. So it is worthwhile to take efforts to extract acetol from the pyrolysis liquid. While the instability of acetol makes the concentrating difficult. Till now there is no report on the method of extraction of acetol from pyrolysis liquid.

In this paper, the concentrating of acetol from wood vinegar was preliminarily probed. The conditions of distillation, solvent extraction, and Na₂CO₃ effect on the concentrating result were tested and phenomena were discussed.

2. Analytical method

The wood vinegar and the concentrated products were analyzed by GC–MS apparatus (Agilent-6890-5972). The column was AB-FFAP (30 m × 0.25 mm × 0.25 μm). Analytical conditions: inlet heater, 275°C; MSD temperature, 150–155°C; temperature program, initial 50°C for 5 min, increase to 110°C by 20°C/min for 5 min, and finally to 230°C by 20°C/min for 6.5 min. The contents of the components in different systems were represented by peak area percentages for relative comparisons under different conditions, since the aim of the work was for qualitative probe.

3. Results and discussion

The raw wood vinegar was analyzed by GC–MS, the total ion chromatogram (TIC) was shown in Fig. 1, and the composition was listed in Table 1. It can be seen from Fig. 1 that water (80.97%) was the predominant component in wood vinegar, and the other main components were acetic acid (7.28%), methyl...
alcohol (4.55%), acetol (3.4%), acetone (0.99%), propanoic acid (0.7%), furfural (0.65%), and phenol derivatives (0.55%). Among the main components, acetol was most distinct in the ratio of content to market price, indicating that it was worthwhile to take efforts to extract acetol from the wood vinegar.

The raw wood vinegar (100 ml) was firstly distilled at atmospheric pressure. Two heating rates were tested, one case was slow heating in the beginning and fast heating later, and the other case was from fast to slow. With distillation going, the evaporated fractions were collected in the order of 3 ml, 10.5 ml, and 4 ml. The composition of each evaporated fraction was analyzed, and the change of the composition with distillation process was shown in Fig. 2. The composition of the latter 50% evaporated fraction was listed in Table 1.

It can be seen from Fig. 2 that the heating rate had very little influence on the content of acetol during the distillation process, and therefore a constant heating rate for distillation was adopted. The contents of methanol, furfural, phenol derivatives were higher in the early 45% evaporated fraction, and then the contents of theirs decreased with distillation going. The contents of acetol and acetic acid were lower in the early distilled fractions, and then increased distinctly after 45% volumetric fraction. It can be seen from Table 1 that the content of acetol in the latter 50% fraction was higher, and the contents of volatile components and phenol derivatives were lower than those in the original raw wood vinegar. So the latter 50% evaporated fraction can be used as the source material for further treatment.

Acetol (145 °C) has similar boiling point with acetic acid (117.9 °C) and has high solubility in water, so the separation of acetol by direct distillation of the water solution with much acetic acid inside is hard. So solvent extraction to transfer acetol from water phase to organic phase was considered. According to the like dissolves the like principle, the solvent like acetone must have high solubility to acetol, but these solvents dissolve with water very well too, so the screen for appropriate solvent is needed. Herein four solvents of toluene, chloroform, ethyl acetate, hypnone were tested. Raw wood vinegar (5 ml) was blended with solvent (5 ml) in a test tube, mixing by fast shaking up and down for 5 min, laying aside for 10 min, and then the organic layer was analyzed by GC–MS. The peak areas of the main components in different solvents were shown in Fig. 3. It can be seen from Fig. 3 that the ratio of ace-

### Table 1

Composition of raw wood vinegar and latter 50% evaporated fraction.

<table>
<thead>
<tr>
<th>No.</th>
<th>RT/min</th>
<th>ID</th>
<th>Raw Area%</th>
<th>L50% Area%</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.</td>
<td>2.11</td>
<td>Acetaldehyde</td>
<td>0.12</td>
<td></td>
</tr>
<tr>
<td>2.</td>
<td>2.42</td>
<td>Acetone</td>
<td>0.99</td>
<td></td>
</tr>
<tr>
<td>3.</td>
<td>2.46</td>
<td>Acetic acid, methyl ester</td>
<td>0.44</td>
<td></td>
</tr>
<tr>
<td>4.</td>
<td>2.84–2.88</td>
<td>Methyl alcohol</td>
<td>4.55</td>
<td>0.038</td>
</tr>
<tr>
<td>5.</td>
<td>3.69</td>
<td>2,3-Butanedione</td>
<td>0.06</td>
<td>0.182</td>
</tr>
<tr>
<td>6.</td>
<td>6.1–7.24</td>
<td>Water</td>
<td>80.97</td>
<td>79.715</td>
</tr>
<tr>
<td>7.</td>
<td>7.5</td>
<td>Propanenitrile</td>
<td>0.03</td>
<td></td>
</tr>
<tr>
<td>8.</td>
<td>9.37</td>
<td>Formamide</td>
<td>0.02</td>
<td></td>
</tr>
<tr>
<td>9.</td>
<td>9.7</td>
<td>2-Propanone, 1-hydroxy-</td>
<td>3.41</td>
<td>4.182</td>
</tr>
<tr>
<td>10.</td>
<td>10.41</td>
<td>2-Cyclopent-1-one</td>
<td>0.04</td>
<td></td>
</tr>
<tr>
<td>11.</td>
<td>10.52</td>
<td>2-Cyclopent-1-one, 2-methyl-</td>
<td>0.01</td>
<td></td>
</tr>
<tr>
<td>12.</td>
<td>10.8</td>
<td>Butanoic acid, 2-oxo-</td>
<td>0.1</td>
<td></td>
</tr>
<tr>
<td>13.</td>
<td>11.49</td>
<td>Acetic acid</td>
<td>7.28</td>
<td>14.241</td>
</tr>
<tr>
<td>14.</td>
<td>12.51</td>
<td>Furfural</td>
<td>0.61</td>
<td>0.078</td>
</tr>
<tr>
<td>15.</td>
<td>13.91</td>
<td>Propanoic acid</td>
<td>0.7</td>
<td>0.972</td>
</tr>
<tr>
<td>16.</td>
<td>14.78</td>
<td>2-Furancarboxaldehyde, 5- methyl-</td>
<td>0.02</td>
<td></td>
</tr>
<tr>
<td>17.</td>
<td>15.43</td>
<td>Butanoic acid</td>
<td>0.03</td>
<td>0.034</td>
</tr>
<tr>
<td>18.</td>
<td>15.95</td>
<td>1-Penten-3-one, 2-methyl-</td>
<td>0.03</td>
<td></td>
</tr>
<tr>
<td>19.</td>
<td>17.81</td>
<td>Cyclooctane</td>
<td>0.06</td>
<td></td>
</tr>
<tr>
<td>20.</td>
<td>18.1</td>
<td>Phenol, 2-methoxy-</td>
<td>0.33</td>
<td>0.128</td>
</tr>
<tr>
<td>21.</td>
<td>18.87</td>
<td>Phenol, 2-methoxy-4-methyl-</td>
<td>0.11</td>
<td>0.025</td>
</tr>
<tr>
<td>22.</td>
<td>19.16</td>
<td>Phenol</td>
<td>0.11</td>
<td>0.099</td>
</tr>
</tbody>
</table>

Raw – raw wood vinegar.
L50% – latter 50% evaporated fraction.
tol to acetic acid in chloroform was the highest, while ethyl acetate had the highest solubility. Herein ethyl acetate was chosen as the extracting solvent, since acetic acid may be eliminated by base treatment.

The latter 50% evaporated fraction (5 ml) was treated by Na$_2$CO$_3$ in a test tube, and then blended with ethyl acetate (5 ml) for solvent extraction. After standing for 10 min the organic layer was analyzed. The influence of the amount of Na$_2$CO$_3$ on the composition of the organic solution was shown in Fig. 4.

It can be seen from Fig. 4 that when Na$_2$CO$_3$ was 0.156 g, the amount of acetic acid, propanoic acid were rather high; acetic acid and propanoic acid disappeared when Na$_2$CO$_3$ was over 0.34 g; the content of acetol increased with increasing amount of Na$_2$CO$_3$, and researched the highest level at 2.15 g; too much Na$_2$CO$_3$ of 3.1001 g made the content of acetol lower. The content of water had a reverse order with acetol. The content of phenol derivatives increased first and then fell off with increasing amount of Na$_2$CO$_3$. It can be explained that acid can be neutralized by Na$_2$CO$_3$, and meanwhile water reacts with excessive Na$_2$CO$_3$ to form hydrates like Na$_2$CO$_3$·10H$_2$O or Na$_2$CO$_3$·7H$_2$O or Na$_2$CO$_3$·H$_2$O. The deduced content of water makes acetol concentrated, while the overmuch Na$_2$CO$_3$ may absorb acetol and makes the content of acetol lower instead.

The distillation of ethyl acetate solution was tested. It was found that acetol can be easily concentrated from 1% to above 40% with bottom temperature of 85–145 °C at atmospheric pressure, while a further distillation of the concentrated acetol system (>40%) was rather hard. The bottom solution (27 ml) of acetol (46.5%) was distilled under a vacuum condition with bottom temperature of 50–125 °C, and 12 ml bottom solution was left after distillation. In the bottom solution, the content of ethyl acetate was distinctly decreased from 29.1% to 3.2%, but the content of acetol did not rise accordingly; instead it slightly declined from 46.5% to 44.7%, while the content of 2-hydroxy-3-methyl-2-cyclopenten-1-one (HMCPO) distinctly increased from 8.6% to 13.5%. In the evaporated phase, the content of ethyl acetate was the highest of 85%, the content of acetol was just 1.2%, and no other heavier components were detected. The last bottom solution (7 ml) was further distilled under a vacuum condition with bottom temperature of 72–150 °C to transfer acetol to the evaporated phase. After distillation, 3 ml evaporated phase was obtained. In the evaporated phase, the content of acetol increased a little to 50.8%, while an unknown compound appeared in a remarkable abundance of 21.4%. It indicates that during the distillation process acetol may convert to some other compounds, and the unknown compound and HMCPO may be the compounds that formed from acetol. The unknown compound was speculated as 5-methyl-6H-pyran-3-one (MPO). The identification of MPO and the possible formation routes of HMCPO and MPO were systematically discussed in another paper. Herein, the possible formation route from acetol to HMCPO is representatively illustrated in Fig. 5. TIC of the evaporated liquid is shown in Fig. 6.

By finely distillation condition control the content of acetol can be increased to some extent. Till now the best level of acetol was 62.4% (area percentage), the second abundant component was its homolog 1-hydroxy-2-butanone (19.6%), the other major components were ethyl acetate (8.1%), acetic acid (6.2%), and water (1.1%), while the yield of acetol was still quite low (4.9%). Herein

![Fig. 3. Extraction ability of different extraction solvents on main components in wood vinegar.](image1)

![Fig. 4. Effect of the amount of Na$_2$CO$_3$ on the contents of main components in ethyl acetate solutions.](image2)

![Fig. 5. Deduced reaction routes for formation of HMCPO (F).](image3)
Acetol (62.5%) was acquired. TIC of the distillate is shown in Fig. 7 and reducing the transfer of heavier components into the distillate. For the increasing of acetol by lessening the conversion of acetol the yield of acetol is defined as the ratio of acetol obtained (product of the area percentage of acetol and the volume of the concentrated solution) to the amount of acetol in the raw wood vinegar (product of the area percentage of acetol and the volume of the raw wood vinegar). The main processes were as follows: the latter 50% evaporated distillate of raw wood vinegar was distilled in 95–107 °C at atmospheric pressure; the bottom solution was treated by Na₂CO₃ and then was filtrated; the filter cake and the filtrate was extracted with bottom temperature 75–85°C, and the distillate with concentrated acetol (62.5%) was acquired. TIC of the distillate is shown in Fig. 7. It can be seen from the comparison between Figs. 6 and 7 that the unknown compound (peak 7, MPO) that may derived from acetol, and the heavier components 8, 9, 10 did not appear in Fig. 7. It indicates that the distillation temperature is sensitive to the content of acetol and the lower treating temperature is advantageous for the increasing of acetol by lessening the conversion of acetol and reducing the transfer of heavier components into the distillate.

4. Conclusion

The acetol concentrating from wood vinegar was preliminarily investigated. It was found that in the process of wood vinegar distillation, heating rate had very little influence on the content of acetol with distillation going. The contents of methanol, furfural, phenol derivatives were higher, and the contents of acetol and acetic acid were lower in the early 45% distilled fraction, and then methanol, furfural, phenol derivatives decreased, and acetol, acetic acid increased distinctly. Ethyl acetate had the highest solubility among the four solvents of toluene, chloroform, ethyl acetate, and hypnone. Excessive Na₂CO₃ made the content of water decrease and acetol increase, while overmuch Na₂CO₃ made the content of acetol lower instead. In the organic solution distillation process, acetol can be easily concentrated to above 40%, while a further distillation of the concentrated system is hard. Conversion of acetol during distillation process may be an important cause to the low yield of acetol, and a lower treating temperature is advantageous for the increasing of acetol.

Acknowledgments

The work is supported by the National Basic Research Program (973 Program), No. 2004CB719704.

References