Black Liquor Gasification Characteristics. 2. Measurement of Condensable Organic Matter (Tar) at Rapid Heating Conditions

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Experiments were performed to investigate tar formation during devolatilization of black liquor at high heating rates, at temperatures from 700 to 1000 °C and 1 bar of total pressure. The tar compounds detected were grouped into two categories, semivolatiles and nonvolatiles, based on their molecular weights and boiling points. The semivolatile tar collected ranged from 0.1% to 5% of the carbon in black liquor, while the nonvolatile tar collected ranged from 0.02 to 1%. However, carbon balances suggested that tar may have accounted for 20% or more of the carbon in black liquor at 900 °C and below. Tar characterization revealed a similarity between the lignin substructure and some of the tar compounds produced. This indicates that kraft lignin was the source of these tar compounds. Tar yields were controlled by a number of competitive formation and decomposition reactions, which are influenced by the residence time, temperature, and gas composition. Low temperatures favored the formation of more aromatic tar species with diversified substituted groups such as toluene and xylenes. These compounds were formed at a finite rate, and their concentrations were increased with gas/particle residence time. Tar species formed more rapidly and decomposed more rapidly at higher temperatures. Nonsubstituted aromatics such as benzene were more stable at higher temperatures and were formed by decomposition of substituted aromatics. Oxidizing gases enhanced both the formation and destruction of tar species, depending on the temperature and residence time.

Introduction

Formation of semivolatile and nonvolatile (condensable) organics (tar) during gasification of biomass and black liquor is of great interest because these compounds are problematic contaminants when the product gas is used as a fuel in gas turbines or as syngas for methanol production. These compounds can also contaminate gas cleanup operations upstream of the turbine or chemical plant, and they represent a potential loss of chemical or fuel. They pose a safety hazard and, in black liquor gasification, a contamination problem for the alkali recovery process.

Tar production has earlier been identified as a problem for low-temperature gasification of biomass, including kraft black liquor.¹,² However, contamination problems with condensable organic matter in green liquor have been reported in a commercial black liquor gasification plant using an entrained-flow gasifier.³ The gasifier at this plant operated at 950–1000 °C.

Though there are a number of studies on tar formation from coal and biomass gasification processes, there are very little data available on tar formation and composition during black liquor gasification. There are but a few reports on tar yields and almost no data on speciation of the tar and condensable organic matter produced. The results reported were from batch pyrolysis and single droplet experiments.⁴ The results from these three studies are summarized in Table 1. All three were conducted at relatively low heating rates, and the tar species were not analyzed.

The objective of the experimental work reported here was to characterize the formation and evolution of condensable and semivolatile organic compounds (tar) during pyrolysis and gasification of black liquor at

| Table 1. Gas, Tar, and Char Yields Reported from Pyrolysis Studies with Kraft Black Liquors |
|-------------------------------------------------|----------------|----------------|
| Feuerstein et al.⁴ | Battacharya et al.⁵ | Gairns et al.⁶ |
| nominal initial particle size, mm | 0.4 | 2.4 |
| dry solids content, % | 65 | 100 | 70 |
| temperature, °C | 400–975 | 620–740 | 400–900 |
| heating rate, °C/s | ~0.1 | ~10 | ~100 |
| residence time, s | ~7000 | 120–900 | 15–130 |
| tar yields | | | |
| % of dry black liquor solids | 2–10 | 9–36 | 7–25 |
| % of dry ash-free matter | 4–18 | 16–63 | 12–44 |
| temp at max tar yield, °C | 570–830 | 700 |

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heating rates comparable to those in commercial, entrained-flow, black liquor gasifiers. This paper is the second in a series that deals with the fate of carbon-containing compounds from pyrolysis and gasification of kraft black liquor at high heating rates. The first paper in this series reported the evolution of light gases during pyrolysis and gasification of black liquor at similar conditions.7

Major problems in research on tar formation and destruction arise from inconsistencies in the definition, collection, and analysis of tar species. Because tar encompasses a wide spectrum of organic compounds, tar has been defined in many different ways. One operational definition of tar from biomass gasification is that it is the organic matter that condenses downstream of the gasifier, under normal process conditions.9-13 Another definition is that tar includes only those organic compounds with boiling points higher than a specific temperature.14-16 A third is that tar is any organic compound that condenses at or below the temperature of the tar-trapping system in their experiments.17,18 To date, no consistent definition of tar has been established within the area of biomass pyrolysis and gasification.

The process of tar production during pyrolysis or gasification of biomass involves several steps. Evans and Milne19,20 characterized the volatile products from biomass pyrolysis and gasification as follows:

(i) Primary products: cellulose-, hemicellulose-, and lignin-derived products such as levoglucosan, hydroxyacetaldehyde, furfurals, and methoxyphenol.

(ii) Secondary products: phenolics and olefins.

(iii) Alkyl tertiary products: methyl derivatives of aromatics such as methylacenaphthylene, methylnaphthalene, and toluene.

(iv) Condensed tertiary products: aromatic hydrocarbons without substituents such as benzene, naphthalene, acenaphthylene, and pyrene.

They noted that the product distribution between each category depends on process parameters such as the oxygen/biomass ratio, residence time, reactor temperature, and type of biomass material and described the effect of time, temperature, and oxygen on the product composition.21

The lack of a standard method of tar sampling has led to a variety of tar collection methods, and this has created problems in comparing results from different studies. Acetone,22-24 methylene chloride,25-33 dichloromethane, methanol, toluene, and water have all been widely used as solvents to condense and collect tar. Nonsolvent methods, such as condensing tar on cotton or fiberglass filters, have also been employed.31,32

Experimental and Analytical Procedures

The measurements of tar formation from black liquor gasification were conducted in a laboratory-scale laminar entrained-flow reactor (LEFR). This type of reactor has two features that are important when obtaining fundamental pyrolysis and combustion data: it provides very rapid heating, and it uses particles that are small enough so that temperature differences within the particles are small. A schematic of the LEFR used in the experiments reported here is shown in Figure 1. This reactor, its operating procedures, and methods used for the preparation of black liquor solids are described in the first paper in this series.7 In this section we describe the experimental and analytical procedures that are specific to the measurement of tar and condensable organic matter.

The gas and solids feed rates used in the experiments were a total gas input rate of 15–20 L/min at room temperature and solids feed rates from 0.3 to 1.5 g of black liquor solids/min. The range of reaction conditions in the LEFR were from 700 to 1000°C and from 0.3 to 1.5 s particle residence time in an atmosphere of 100% nitrogen at 1 bar of total pressure. A limited number of experiments were performed with water vapor and CO2 present to evaluate the effect of these mild oxidizing agents on the distribution of organic products. The concentrations of water vapor and CO2 employed were both 12 vol % in nitrogen. This is roughly the concentration of both gases expected during gasification of black liquor containing 20 wt % water by partial oxidation with elemental oxygen.

The products analyzed from the experiments described in this paper were the condensable organic and tar compounds. They were collected with a three-stage scrubber that also collected the char residue produced.
A product collector between the reaction zone and the scrubber was used to cool the products, thereby quenching any high-temperature chemical reactions. The collector had a porous inner surface along its full length, through which nitrogen flowed into the collected reaction products. The nitrogen flux was sufficient to prevent thermophoretic deposition of aerosols on the inner surface of the collector. The scrubber was close-coupled to the exit of the product collector (see Figure 1). The close coupling shortened the distance between the reactor exit and the scrubber, which minimized condensation and collection of tar in the gas transport line. To ensure capture of the widest range of tar compounds, each experiment was conducted twice, using a different gas scrubbing solvent (methanol or methylene chloride) in each of the replicate runs.

Collecting tar by this method has the advantage of processing all of the products of pyrolysis or gasification at a moderate temperature (250–300 °C) where at least many of the tar compounds would not have condensed prior to entering the scrubbers. However, the method has several limitations. First, because the gases are not filtered prior to scrubbing, any soluble organic matter still in the char residue is extracted and collected as tar. Second, some of the tar compounds may be reactive and form higher molecular weight compounds that are insoluble in the scrubbing solutions. Third, some of the tar compounds may adsorb on the high surface area carbon residue, thus being removed from solution. Fourth, there is no way to distinguish between char and soot that may have been formed during thermal cracking of tar compounds. Soot has been observed qualitatively during devolatilization of kraft black liquor, but quantification of soot production from black liquor has never been reported.

Samples of the tar-containing scrubber solutions from two selected experiments were sent to the Ecology and Environment Laboratory, Lancaster, NY, for a screening analysis of tar components. The results were used in the development of analysis procedures employing gas

Table 2. Some of the Major Black Liquor Tar Species IDENTIFIED

<table>
<thead>
<tr>
<th>Compound</th>
<th>Structure</th>
<th>BP (°C)</th>
<th>Compound</th>
<th>Structure</th>
<th>BP (°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Benzene</td>
<td></td>
<td>80</td>
<td>Toluene</td>
<td></td>
<td>111</td>
</tr>
<tr>
<td>o-, m-, p-Xylene</td>
<td></td>
<td>139-145</td>
<td>Methylstyrene</td>
<td></td>
<td>170</td>
</tr>
<tr>
<td>Indene</td>
<td></td>
<td>181</td>
<td>Phenol</td>
<td></td>
<td>182</td>
</tr>
<tr>
<td>Naphthalene</td>
<td></td>
<td>218</td>
<td>2,6-Dimethoxy-phenol</td>
<td></td>
<td>234</td>
</tr>
<tr>
<td>Trimethoxy-benzene</td>
<td></td>
<td>247</td>
<td>Hydroxy-methoxy-benzoic acid</td>
<td></td>
<td>250</td>
</tr>
<tr>
<td>Acenaphthene</td>
<td></td>
<td>279</td>
<td>Biphenylene</td>
<td></td>
<td>(m.p. 109°C)</td>
</tr>
<tr>
<td>Anthracene</td>
<td></td>
<td>340</td>
<td>Phenanthrene</td>
<td></td>
<td>336</td>
</tr>
<tr>
<td>Phenalene</td>
<td></td>
<td>292</td>
<td>Fluoranthene</td>
<td></td>
<td>375</td>
</tr>
<tr>
<td>Perylene</td>
<td></td>
<td>350-400</td>
<td>Pyrene</td>
<td></td>
<td>404</td>
</tr>
</tbody>
</table>
chromatography (GC) with a headspace injection technique\textsuperscript{34} to identify and quantify the lighter tar compounds collected in the methanol scrubber solutions. Concurrent analysis using GC/MS was performed for quantification of heavier tar components collected in methylene chloride solutions. Because these heavy components were present at very low concentrations, the scrubber solutions were concentrated by evaporation before injection into the analyzer.

**Results and Discussion**

The kraft lignin fragments in black liquor, although having undergone digestion in strong alkali solutions at 160–170 °C, still consist mainly of a two-dimensional, cross-linked network of aromatic fragments. This kraft lignin is composed of mainly individual benzene rings connected by aliphatic and/or ether linkages. Figure 2 shows the proposed structure of a pine kraft lignin molecule as depicted by Marton.\textsuperscript{35}

Preliminary analysis results of tar from black liquor pyrolysis revealed a wide variety of organic aliphatic and aromatic compounds ranging from semivolatile, single-ring aromatic compounds to multiring, nonvolatile aromatic compounds. A number of organosulfur compounds and long-chain aliphatic hydrocarbons were also detected in smaller amounts. The major tar components identified are shown in Table 2, along with their melting and/or boiling points. Figure 3 is a sample of a typical gas chromatogram that shows some of these compounds.

**Source of Black Liquor Tars.** The results of characterization and quantification of black liquor tar suggest the source of these compounds. The chemical species in kraft black liquor consist mainly of alkali (kraft) lignin, hydroxy acids, extractives, sodium, sulfide, thiosulfate, and sulfate, along with smaller amounts of other components such as methanol, potassium formate, acetic, and chloride. Of these major components, kraft lignin is the only one that is composed mainly of aromatic substructures.

A comparison of the major tar species from black liquor devolatilization with the aromatic substructures of lignin suggests that those tar compounds are very likely the result of thermal decomposition of lignin and re-formation of the lignin-derived constituents. Many of the tar species identified, such as 2,6-dimethoxyphenol and hydroxymethoxybenzoic acid, are obviously part of lignin substructures. During the devolatilization process, some weak bonds that connect the aromatic substructure of lignin may be broken to form light tars, while re-formation (thermal condensation) of broken aromatic groups results in the formation of heavier multiring tars.\textsuperscript{36}

**Quantitative Determination of Black Liquor Tars.** Because there is a fine distinction between the behavior of semivolatile and nonvolatile tar compounds
in terms of their chemical properties and collection methods, the following discussion begins with the results of the measurements of semivolatiles, followed by the findings of the nonvolatile compounds. In the present work, we define semivolatile tar species to be those with no more than 10 carbon atoms and nonvolatile tar species to be those with more than 10 carbon atoms. With these definitions, most semivolatile tar species have boiling points below 250 °C. Nearly all nonvolatile tar species had boiling points above 300 °C.

Formation of Semivolatile Tar Compounds

Effect of the Temperature and Residence Time under Pyrolysis Conditions. The semivolatile tar species were collected by passing the pyrolysis products (gas, char, and fume) through methanol-filled scrubbers. The most abundant semivolatile tar species were benzene, naphthalene, toluene, xylenes, and methylstyrene. A number of chemicals present in much smaller quantities were also found, some of which were identified and others which were not.

Figure 4 illustrates the change in the benzene concentration in the product gas with increases in the residence time and reactor temperature. At 800–1000 °C, the benzene concentration increased with both residence time and temperature, while there was no significant change at 700 °C. As much as 1.4% of the carbon input had been converted to benzene at 1000 °C in 1.3 s. The increase at higher temperatures resulted from dissociation of other heavier, substituted aromatic compounds to a more stable, nonsubstituted compound, benzene. At 700 °C, carbon–carbon bond dissociation is probably still sluggish, resulting in a relatively low and constant concentration of benzene as well as of other semivolatiles at longer residence times.

Figure 6. Toluene vs residence time and reactor temperature.

Figure 7. Sum of o-, m-, and p-xylene vs residence time and reactor temperature.

Figure 8. Methylstyrene vs residence time and reactor temperature.

Figure 9. Sum of all semivolatile species measured vs residence time and reactor temperature.

Figure 10. Conversion to C_{4}–C_{10} at a residence time of 0.6 s (% of C input).

Figure 5 shows the concentration profiles for naphthalene. The concentration of naphthalene increased with residence times at 700–900 °C. Unlike benzene, its concentration decreased rapidly with a residence time at 1000 °C. Naphthalene is readily cracked catalytically at 800–900 °C, and conversions of 10–20% can be achieved even without catalysts at 900 °C and space velocities of less than 1 s\(^{-1}\).\(^{37}\) The data in Figure 5 indicate that naphthalene is much less stable at 1000 °C than at lower temperatures.

Figures 6–8 show the conversion to substituted single-ring compounds: toluene, xylenes, and methylstyrene. These compounds, as well as other substituted aromatics not shown here, exhibited a similar concentration profile. A very small amount of these compounds was detected at 700 °C and the shortest residence time (0.3 s). At longer residence times, their concentrations increased but were still relatively low in comparison...
were highest at the shortest residence time and destruction reactions began early. Hence, the tar levels decreased as the residence time increased; this indicated the onset of tar thermal destruction reactions at 800 °C (not shown), the concentrations increased with the residence time, reached a maximum, and then started to decrease. As mentioned earlier, the reduction in the amounts of these compounds may have resulted from the thermal dissociation of the compounds with substituted branches to the more stable compound benzene.

Formation of semivolatiles took place rapidly at 1000 °C. The highest concentrations of these substituted aromatics were measured at the shortest residence time at this temperature. However, the concentrations decreased rapidly with increasing residence time, probably via the competitive thermal destruction reactions at high temperature.

To show more clearly the overall conversion of semivolatile tar, the concentrations of all of the semivolatile species identified were summed and plotted in Figure 9. In general, at low temperatures the amount of semivolatile compounds increased as the residence time increased. The total concentration leveled off at 700 °C, probably because of the limited extent of organic carbon bond breaking at this low temperature.

In contrast, the total concentration of semivolatiles continued to increase with the residence time at 800 °C, suggesting the dominance of semivolatile tar formation reactions at this intermediate temperature. At 900 °C, the tar concentrations reached a maximum and started to decrease as the residence time increased; this indicated the onset of tar thermal destruction reactions at higher temperatures. At the highest experimental temperature, 1000 °C, both the tar formation and thermal destruction reactions began early. Hence, the tar levels were highest at the shortest residence time and decreased as the residence time increased.

Effect of Different Gasification Conditions. To study the effect of gas composition on tar formation, a limited set of experiments was conducted using 12% water vapor and 12% water vapor/12% CO₂ in nitrogen as the feed gases. The results, plotted as the percent of carbon input converted to C₄–C₁₀ tars, are displayed in Figures 10 and 11 for residence times of 0.6 and 1.0 s, respectively. The percentage of carbon input converted to C₄–C₁₀ tar compounds increased with temperature in all three gas environments. The amount converted ranged from 1.2% at 700 °C in nitrogen to as much as 4.9% at 1000 °C in 12% water vapor (both are at 0.6 s). At 0.6 s (Figure 10), the addition of oxidizing gases increased moderately the formation of tar compounds. The effect of oxidizing gases was greatest at 1000 °C, at which temperature 2.9%, 4.9%, and 4.2% of the carbon input was converted to tar in gas atmospheres of 100% nitrogen, 12% water vapor, and 12% water vapor/12% CO₂, respectively. This may result from greater dissociation of larger black liquor constituents promoted by these gases.

At the longer residence time (Figure 11), more tar was present in a nitrogen environment than in the presence of water vapor and CO₂ at 900–1000 °C, while less tar was measured at 800 °C in nitrogen. This is the result of the competing tar formation and destruction processes. Oxidizing gases increase the extent of conversion of organic matter to tar, which is why more tar is present in their presence at 1.2 s and 800 °C than in nitrogen. At 900 and 1000 °C, tar destruction dominated over tar formation. At these temperatures and the longer residence time, the oxidizing gases were effective in destroying tar species so that less tar was present in the presence of oxidizing gases than in nitrogen.

In general, the extent of semivolatile tar reactions is controlled by the dynamics of the competitive formation and destruction reactions of these compounds. The formation reactions include the dissociation of the larger organic components formed during primary devolatilization. Both formation and destruction reactions are influenced by the residence time, temperature, and gas composition. Oxidizing gases initially facilitate the formation of semivolatiles by dissociation of larger components, while later they destroy these components.

Evolution of Nonvolatile Tars from Pyrolysis of Black Liquor. Nonvolatile organics are heavier compounds with such low vapor pressure that they do not vaporize appreciably at room temperature. In this study, these compounds are defined as any organic matter with more than 10 carbon atoms in the molecule. Methylene chloride was used as a solvent to ensure the best possible collection of these tar compounds, which are mainly polynuclear aromatics and aliphatic hydrocarbons.

Because of the very dilute nature of these nonvolatile tar samples collected in methylene chloride, concentration by a factor of 30 was required before GC/MS injection in order to be able to detect the tar constituents. The GC/MS analysis results revealed a wide variety of organic compounds. Some of the compounds identified were acenaphthylene, anthracenedione, methylphenalenes, phenalene, phenylenes, and phenanthrene. There were also unknown polyaromatics, phenolics, and long-chain hydrocarbons. Figure 12 contains an example of a chromatogram from the quantification of these compounds. A mass spectrum of 1H-phenalenone, one of the compounds identified, is shown in Figure 13.

To account for the unknown compounds, their concentrations were estimated based on the response of acenaphthylene. This standard was selected based on the average mass number of these unidentified compounds. The concentrations of each compound were then summed and reported as the total condensable tars (C₁₀–C₂₀), as plotted in Figure 14.

With a reactor temperature of 700 °C, the nonvolatile tar levels increased from 0.02% of the carbon in black liquor at 0.4 s residence time to 0.4% at the residence...
time of 1.3 s. The corresponding values at 800 °C were 0.04% of the carbon input at 0.4 s and 0.7% at 1.3 s residence time. The low tar levels at short residence times and low reactor temperatures suggest that the nonvolatile tar formation reactions (dissociation of a nonsubstituted C–C bond in BLS) had not yet commenced at these conditions.

At 900 °C, the tar concentrations increased from 0.3% at 0.4 s to a maximum of 0.8% and decreased as the residence time increased. This result suggests that, at this temperature, the tar formation reactions started early, as did the competitive tar destruction reactions. This finding was also confirmed by the report on biomass tar formation by Kinoshita et al., who found that the destruction of aromatic hydrocarbons proceeded measurably at temperatures above 850 °C.

At the highest experimental temperature, 1000 °C, the highest tar content, equivalent to 1.0% of black liquor carbon, was measured at the shortest residence time. The concentrations then decreased to 0.3% at the longest residence time. The highest value, 1.0%, does not represent the maximum obtainable condensed tar formation from black liquor pyrolysis because the quantity may have been higher at shorter residence times than could be achieved with the LEFR. A similar implication applies to the experiments at 700 and 800 °C, at which temperatures the tar concentrations had not yet reached the maximum at the longest experimental residence times.

Conclusions

In LEFR experiments performed to investigate tar formation during devolatilization of black liquor at high heating rates, the tar compounds detected were grouped into two categories, semivolatiles and nonvolatiles, based on their molecular weights and boiling points. Over the range of experimental conditions employed, semivolatile tar yields ranged from 0.1% to 5% of the carbon in black liquor, while the nonvolatile tar accounted for 0.02–1% of the carbon in black liquor. Tar characterization revealed a strong similarity between the lignin substructure and some of the tar compounds produced. This suggests that kraft lignin was the source of these tar compounds.

Tar yields were controlled by a number of competitive formation and decomposition reactions, which are influenced by the residence time, temperature, and gas composition. In general, low temperatures favor the formation of more aromatic tar species with diversified substituted groups such as toluene and xylenes. These compounds formed relatively slowly, at a rate measurable within the time frame of the experiments, and their concentrations increased with the residence time. Tars formed more rapidly and decomposed more rapidly at higher temperatures. Nonsubstituted aromatics such as benzene were more stable at higher temperatures and were formed by decomposition of substituted aromatics. Oxidizing gases enhanced both the formation and destruction of tars, depending on the temperature and residence time.
In general, the findings are comparable to those of coal and other biomass gasification studies with respect to both the formation levels and tar species.

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Literature Cited


