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Wood Waste Combustion in Boilers

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Information on the Sulfur Content of Bark and its Contribution to SO₂ Emissions when Burned as a Fuel

WOOD WASTE
COMBUSTION IN
BOILERS
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References 10 & 23

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Conjecture exists about the SO₂ emissions resulting from the burning of wood residues since current New Source Performance Standards for large power boilers permit the use of the Btu in wood residues in calculating allowable SO₂ emission rates. The concern is based on available knowledge of the sulfur content of bark and wood residues which, if stoichiometrically converted to SO₂ would account for SO₂ levels of about 130 ppm in the flue gas. This information is apparently the background for selection of an emission factor of 0.375 lb SO₂/million Btu of wood residue fired that is included in EPA resource documents. This paper describes a field study carried out to determine the amount of SO₂ generated when burning representative bark. The study involved a sulfur fuel balance around the combustion device by determining sulfur content of the bark fed, and sulfur leaving the boiler in solid and gaseous forms, namely ash, fly ash, and SO₂. The study showed that just over 5% of the sulfur contained in the bark was emitted as SO₂ which amounted to 0.001 to 0.02 lb SO₂/million Btu in the bark fed. The remainder of the sulfur was accounted for in the ash combustion products. The findings support the conclusion that the sulfur content of wood is not stoichiometrically converted to SO₂.

references were for the most part not specific as to the specie of bark involved. The EPA's emission factors for wood waste-fired boilers are based on the same range of 0 to 0.2% sulfur content, where an arbitrary average of 0.1% is selected, resulting in an emission factor of 0.375 lb SO₂/million Btu (86% stoichiometric conversion). These values suggest gaseous concentrations of SO₂ on the order of 130 ppm while the limited data available indicated measured concentrations approaching one-tenth of these levels.

In order for the pulp and paper industry to meet their commitment to (a) incrementally decrease purchased energy consumption over the next several years, or (b) become energy sufficient, increasing emphasis will be placed on the utilization of bark and wood residues as a primary fuel. Although it is logical to expect that appropriate concessions might be offered relative to allowable emission levels in order to encourage the use of these energy resources, current indications are that increasingly more attention will focus on these sources insofar as regulatory action is concerned. This paper addresses one of the issues which has already been raised regarding the emissions from burning wood residues, namely their SO₂ contribution as a result of their sulfur content.

Background

Recently there has been conjecture in EPA about the SO₂ derived from the sulfur content contained in typical tree

barks. This question arose due to the recent amendments to Subpart D, Standards of Performance for New Stationary Sources (40 CFR 60). Essentially this regulation as amended by the EPA November 22, 1976, (41 FR 51397), permits the use of the Btu content of wood in calculating allowable SO₂ emissions from combination fuel-fired boilers. The issue has been raised as to the levels of sulfur contained in barks, and the subsequent emission levels of SO₂ which would be associated with the combustion of these fuels. Subsequently, a project was included in the NCASI 1978 technical studies program to address these issues.

Published Information

In contrast to the extensive literature available on the chemistry of wood, relatively little is published on the chemistry of bark. Nevertheless, limited information was located from seven sources, suggesting that the sulfur content of bark may vary from 0 to 0.2% on a dry weight basis. However, these

Objectives

Consistent with the issues which have been raised, i.e., the SO₂ emission levels associated with the combustion of bark and wood residues in dedicated boilers or combination fuel-fired boilers, a straightforward investigation was undertaken. Accordingly the objectives of this investigation were to (a) determine what was known about the sulfur content of bark (and wood residues) based on published information, and (b) perform field testing at selected sites to determine the fate of sulfur contained in bark and wood residue type fuels when fired in boilers burning bark or sulfurless fossil fuel. During these investigations, an attempt was made to account for all of the sulfur, to the extent possible, by developing a sulfur balance around the boiler system.

The investigative efforts described in this paper involved emission measurements, laboratory analysis, and data compilation associated during the operation of four different bark boilers.

Investigative Program and Procedures

Scope of Work

In order properly to address the pertinent issues, the following elements

were considered a minimum to support this investigative effort:

1. Compile a summary of the available information on the sulfur content of bark and wood.

2. Perform field testing at selected sites to determine the fate of sulfur contained in bark and wood residue type fuels when fired in dedicated boilers. During these investigations, an attempt was made to account for all of the sulfur, to the extent possible, by obtaining material samples and measurements as follows:

a. The SO₂ emission levels in boiler stack gases were continuously monitored for sufficient duration, during a stable operating period.

b. Samples of particulates being emitted during these test periods were collected and analyzed for sulfate content. Also, samples were collected from the particulate control device for the same purpose.

c. Samples from the boiler ash hopper were also collected and analyzed for sulfates.

d. A composite sample of the bark being fired was collected and analyzed for total sulfur content.

e. The pertinent boiler operating information was recorded during the test periods of each site.

3. The results of these analyses were used to develop a sulfur distribution profile for the specific fuel being burned at each test site.

4. It was also anticipated that in projecting the fate of the available sulfur, additional insight would be gained relative to any SO₂-particulate interactions.

Summary of Published Information Relative to Sulfur Content of Bark and Wood Waste

Sulfur Content of Bark. In contrast to the extensive technical literature available on the chemistry of wood, relatively little exists on the chemistry of bark. Nevertheless, limited information was located from several sources,¹⁻⁷ suggesting that the sulfur content of bark may vary from 0 to 0.2% on a dry weight basis. However, these references were for the most part not specific as to the specie of wood involved.

Based on studies by the Institute of Food and Agricultural Sciences, University of Florida¹ to determine the components of forest fire smoke, sulfur oxides have not yet been detected in forest fire smoke, and only organic soils contain more than a negligible amount. The EPA's *Compilation of Air Pollutant Emission Factors*² states that bark contains less carbon and nitrogen than wood, but more sulfur, with the amount

quoted as ranging from 0 to 0.075% by weight. Another EPA reference source³ quotes the amount of sulfur in bark to range from 0.05 to 0.075% by weight.

Ultimate analysis of 4 Douglas Fir barks used in pyrolysis development work performed by Boucher, *et al.*,⁴ suggested sulfur content to range from 0.04 to 0.16% by dry weight. A summary contained in yet another reference⁵ indicates the sulfur content for a variety of barks to range from a trace to 0.1% by weight.

The EPA's emission factor for wood waste-fired boilers, contained in *Environmental Pollution Control, Pulp and Paper Industry, Part I, Air*,⁶ is based on a range of 0 to 0.2% sulfur content, where an arbitrary average of 0.1% is selected. The value contained in this reference projects an emission level of 0.375 lb SO₂/million Btu (86% stoichiometric conversion of sulfur content). These values would further suggest gaseous concentrations of SO₂ on the order of 130 ppm, while the limited data available from the literature⁷ indicate measured concentrations approaching about one-tenth of these levels.

Other Physical and Chemical Properties of Bark. There are other important properties of bark which should be considered in an investigation addressing the potential SO₂ emissions from the combustion of bark. One of these is the ash content of bark. Published data⁸ show the ash content of bark to vary from 0.5 to 10.0%, with the greater portion of these values falling between 2.0 and 6.0%. However, the actual values encountered in the field will be somewhat higher due to varying wood composition, and the amount of dirt carried with the bark resulting from its contact with soil.

A second consideration is bark ash composition. Bark ashes are mainly composed of inorganic oxides, carbonates, and sulfates. The oxides of silica and calcium usually account for more than half of the ash content while oxides of iron, titanium, aluminum, magnesium, manganese, and carbonates of calcium are also present. The earlier cited reference data indicates ash sulfate (as SO₃) content ranging from 1.4 to 7.4%.

The properties of bark which have been discussed in this section will later be shown to have a substantial influence on the distribution of sulfur compounds in combustion products resulting from the burning of bark.

Need for Development of Sulfur Balance around Boiler Systems in This Study

During the initial stages of this investigation, preliminary testing to de-

termine SO₂ levels in flue gases resulted in much lower values than anticipated, based on the fuel sulfur content. Previous investigative work conducted by the NCASI⁹ revealed that the ash products of combustion do indeed react with SO₂ generated during combustion. It is also not known how much of the sulfur content of the fuel was originally in a sulfate form and not available for SO₂ generation. Consequently, in order to enhance the validity of this investigative effort, it was deemed imperative to develop a sulfur balance around the boiler system studied at each site, by including the following elements:

1. The SO₂ emission levels in boiler stack gases were continuously monitored for sufficient duration during a stable operating period.

2. Samples of particulates emitted during these test periods were collected for analysis of sulfate content. Also, samples were collected from the particulate control device for the same purpose.

3. Samples from the boiler ash hopper were also collected and analyzed for sulfates.

4. A composite sample of the bark fired was collected and analyzed for total sulfur content.

5. The pertinent boiler operating information was recorded during the test periods at each site.

Testing and Analytical Procedures Utilized

The testing and analytical procedures which were utilized to develop the required data will be summarized in this section.

Stack Gas SO₂ Determinations. Testing was performed on boiler flue gases using a Barton coulometric titrator to determine SO₂ concentrations. The decision to oxidize the gas sample thermally prior to analysis with the Barton titrator was predicated on the possibility that organic constituents contained in the flue gases might generate a bromine demand, thus resulting in an erroneously high indication of SO₂ concentration. The tests were conducted for a minimum duration of four (4) hours and were performed in accordance with the equipment and procedures outlined in NCASI AQITB No. 89.¹⁰

Analysis of Sulfur in Bark and Ash Samples. The sulfur analysis on all samples obtained during this investigation was performed in duplicate by an independent laboratory, which used a Leco DB-64 digital titrator for this purpose. The DB-64 Sulfur Titrator automates the familiar iodate titration used in the determination of sulfur by the combustion method, and is further

Table I. Sulfur distribution in dedicated bark boiler systems.

Mill No.	Bark feed lb/hr Dry Wt.	Percent ash in bark	Sulfur in bark		Sulfur released to atm. via stack		Heat Input MM Btu/hr	lb SO ₂ per MMBtu	Percent of total		
			Percent	lb/hr	Percent of total	lb/hr			Contained in		Discharged w/Grate ash
									Fly ash	Hopper ash	
1	28,090	1.3	0.068	19.1	0.7	0.134	257.6	0.104×10^{-2}	84.2	1.8	13.3
2	15,275	1.3	0.010	1.7	9.6	0.163	156.0	0.208×10^{-2}	31.0	3.8	55.6
3	18,000	2.5	0.060	10.4	5.9	0.614	144.8	0.84×10^{-2}	86.8	5.0	4.0
4	30,600	3.3	0.134	40.8	6.5	2.65	247.5	2.142×10^{-2}	-84.4-		5.1
									(By difference)		

described in Leco Bulletin No. 200-734.¹¹

Analysis of Sulfate in Ash Samples. In addition to having all ash samples analyzed by the Leco Furnace method for sulfur, sulfate determinations were also performed in the NCASI Southern Regional laboratory using the gravimetric method (barium chloride precipitation)¹² as specified in *Standard Methods*.

In utilizing this procedure on the bark samples, the material was "ashed" in the laboratory. This step also provided information on the ash content for each of the bark samples.

Results

The investigative efforts covered in this report resulted from the field testing, laboratory analysis, and data compilation associated with the operation of four different bark boilers.

Sulfur Content of Bark

The bark fuel supply at each of the mill sites consisted of a mixture from several sources such as that resulting from debarking of roundwood stored at the mill, and purchased bark from sawmills and other sources. Although the dominant specie was pine bark in all cases, there were substantial amounts of hardwood bark in the mixture as well. These barks were derived from wood harvested from the lower quadrant of the Southeastern United States (Alabama, Florida, and Georgia), the area essentially being a square of 400 miles (160,000 square miles).

Sulfur content of composite bark samples taken from each of the four study sites was 0.068, 0.010, 0.060, and 0.134% on a dry weight basis. These values are well within the ranges which have been reported in the literature surveyed.

Sulfur Contained in Ash Materials of Combustion

At each study site ash samples were taken at the points where these materi-

als are purged from the system: e.g., boiler grate ash, primary collector hopper fly ash and fly ash discharged with flue gases. Analysis of these samples showed that 90% or more of the feed fuel sulfur content is contained in (or on) these ash materials, the actual values being 99.3, 90.4, 95.1, and 93.5%. In the case of the higher value (99.3%), a large portion of the primary collector hopper fly ash was reinjected into the boiler. This provided a finer ash with longer retention times to react with SO₂, consequently resulting in almost complete adsorption of SO₂ gases generated during combustion.

In the case of the lower value (90.4%), analysis indicates that the flue gas fly ash contained the lowest amount (31.0%) of total sulfur and the grate ash contained the highest (55.6%) amount, suggesting that the bark size or some other physical factor is responsible for this distribution shift. Since this source was a gas and bark-fired boiler, the NO_x emission levels were high, suggesting a high combustion temperature which inhibits SO₃ formation and the subsequent sulfate specie formation.

Sulfur Emitted as SO₂ in Stack Gases

As indicated in the above discussion, for the sources sampled, in the most extreme case, less than 10% of the total sulfur content of bark fuel was released as SO₂ via the stack gas. These values for the four sources concerned were 0.7, 9.6, 5.9, and 6.5%. The higher percentage value of 9.6 occurs at the source with lowest fuel sulfur content (0.01%), and the probable causes for this result are discussed in the previous section.

A summary of all the pertinent data relative to this investigation is contained in Table I.

Discussion

Chemical and Physical Analysis of Bark and Wood Waste

The properties of wood residues and bark fuels can vary so greatly that a standard specification is not possible.

The differences should be recognized and accounted for in the engineering and operation of wood-fueled systems. Table II summarizes the analysis for several properties of selected wood species.

The ash content of wood residues is generally low, but still is significant when large quantities are burned. The ash content of bark usually is greater than that of wood because handling and harvesting of logs frequently causes dirt and sand to cling to the bark. Saltwater transport and storage of logs also can add to the ash content by deposition of sea salt in the wood or bark.

Review of the Combustion Mechanism

The basic process of burning wood-refuse fuels requires the evaporation of moisture, the distillation and combustion of volatile components, and the combustion of the remaining carbon materials. These three steps are accomplished either separately or simultaneously depending on the type of equipment that is selected for the particular installation. Boiler emissions are affected by the size distribution of fuel, firing method, reinjection of fly carbon (ash), furnace vertical velocity and residence time, and overfire air.

Factors Affecting Sulfur Distribution in Combustion Products

The issues which have been raised generate further interest in the sulfur content of wood residues and in the distribution of the sulfur in the products of combustion. Earlier work by Kaiser¹³ discusses the apparent effect of alkaline components of ash in uniting with sulfur oxides, and certainly the presence of sulfate sulfur in ash products of wood waste combustion has been established in the references quoted in this report, as well as that determined in our own laboratory.

The variables which affect the sulfur distribution are closely related to those cited in the previous section which also influence overall emission levels, i.e., size distribution of fuels, reinjection of fly

ash, residence time and velocity, and combustion temperature. Also, the fuel composition such as sulfur content (amount as free sulfur or sulfate) and ash content (and composition) may exert an effect as well.

Factors Contributing to SO₂ Emission Levels from Combustion of Bark

The SO₂ emission levels from bark and wood waste boilers have been shown to be extremely low (10 ppm or less) because of two major reasons, (a) the initial sulfur content of fuel is extremely low (less than 0.2%), and (b) most of the sulfur (90% or more) is combined with the ash products of combustion.

Conclusions

1. The sulfur content of the barks fired ranged from 0.01 to 0.134% by weight on a dry basis. This resulted in a sulfur input to the boilers ranging from 1.7 to 40.8 lb/hr.
2. The percentage of total sulfur fed which was released to the atmosphere via the stack as SO₂ ranged from 0.7 to 9.6%. Sulfur dioxide concentrations ranged from <1 to 10 ppm or 0.1 × 10⁻² lb to 2.14 × 10⁻² lb of SO₂/10⁶ Btu.
3. The total sulfur accounted for, based on calculations from analysis and material flow ranged from 86 to 113% of that contained in the bark feed.

4. In the case of the sources investigated only 10% or less with an average of just over 5% of the fuel sulfur content was emitted as SO₂. This fact is further substantiated by the sulfate content of the ash products of combustion, which are discharged at various points in the operation. Table I contains a summary of all pertinent data, and as indicated, all of the sulfur contained in the fuel is accounted for as SO₂, or as sulfate in ash released from the (a) boiler grate, (b) mechanical collector hoppers, and (c) the fly ash discharged with the exit gas.

5. The reaction of sulfur, oxygen, and ash minerals to produce sulfates in the combustion process is responsible for preventing the full conversion of the bark and wood waste sulfur to SO₂ in the flue gases. Some of the sulfur may be in sulfate form in the bark and wood waste before combustion. That SO₂-SO₃ will unite with metal oxides in the gas phase is well known from the use of pulverized dolomite and other minerals to control sulfur oxide emissions from oil-fired power boilers. Sulfates of iron, magnesium, sodium, and calcium, etc., are produced in the gas phase of such boilers.

6. Based on work performed by others,^{13,14} it may be inferred that the sulfur content of boiler fly ash increases with time of contact with the flue gases, and possibly with the fineness of dust par-

ticles. Also, the alkali content of the fly ash is highest in the emitted fine ash. The greater time of contact and higher alkali content of the finer fly ash may have a combined effect in fixing sulfur, such as by reacting with SO₂ and SO₃ in the combustion Gases.

References

1. D. R. Crowe, Editor, "Recent Developments in Forestry Research," IFAS, U of Fla., Resources Report 3, Aug. 1976.
2. "Compilation of Air Pollutant Emission Factors," Office of Air Programs Publication Number AP-42, U.S. EPA, RTP, NC, Feb. 1972, pp. 1-11.
3. "Control Techniques for Sulfur Oxide Air Pollutants," Office of Air Quality Planning and Standards, U.S. EPA, Nov. 1972, pp. 2.2.5-11.
4. F. B. Boucher, E. W. Knell, G. T. Preston, and G. M. Mallan, "Pyrolysis of Industrial Wastes for Oil and Activated Carbon Recovery," EPA-600/2-77-091, May 1977, p. 14.
5. *Steam, Its Generation and Use*, the Babcock and Wilcox Company, New York, 1963, pp. 3-44.
6. "Environmental Pollution Control, Pulp and Paper Industry, Part I, Air," U.S. EPA Technology Transfer, EPA-625/7-76-001, Oct. 1976, pp. 16-3.
7. D. R. Moody, "Advances in utilizing wood residue and bark as fuel for a gas turbine," *Forest Products Journal* 26(9): 65 (Sept. 1976).
8. R. W. Boubel, et al., "Control of Particulate Emissions from Wood-Fired Boilers," Stationary Source Enforcement Series, EPA 340/1-77-026.
9. "Sulfate in Combination Fuel-Fired Boiler Stack Particulate Catch-Possibility of Contribution from SO₂," NCASI Special Report 77-01, Feb. 1977.
10. "A Guide to the Design, Maintenance and Operation of TRS Monitoring Systems," NCASI Atmospheric Quality Improvement Technical Bulletin No. 89, Sept. 1977.
11. "Leco DB-64 Digital Titrator," Bull. No. 2-0-734, Oct. 1972, Leco Corporation, 3000 Lakeview Avenue, St. Joseph, MI 49085.
12. *Standard Methods*, 12th Edition, 1965, 287.
13. E. R. Kaiser, "The sulfur balance of incinerators," *JAPCA*, 18: 171 (1968).
14. A. Liberti, D. Brocco, and M. Possanzini, "Adsorption and oxidation of sulfur dioxide on particles," *Atmos. Environ.* 12: 255 (1978).

Table II. Analysis of some selected wood refuse burned as fuel.^a

Item	Jack Pine	Birch	Maple	Western Hemlock
Proximate analysis, percent				
Ash	2.1	2.0	4.3	2.5
Volatile	74.3	78.5	76.1	72.0
Fixed carbon	23.6	19.2	19.6	25.5
Ultimate analysis, percent				
Carbon	53.4	57.4	50.4	53.6
Hydrogen	5.9	6.7	5.9	5.8
Sulfur	0.0	0.0	0.0	0.0
Nitrogen	0.1	0.3	0.5	0.2
Ash	2.0	1.8	4.1	2.5
Oxygen (by difference)	38.6	33.8	39.1	37.9
Heat value, Btu/lb (bone dry)	8930	8870	8190	8885
Ash analysis, ppm				
SiO ₂	16.0	3.0	9.9	10.0
Al ₂ O ₃	6.3	0.0	3.8	2.1
Fe ₂ O ₃	5.0	2.9	1.7	1.3
CaO	51.6	58.6	55.5	53.6
CaCO ₃	4.9	13.0	1.4	9.7
MgO	5.5	4.2	19.4	13.1
MnO	1.6	4.6	1.0	1.2
P ₂ O ₅	2.8	2.9	1.1	2.1
K ₂ O	4.1	6.6	5.8	4.6
Mn ₂ O	3.1	1.3	2.2	1.1
TiO ₂	0.2	Trace	Trace	Trace
SO ₃	2.6	3.2	1.4	1.4
Fusion point of ash, °F				
Initial	2450	2710	2650	2760
Softening	2750	2720	2820	2770
Fluid	2760	2730	2830	2780
Weight, lb/ft ³ (bone dry)	29	37-44	31-42	26-29

^a Average moisture of about 50% as received at firing equipment. Adapted from information compiled by the Stream Power Committee of the Canadian Pulp and Paper Association.

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