

TERTIARY RESOURCE RECOVERY FROM WASTE POLYMERS VIA PYROLYSIS: POLYPROPYLENE

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ABSTRACT

Polypropylene is a significant component of mixed plastic waste from which fuels and chemicals can be recovered via thermal or catalytic degradation. Pyrolysis of polypropylene was investigated at a temperature of 420°C and reaction times ranging from 10 to 180 minutes. Total conversion reached approximately 60% at 90 minutes, and no significant change was observed for longer reaction times. The selectivity to monomer, propylene, achieved a plateau at approximately 10% after a reaction time of 90 minutes. The overall product distribution can be explained by the typical free radical mechanism with the dominant products as alkenes in the form of C_{3n} , alkanes in the form of C_{3n-1} , and dienes in the form of C_{3n-2} .

I. INTRODUCTION

In recent years, post-consumer wastes have caused increased concern because of the escalation of municipal solid wastes (MSW) generated. In 1995, 208 tons of MSW were generated, and it increased to 340 tons in 1998, with more than 60% of MSW landfilled. The decreasing availability of landfill space and the inefficient use of post-consumer products through landfilling, have heightened the attention paid to recycling of MSW over the past decade.

Plastics make up a significant portion of post-consumer products. In the United States alone, over 70 billion pounds of plastics are manufactured annually, while only 10% of this amount is recycled or incinerated. In 1995, 9.1 weight percent of MSW was composed of plastics, with a total of 30% by volume. Among the plastic waste, 15.3 weight percent contained polypropylene.

Currently, the recycling of plastics can be divided into four categories - primary, secondary, tertiary, and quaternary. Primary recycling simply reuses the plastics as products that have similar properties to the discarded materials. Secondary recycling, also known as material or mechanical recycling, is achieved by melting, grinding, and reforming plastic waste mixtures into lower value products. Tertiary recycling converts discarded plastic products into high-value petrochemical or fuel feedstocks. Quaternary recycling uses combustion or incineration to recover energy from plastic products. Since primary and secondary recycling have limitations on the properties and uses of the final products, and quaternary recycling is an insufficient use of resources and has a negative public image because of release of CO_2 and airborne particles, tertiary recycling promises the best long-term solution. However, tertiary recycling is not economical at present. One of the biggest costs is the sorting of the original polymers. Therefore, processing of multicomponent polymeric wastes may provide a potential solution. To establish a baseline to which pyrolysis of mixed plastic wastes containing polypropylene can be compared, the thermal degradation of neat polypropylene was examined.

II. EXPERIMENTAL

Batch pyrolysis experiments were carried out by loading 20 mg of polypropylene (PP) into a 3.1-ml glass ampoule (Wheaton). The polypropylene was obtained from Aldrich Chemical ($M_w=127,000$, $M_n=54,000$) in powder form. After purging with argon for 2 minutes, each ampoule was sealed using an oxygen/propane flame, and then the sample was reacted in an isothermal fluidized sand bath at 420°C. Reaction times ranged from 10-180 minutes. Upon completion of the reaction, the ampoule was removed from the sand bath and quenched in another sand bath set at ambient temperature. Three replicates were performed for each reaction time.

Gaseous products were analyzed by putting the ampoule inside a 53-ml flask with a Tygon tube on one end and an injection port on the other. Both ends were then sealed with septa. The flask was purged with helium for 10 minutes and, after the ampoule was broken, allowed to equilibrate for 30 minutes. Two ml gas samples for the 10 minute reaction runs and 1 ml samples for the other runs were then taken using a gas-tight syringe. Gaseous products were then identified and quantified against known standards using a Hewlett Packard 5890 Series II Plus Gas Chromatograph equipped with a thermal conductivity detector (TCD) and a 6 ft stainless steel Porapak Q column (Supelco).

Liquid and solid products were extracted with 1.5 ml HPLC grade methylene chloride overnight. The product solution was first passed through a 0.45- μ m polypropylene filter (Alltech) attached to a syringe and then passed through a Waters Gel Permeation Chromatograph (GPC). Products with molecular weights less than ~400 g/mol were collected with the fraction collector attached to the GPC outlet. An external standard (biphenyl) was added after fraction collection. Product identification and quantification were achieved using a Hewlett Packard 6890 Series Gas Chromatograph-Mass Spectrometer and a Hewlett Packard 6890 Series Gas Chromatograph with a flame ionization detector (FID), each equipped with a Hewlett Packard 30 m crosslinked 5% Ph Me Silicone capillary column.

The percent conversion of PP, X, was defined according to the equation:

$$X = \frac{W_g + W_l}{W_o} \times 100\%$$

where W_g is the weight of gaseous products, W_l is the weight of liquid products with carbon number less than or equal to 25, and W_0 is the initial weight loading of PP. Selectivity, S , of a certain species A was based on the following equation:

$$S = \frac{W_A}{W_g + W_l} \times 100\%$$

where W_A is the weight of species A. Product yields were normalized by dividing the millimoles of each product by the initial molar loading of propylene repeat units. Finally, error bars shown in the figures represent the standard deviations of experiments that have been triplicated.

III. RESULTS

The overall conversion of neat pyrolysis of polypropylene increased with respect to reaction time, as illustrated in Figure 1. After 90 minutes of reaction, the conversion reached approximately 60%, and no significant change was observed at longer reaction times. This suggests that little additional conversion can be achieved even for very long reaction times at this temperature in a closed batch reactor of 3.1 ml. The selectivity of polypropylene monomer, propylene, showed similar behavior, achieving a selectivity of approximately 10% after 90 minutes of reaction as shown in Figure 2.

If the products were divided into three fractions, C_1 - C_4 , C_5 - C_{10} , and C_{11} - C_{25} , respectively, the yields of these fractions behaved differently. As shown in Figure 3, the yield of the C_1 - C_4 fraction increased with reaction time, whereas the C_5 - C_{10} fraction reached a maximum around 120 minutes and no significant change was observed at 180 minutes. Finally, the C_{11} - C_{25} fraction reached a maximum around 60 minutes. These results suggest that as reaction time increased, the heavier products decompose to lighter ones.

The reaction products of polypropylene pyrolysis consisted of four major categories - alkanes, alkenes, dienes, and aromatic compounds. Lower molecular weight species were found in higher yields whereas there were notable decreases in the yields with carbon numbers greater than ten. For alkanes, the most dominant product was ethane (C_2). In addition, pentane (C_5), 4-methylheptane (C_9), C_{11} , C_{14} , and C_{17} were found in the highest yield; the alkanes were thus dominated by products with carbon numbers C_{3n-1} , with $n=1, 2, 3, 4, \dots$, as shown in Figure 4. The yields of the majority of the alkanes increased with respect to reaction time. For alkenes, propylene was the most dominant product with propylene oligomers (C_6 , C_9 , C_{12} , C_{15} , C_{21} , and C_{24}), i.e., C_{3n} , $n=1, 2, 3, 4, \dots$, as the other major olefinic products. As shown in Figure 5, yields of alkenes with carbon numbers greater than five all reached maximum values then decreased when reaction time increased. However, yields of lighter alkenes (with carbon numbers less than five) increased monotonically with reaction time. Dienes, which were found beginning with C_7 and were present in relatively low yields, appeared as C_7 , C_{10} , C_{13} , C_{16} , C_{19} , C_{22} , and C_{25} , i.e., C_{3n-2} , $n=3, 4, 5, 6, \dots$ (not shown). They also appeared to reach maximum values then decrease except for C_7 . Finally, aromatic compounds were also found as minor products. Their yields were comparable in magnitude to the diene yields. The yields of aromatic compounds generally increased with respect to reaction time (not shown).

As noted above, the product distribution showed that most alkenes appeared in the form of C_{3n} , whereas alkanes and dienes appeared in the form of C_{3n-1} and C_{3n-2} , respectively. This product distribution is in agreement with observations reported in the literature [1-2] and can be explained by the mechanism illustrated in Figure 6, which was based on the one proposed by Tsuchiya et al. [3]. The initiation step of the free radical mechanism is simply to break any of the PP long chains into two shorter end-chain radicals. The end-chain radicals (or mid-chain radicals formed subsequently) may abstract hydrogen from a PP long-chain to form a tertiary radical, as shown in Figure 6(a). Upon undergoing β -scission, the tertiary polymer radical is broken into two parts, one with a double bond on the end (denoted as I), and the other with a secondary free radical (denoted as II). When the polymer chain I is attacked by another free radical and β -scission occurs, dienes (in the form of C_{3n-2}) and alkenes (in the form of C_{3n}) can be formed, as shown in Figure 6(b). On the other hand, polymer chain II can undergo three kinds of reactions such that alkanes (in the form of C_{3n-1}) and alkenes (in the form of C_{3n}) can be formed. Figure 6(c) shows three possible reaction pathways of polymer chain II. Although other steps not explicitly drawn are possible, the formation of C_{3n} alkenes, C_{3n-1} alkanes and C_{3n-2} dienes as the dominant products suggests that the mechanism in Figure 6 captures the major reaction pathways.

ACKNOWLEDGMENT

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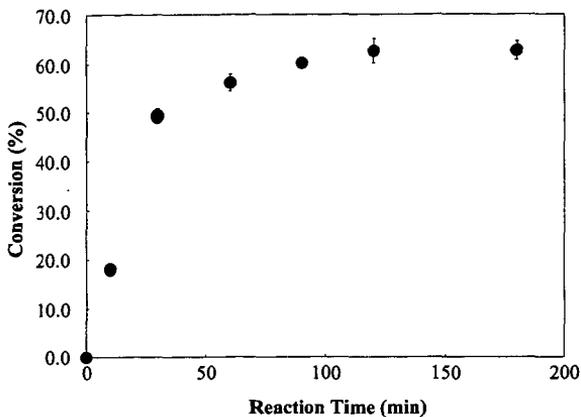


Figure 1 : Conversion of polypropylene as a function of reaction time.

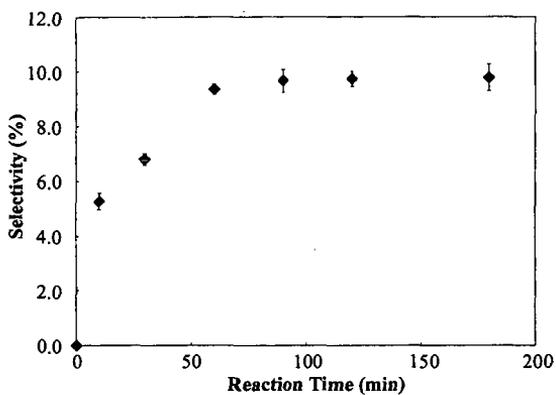


Figure 2 : Selectivity of propylene as a function of reaction time.

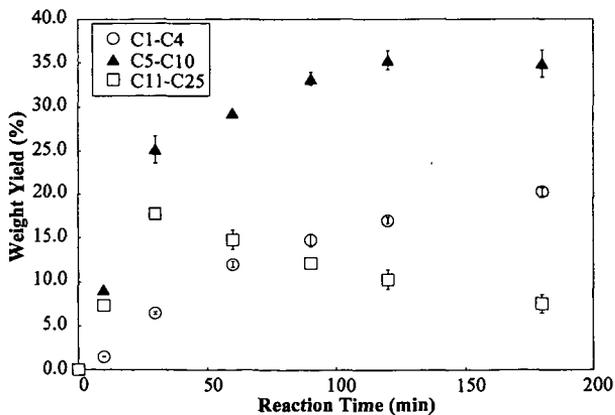


Figure 3 : Weight yields of different product fractions as a function of reaction time.

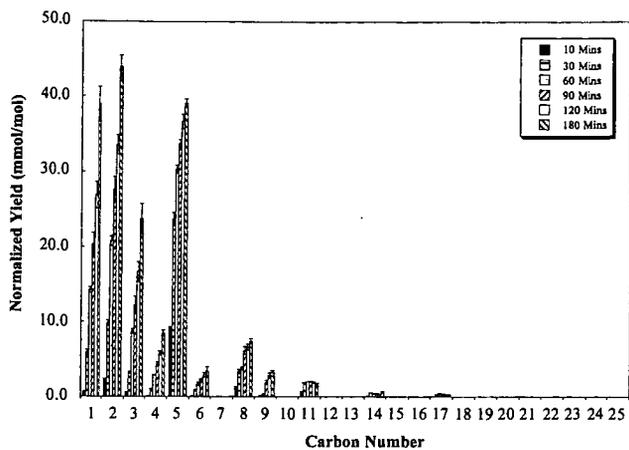


Figure 4 : Comparison of normalized yields of alkanes as a function of reaction time and carbon number.

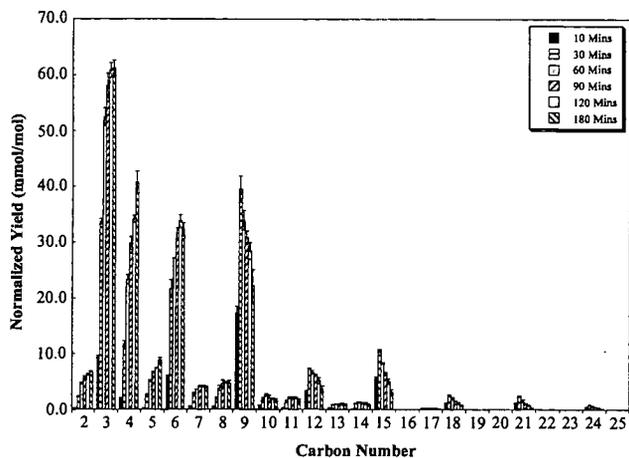


Figure 5 : Comparison of normalized yields of alkenes as a function of reaction time and carbon number.

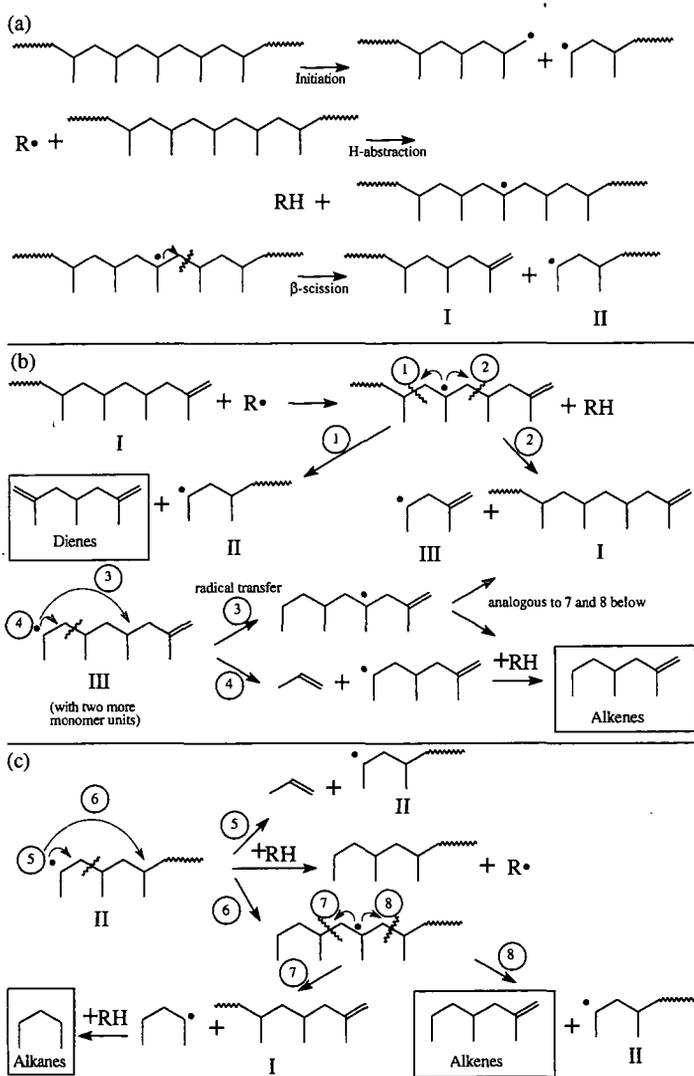


Figure 6: (a) Formation of two kinds of polymer chains (I and II) through bond fission, hydrogen abstraction and β -scission and proposed reaction mechanisms of polymer chains (b) I and (c) II.

Combustion of Coal Washery Rejects in a Circulating Fluidized Bed
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KEYWORDS: Fluidized bed combustion, washery rejects, coal

INTRODUCTION

The CANMET Energy Technology Centre, sponsored by Luscar Ltd and the Alberta Government, carried out a series of combustion trials on a number of washery rejects, to determine whether they could be burned in an environmentally acceptable manner using both conventional and advanced combustion technologies - namely fluidized bed combustion (FBC). The facilities used were a pilot-scale research boiler (PSRB) and CANMET's 0.8 MWth circulating fluidized bed boiler (CFBC). The program was sponsored by the Alberta Government (Western Diversification) and Luscar Ltd. This paper presents details of the CFBC pilot plant trials only.

EXPERIMENTAL

Test Materials

The three fuels burned in the reactor were: raw coal (Obed No.4), Obed Jig Rejects (Obed No.7) and Obed Jig Middlings (Obed No. 10). These fuels required a sorbent, Cadomin limestone (Genstar Cement Ltd), to achieve the allowable SO₂ emissions levels recommended under the National Guidelines for Stationary Sources. This particular limestone had been previously tested by CANMET using a TGA and was shown to be only a moderately reactive sorbent. As some difficulties were experienced in achieving adequate sulphur capture under the test conditions employed, a trial was also carried out using Havelock limestone (a relatively reactive eastern Canadian limestone).

Test Methods

The pilot-scale CFBC unit used has been described extensively elsewhere [1]. The major features of this versatile facility include a refractory lined combustor 405 mm in diameter and 7 m high, a refractory lined hot cyclone and an inclined L-valve loop seal system for recirculation of solids (Fig. 1). Four retractable bayonet type vertical cooling tubes permit the control of the combustor temperature during operation at various test conditions. It is complemented by a comprehensive instrumentation and control system, which is described elsewhere [1]. The combustor is designed to operate at temperatures up to 1100 °C and at a superficial gas velocity of up to 8 m/s.

CFBCs typically operate at combustion temperatures between 800 °C and 950 °C. Lower temperatures normally reduce combustion efficiency to unacceptable levels, decrease sulphur capture and increase products of incomplete combustion. Higher temperatures by contrast, run the risk of producing bed agglomeration, increasing NO_x emissions to unacceptable levels, and also reducing sulphur capture.

Initial operation of the facility has demonstrated a satisfactory performance of the combustor and ancillary equipment. In addition, the unit has been successfully used with high sulphur petroleum coke and pitch. The unit has also been used to generate ash from the CFBC combustion of high sulphur coals in order to study various ash management applications.

The research facility generates a database useful for the design and process optimization of full-scale units, study of emissions of pollutants, and prediction of the combustion performance of feedstocks.

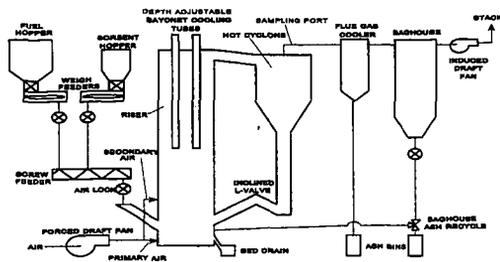


Figure 1. Schematic of CANMET's 0.8 MW(th) CFBC pilot plant

RESULTS

Table 1. Combustion results

Test and Date	Bed Temperature (°C)	Ca/S	NO _x (ng/l)	SO ₂ (ng/l)	Sulphur Capture Efficiency (%)	Combustion Efficiency (%)
Obed No. 4 Oct. 29-30/ 92	850	0	155.3 ± 8.7	370.3 ± 31.9	26	99.0
	850	2.2	151.8 ± 7.7	354.1 ± 53.7	28	-
Obed No. 7 Nov. 3-4/92	850	0	149.5 ± 10.1	562.5 ± 34.9	14	98.2
	850	4.9	144.9 ± 11.7	377.9 ± 74.3	32	98.9
	800	4.9	100.9 ± 5.5	224.1 ± 31.5	49	97.7
Obed No. 10 Nov. 5-6/92(*)	850	0	117.8 ± 8.6	422.0 ± 69.0	14	99.0
	850	2.8	107.2 ± 5.1	313.5 ± 25.2	30	98.8
	800	2.8	72.7 ± 8.0	185.7 ± 9.2	63	98.0
	900	2.8	135.1 ± 4.1	395.2 ± 24.4	38	99.1
Obed No. 4 Nov. 10/92	800	0	103.6 ± 10.4	316.8 ± 65.6	26	98.5
	800	2.7	97.6 ± 10.4	264.3 ± 62.4	31	98.3
Obed No. 7 Nov. 12/92	800	0	113.2 ± 14.7	218.4 ± 79.2	-	-
	900	5.5	187.9 ± 4.9	403.7 ± 50.4	44	99.0

(*) Trial with Havelock limestone

Table 1 (above) presents results from the CFBC combustion trials.

DISCUSSION

Sulphur Capture Results

As indicated in Table 1, the natural Ca/S molar ratio of all of the fuels tested is relatively high. These high levels of alkali metals versus fuel sulphur content could potentially result in a significant inherent capture if the calcium was present in a suitable form. Sulphur removal without limestone addition observed by CANMET for FBC combustion of Canadian fuels appears to average about 28% [2], and captures of over 90% have been observed for one Western Canadian subbituminous coal using both circulating and bubbling FBC technology [3,4]. Similar data have been reported elsewhere, e.g., inherent captures of up to 75% have been reported for British coals [5].

However, one important difference between capture due to ash components and limestone in FBC systems was that the optimum capture temperature for ash appears to be about 750 °C. This is a full hundred degrees below the optimum temperature for most limestones [5].

Combustion Efficiency

The combustion efficiency data follow the expected trend increasing with increasing bed temperature. No other experimental parameter over the range used in this test series seems to have a significant effect on the combustion efficiency. The variation in combustion efficiency from 97.7 to 99.1% is very small, with typical combustion efficiency being about 99% for bed temperature of 850 °C.

Nitrogen Oxides Emissions

NO_x emissions vary from 73 to 188 ng/J, which are well below levels typically seen from conventional combustion. Surprisingly there appears to be no effect associated with the addition of limestone, which might have been expected to increase NO_x emissions. Limestone is well known to be able to increase NO_x emissions in CFBC's due to its ability to catalyze NH₃ oxidation (from fuel volatiles) [6]. Perhaps the explanation is that limestone is simply not present in sufficiently high absolute quantities to have a significant impact, despite the high Ca/S molar ratios used in this study. However, the data clearly show that NO_x appears to increase with bed temperature which is as expected.

Sulphur Dioxide Emissions

For the most part, the National Guideline for Stationary Sources (258 ng/J) is exceeded (Table 1). However, the use of Cadomin limestone with Ca/S molar ratio of greater than 5 does allow this guideline to be met at 800 °C and SO₂ emissions should not be a problem for sufficiently high Ca/S molar ratios.

CONCLUSIONS

Three fuels, Obed No. 4, Obed No. 7 and Obed No. 10, have been burned in a CFBC combustor. All of these fuels are highly reactive and at typical CFBC operating conditions (850 °C and 3% O₂), it appears that combustion efficiency (based on unburned carbon loss) is 99.0% which is typical of such very reactive fuels. Inherent sulphur capture was shown to be small and to decrease with bed temperature, and appeared to be directly related to the degree of pyritic sulphur in the fuel which suggests that the "apparent capture" is due to carryover of unreacted pyritic sulphur. Cadomin limestone is only likely to be effective in achieving emission guidelines when it is used at Ca/S molar ratios of greater than 5. NO_x emissions are all below the current guidelines. Other emissions such as CO and N₂O appear to be low and are unlikely to pose problems. CO and N₂O emissions decrease with increasing bed temperatures as expected and interestingly, limestone appears to have a small positive effect in reducing CO levels. CFBC appears to be an entirely satisfactory technology for burning these fuels and based on these results would have no problem in achieving

good combustion performance and low emissions.

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Combustion of Pig Lard in an Industrial Boiler

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Keywords: Combustion, boiler fuel, pig lard, low emissions.

INTRODUCTION

The changing or loss of markets for lard and grease is a major concern for the hog processing industry. The U.S. capacity for the daily processing of hogs in July 1999 was 389,820 hogs per day [1]. After rendering, each hog will produce an average of 2.60 gallons of choice white grease (CWG) and 1.43 gallons of lard [2]. This equates to nearly 600 million gallons of combined products a year. Of the total animal product entering the slaughterhouses and meat processing and packing plants, some 60% leaves as appropriate for human use; the remaining 40% goes to the rendering plant, and 80% of the rendered material returns to animal feedstuffs [3]. Should legislative action prohibiting feeding animal by-products to animals consumed by humans occur, lard and CWG will then have to compete with the other non-food markets. It should be noted that not all of the lard and grease is currently used in the animal feed industry; hog by-products are sources of chemicals that are used in the manufacture of a wide range of products, e.g., cosmetics, insecticides, weed killers, lubricants, etc. [1].

In the study Penn State worked closely with Hatfield Quality Meats and Lehigh University. Although Hatfield currently has markets for the lard and CWG, they wanted to explore options should they lose their current markets through the changing demographics of lard consumers, or legislative action banning the use of animal by-products in animal feed for animals that are consumed by humans. Should these occur, then Hatfield will have a potentially massive and difficult disposal problem.

One option is to use the lard and the CWG as boiler fuels. Hatfield has three No. 6 fuel oil boilers in their main processing plant. The watertube boilers are of D-type design with one rated at 800 Hp and two rated at 650 Hp. Cleaver Brooks manufactured the 800 Hp boiler while the 650 Hp boilers were manufactured by Keeler Dorr-Oliver. Typically, when the 800 Hp boiler and one 650 Hp boiler are in operation they consume about 35,000 gallons of No. 6 fuel oil per week. Therefore, should lard and/or CWG prove to be an adequate fuel for firing industrial boilers, Hatfield would produce enough products in-house to meet their weekly fuel quota.

The objective of this study was to perform the analysis of CWG, semi-finished lard, finished lard and No. 6 fuel oil, and to compare the firing and handling characteristics of semi-finished lard, finished lard and No. 6 fuel oil in Penn State's research boiler. Should lard and CWG be candidates for boiler fuels, then they could be utilized in Hatfield's boilers and marketed to other boiler operators, both industrial and utility. From the utility perspective, the lard and CWG could be used as the start-up fuel in coal-fired boilers as a direct replacement for No. 6 in oil-fired boilers [4].

EXPERIMENTAL

Fuel Characterization

Ultimate analysis was performed on all feedstocks using a LECO CHN-600 instrument for total carbon, hydrogen, and nitrogen contents, and a LECO SC-132 sulfur determinator was used for total sulfur determination. As-fired heating values (in Btu/lb) were determined using a Parr Adiabatic Calorimeter. Viscosity measurements were taken using a Brookfield DVIII viscometer with a #21 spindle, at 100, 120, 140 and 160°F for the No. 6 fuel oil, CWG, and lard samples. Spindle speed rate was varied to establish whether the samples exhibited Newtonian or non-Newtonian fluid characteristics. Simulated distillation gas chromatography (SimDis GC) was performed on all samples using a Hewlett Packard 5890 plus gas chromatograph fitted with an FID and a Restek MXT-500 Sim Dist column (6 meter x 0.53 mm ID x 0.15µm df).

Research Boiler and Ancillary Components

The design and operation of the research boiler used in this study has been described previously [2]. The typical operating procedure of the boiler involved preheating the system with natural gas until the refractory-lined quarl (divergent burner throat) reached a predetermined temperature. This took approximately four hours. The natural gas flow was then reduced, and the No. 6 fuel oil and lard flow increased until the required thermal input was obtained with satisfactory flame appearance. Tests were conducted for three, six, and three hours, firing No. 6 fuel oil, finished lard, and semi-finished lard, respectively. Approximately 100 gallons (2 drums) of the finished lard and 100 gallons of the semi-finished lard were used during the testing.

The lard was heated and mixed before being transported to the feed tank where it was heated continuously to maintain a temperature of $\approx 130^{\circ}\text{F}$. The following information was collected:

- Fuel firing rate;
- Fuel pressure;
- Combustion air flow and temperature;
- Atomizing air mass flow rate and pressure;
- Flame character, stability, and quality (quantitative);
- Boiler and system operating temperatures and pressures;
- Steam flow rate and pressure; and
- Continuous stack gas composition (O_2 , CO_2 , CO , NO_x , and SO_2).

RESULTS AND DISCUSSION

Fuel Characterization

The data from the determination of the fuel characteristics are shown in Table 1. The lard samples contained less carbon and more oxygen than the No. 6 fuel oil. In addition, the lard samples contained essentially no sulfur. The heating value of the lard samples was $\approx 16,900$ and $17,000$ Btu/lb for the semi-finished and finished lard samples, respectively, compared to $\approx 18,500$ Btu/lb for the No. 6 fuel oil sample.

The CWG sample contains slightly more sulfur than the lard samples (0.2% vs. $\leq 0.1\%$) but much less than the No. 6 fuel oil. The heating value of the CWG is similar to the lard samples.

Table 1. Fuel Analysis

	Semi-Finished Lard	Finished Lard	Choice White Grease	No. 6 Fuel Oil
Ultimate Analysis (% as fired) ^a				
Carbon	77.7	77.4	77.9	85.8
Hydrogen	12.0	11.5	13.6	12.1
Nitrogen	0.4	0.6	0.2	0.6
Sulfur	0.0	0.1	0.2	1.5
Oxygen (by difference)	9.9	10.4	8.1	-
Heating Value (Btu/lb, as fired)				
	16,941	16,990	16,977	18,454
Viscosity (cSt) ^b				
100°F	70	97	91	1,357
120°F	23	25	26	520
140°F	17	17	17	232
160°F	-	-	13	128
Boiling Points (°C) ^c				
< 260	0.7	0.8	0.5	8.9
280 to 450	5.1	1.9	20.9	29.3
450 to 540	1.8	1.1	11.6	12.5
540 to 700	91.6	95.3	65.6	38.3
> 700	0.3	0.3	0.9	9.8

^a Fuel oil analysis normalized to 0% oxygen because oxygen, by difference, was -0.6%

^b Measured using a Brookfield DVIII viscometer, a #21 spindle.

^c Measured using a Hewlett Packard 5890 plus gas chromatograph fitted with a FID and a Restek MXT-500 Sim Dist column.

Figure 1 is a plot of viscosity (in centistokes) as a function of temperature for the samples analyzed in this study. For comparison, the viscosities of Nos. 4 and 5 fuel oils at 100°F are also shown [5]. The CWG and lard samples became very fluid over a small temperature rise and exhibited signs of being shear-thinning fluids, i.e. when more force is applied (faster spindle speed), the lower the measured viscosity. Semi-finished lard exhibited the lowest viscosity values; however, the viscosities for the CWG and lard samples fell in a narrow range. The differences in measured viscosity were mainly due to the relative concentrations of the components, e.g. the finished lard had proportionately more of the higher boiling constituents than the semi-finished lard

(95.3% to 91.6% in the 540-700°C boiling range). This is due to the fact that higher boiling constituents are usually more viscous than the lower boiling constituents. The viscosities of the lard and CWG samples indicate that they should handle and atomize easier than No.6 fuel oil and are probably more like No. 5 fuel oil.

SimDis GC was performed on each of the samples to determine their boiling point distributions (see Figure 2). This was done to compare the boiling characteristics of the lard and CWG samples with No. 6 fuel oil. The SimDis GC of the semi-finished lard shows that 91.6 wt.% of the sample boils between 540-700°C, and that there is a smaller proportion (5.1 wt.%) boiling between 260-450°C. Further refining to produce the finished lard reduces the quantity of constituents that boil below 540°C by 50% from 7.6 to 3.8 wt.%. Consequently, the proportion of 540-700°C boiling constituents increases to 95.3 wt.%.

The CWG has two distinct regions with different boiling points (see Figure 2a). Two thirds of the sample boils between 540-700°C. The majority of the rest boils between 300-540°C, while the entire sample boils below 750°C.

Figure 2d shows that No. 6 fuel oil has constituents that cover a wide range of boiling points. Over 50 wt.% boils below 540°C, and almost 10 wt.% boils above 700°C (for the lard and CWG samples < 1 wt.% boiled in the +700°C range). In addition 1 wt.% of the No. 6 fuel oil did not elute from the column, and thus had a boiling value of +770°C.

It is the presence of the very high boiling material and their physical interactions with the lower boiling constituents, that causes the high viscosity in the No. 6 fuel oil.

Materials Handling and Combustion

No. 6 fuel oil

The No. 6 fuel oil was heated to 130°F in the feed tank before firing in the boiler. Although No. 6 fuel oil is typically preheated to 200°F [5], it was heated to 130°F in order to have a direct comparison with the lard tests.

The research boiler was fired on natural gas for a period of four hours before switching over to the No. 6 fuel oil. The transition from natural gas to No. 6 fuel oil occurred over approximately a 20-minute period until the desired air and fuel flow rates were obtained. The No. 6 fuel oil was burned for a period of three hours. During this period, the operating conditions were varied to establish the lowest O₂ level the boiler would operate at without adverse impact on CO emissions. This was found to be ≈ 2.0%; consequently, the lard tests were then conducted at similar O₂ levels. The combustion data listed for the No. 6 fuel oil in Table 2 are for a 0.65 hour period of steady-state testing with 2.0% O₂ in the flue gas. No problems related to the handling or combustion of the No. 6 fuel oil were encountered.

Finished and Semi-Finished Lard

Both the finished and semi-finished lard had similar handling characteristics. The samples were heated to above ≈105°F, in order to 'melt', and homogenize them into a consistent liquid mixture. The lard samples were then transported into the feed tank where the temperature was maintained at ≈130°F. Except for heating, no processing of the lard was needed before combustion.

When firing the lard samples (which were done on separate days) the boiler was fired on natural gas for 4-4.5 hours before switching over to the lard. The transition from natural gas to lard required approximately ten minutes until the desired air and fuel flow rates were obtained. The finished lard was burned for six hours and the semi-finished lard was burned for three hours. No problems related to the handling or combustion of the lard samples were encountered.

The lard flames can best be described as having a small initial blue 'natural gas-like' flame followed by an 'oil-like' bright, central jet, surrounded by a grayish flame. The distinct separations in the flame are likely a result of the combustion differences of the discrete constituents of the lard.

The lard flames were well anchored during the tests. There was no change in the flame character over the time each fuel was tested. The lard flames were significantly longer than either the natural gas or No. 6 fuel oil flames, and were self-sustaining.

The emissions remained fairly steady throughout the tests. Interestingly, the NO_x and SO₂ emissions from the lard tests were lower than when firing the No. 6 fuel oil. The nitrogen content of the lard samples is similar to that of the No. 6 fuel oil; hence, the lower NO_x emissions are likely due to the presence of water or other constituents in the fuel, which resulted in a different flame structure (i.e., longer flame), and possibly a lower flame temperature. No flame measurements were taken during the tests. There is no appreciable sulfur in the lard samples; therefore, no SO₂ emissions were observed. The CO emissions when firing the lard were slightly higher than when firing the No. 6 fuel oil. This is because the O₂ level was not optimized for the lard tests. Instead the O₂ levels were kept to that of the No. 6 fuel oil test.

SUMMARY

In comparison with No. 6 fuel oil, the lard samples evaluated in this study possess very good materials handling and combustion characteristics. During combustion, the lard samples produced no sulfur emissions, and two thirds less NO_x than No. 6 fuel oil. With the correct firing system reconfigurations, lard and possibly CWG could be used as fuels for industrial-scale boilers, or as start-up fuel for utility boilers.

Table 2. Combustion Data

	#6 Fuel Oil	Finished Lard (Overall)	Semi-Finished Lard (Overall)
Length of Test (h)	0.65	5.90	2.53
Fuel Injection Temperature (°F)	140	130	130
Fuel Firing Rate (million Btu/h)	1.74	1.74	1.72
% O ₂	2.2	2.0	2.2
% CO ₂	14.4	14.7	14.6
ppm CO @ 3% O ₂	111	145	147
ppm NO _x @ 3% O ₂	395	137	135
ppm SO ₂ @ 3% O ₂	784	0	0

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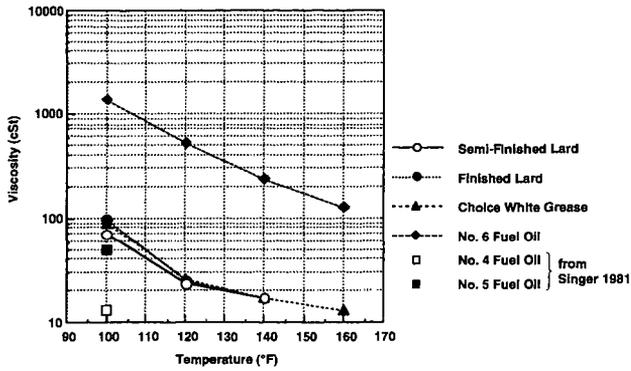


Figure 1. Viscosity as a function of temperature using a Brookfield DVIII viscometer with a #21 spindle.

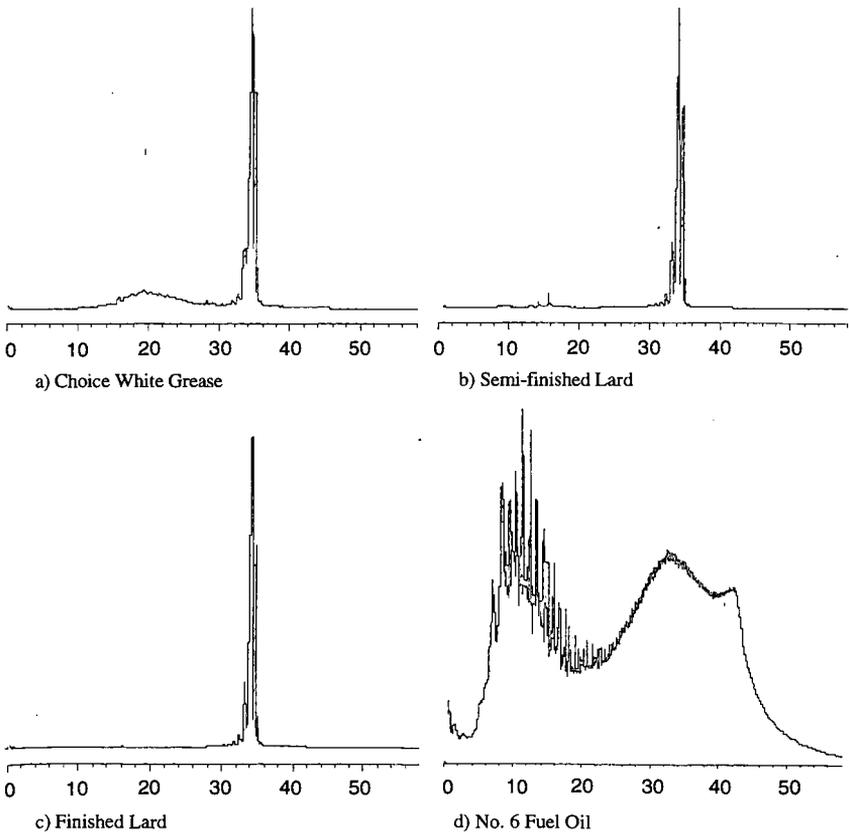


Figure 2. Simulated distillation chromatograms of samples evaluated in this study

CONSTRUCTION/DEMOLITION WOOD AS FUEL FOR COFIRING

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Key words: cofiring of wood and coal, stoker boiler, urban wood waste

INTRODUCTION

National interest in the combustion of wood and wood/coal mixtures is growing rapidly in response to the world-wide concern for global warming, the U.S. concern for SO₂ and NO_x emissions, and regional interest in expanding the utilization of forest products and byproducts. The wood/coal cofiring program at the University of Pittsburgh has focused its early work on the use of clean urban waste. A design requirement of the program was that the cofiring be accomplished by providing a wood-coal fuel blend that could be utilized by the boilerhouses as a regular fuel shipment without modification or capital expenditures. Three demonstrations of cofiring wood and coal, up to 12% wood by BTU content, have been conducted at two local boilerplants. The first project, conducted in 1997, under this program was a demonstration at the traveling-grate stoker boiler of a Pittsburgh Brewing Company (PBC)¹. In May 1999, a second demonstration was completed at a federally owned spreader stoker operated by the National Institute of Occupational Safety and Health (NIOSH)². The third demonstration was conducted at PBC in October 1999. The principal wood used in all the demonstrations was broken pallets tub-ground to a mulch-like in its consistency. Combustion has been very acceptable, but further development work is underway to achieve acceptable feeding characteristics of the mixture through the receiving grill and pit of the boilerplants. The prime objective of the University of Pittsburgh's wood/coal cofiring program is the successful introduction in western Pennsylvania of commercial cofiring fuel for stoker boilers. This paper summarizes the results of the demonstrations at PBC and NIOSH along with observations on the identification of specific sources of urban wood, and the processing required to produce a cofiring fuel.

PROJECT DESCRIPTION

PBC Demonstration I Steam for brewing, bottling and space heating is produced at the boilerhouse, which contains a gas-fired boiler and two traveling-grate stokers. The stokers are rated at 42,000 lb steam/hr (140 psig) and do not have emissions control equipment. Allegheny County Health Department (ACHD) has primacy for air quality assurance. ACHD generally requires that coal-fired boilers (above 0.5 MMBtu/hr thermal input) emit less than 1.2 lb/MMBtu of SO₂ with an allowable opacity of less than 20%. ACHD performs visible inspections of stack plumes to check opacity and ensure that boilerhouses do not become nuisance problems for neighbors. Stoker coals used in Allegheny County usually arrive by river barge from low-sulfur mines in the Virginia/West Virginia/Kentucky region. Such low-sulfur, stoker-sized coals can cost up to \$56/ton when delivered to the boilerplants.

Junior pea stoker coal - ¾ inch by ¼ inch - is delivered to the PBC by tri-axle truck (25 tons) from the Colona Terminal, a transfer station twenty miles west of the plant. Coal is dumped directly into a feed pit, which has a bucket elevator to convey the coal to one of two day bins located above the operating boiler. The feed pit is covered by a grizzly, for vehicle and personnel access, with openings of about 7-inches square. A paddle wheel feeder directs coal from the pit to the bucket elevator, which then transports it to the chute that supplies the day bin. Two chutes of about two feet square convey at the fuel from the day bin to a small hopper. Fuel is then fed by gravity from the small, open hopper onto the traveling grate that has an adjustable gate to set the initial fuel bed height above the grate. The fuel firing rate, set by the grate speed, is determined by a Bailey PID controller.

The first wood obtained for testing was screened tub-ground pallet pieces. Early in the test program, the size consist of this material was 1¼ inch by zero, but later it was changed to 1¼ inch by ¼ inch. The test was expanded to include a second urban wood waste - a 1 inch by zero chipped clearance wood. Fifteen 3-4 hour tests of 5% to 40% wood fuel blends (by volume) were conducted to evaluate the fuel flow/handling characteristics with PBC's existing conveying system. The blended fuels were prepared from wood and coal stored in two open piles near the boilerhouse, using a small front-loader bucket to assist with mixing, before the coal/wood fuel blends were loaded into the day bin. In addition, several 24 hour tests and a 72 hour test with flue gas monitoring provided by the Federal Energy Technology Center (FETC) were conducted to evaluate the boilerplant's ability to operate at steady state with a wood/coal mixture. These mixtures were prepared at Colona Terminal by layering the coal and wood onto the bed of a regular tri-axle delivery truck.

NIOSH Demonstration The NIOSH boilerhouse produces steam for the center's district heating system. The boilerhouse contains two gas-fired boilers and a spreader stoker Keeler boiler. The boiler is rated at 55,000 pph at 200 psig (but normally operates at 100 psig) with a baghouse for emissions control. As at PBC, ACHD has primacy for air quality assurance at the boilerplant and requires the use of low-sulfur compliance coal.

The junior pea stoker coal comes by barge from eastern Kentucky to a transfer station on the river and is trucked from the transfer station to the plant in 25-ton loads. Coal is dumped directly into a receiving

hopper. The coal receiving hopper is situated below a steel grate with openings a minimum of 5" by 8". A Syntron coal feeder picks up the coal onto a belt conveyer, which takes the coal up an elevation of 20 feet to a bucket elevator. The bucket elevator elevates the coal six stories to hoppers. From these hoppers the coal goes down through ducts onto a horizontal paddle conveyer that unloads the coal into a bunker. There are twelve gates at the bottom of the bunker. Another horizontal conveyer receives the coal from any one of the selected gates and delivers the coal to the Detroit Roto Grate stoker spreader feeder system.

There are three 18" feeders with a capacity of 500 to 2000 pounds per hour each. The boiler is also designed with an overfire air system to return the flyash. The stokers throw the coal to the back of the boiler, while a moving grate travels from back to front. The coal burns both above the grate in suspension and on the grate. A large number of fine fuel particles leave unburned from the firebox. The finer particles go through the economizer while the heavier ones are reinjected into the boiler by a stream of over fire air. The bottom ash falls into a hopper.

The wood for all test burns was a nominal 1¼ inch by ¼ inch tub-ground pallet waste. The screen and outlet of a tub grinder were modified from the settings used in the PBC demonstration to produce more "chunks" and fewer "stringers" from that used at PBC. Four-hour test burns of 10%, 20%, 30% and 40% wood by volume were conducted in mid-May 1999. The 10% and 20% wood fuel blends were prepared by mixing the wood and coal on the pad, while the 30 and 40% blends were prepared by layering the coal and wood onto the bed of the delivery truck. A 48-hour test burn was conducted using a fuel blend of approximately 33% wood by volume.

PBC Demonstration II In October 1999, two 4-ton mixtures of wood/coal fuel blend were test fired in one of PBC's stoker boilers. The wood component of the fuel blend was prepared by a modified method that produced a more cubic wood particle. Additionally, the wood and coal were mixed at the wood processor's site with a FECON blender to 50% wood by volume or about 12% by BTU content.

ACCOMPLISHMENTS

Fuel Conveyance: PBC Demonstration The demonstration showed that fuel conveyance plays a critical role in the ability of a stoker boiler to handle and feed wood/coal blends. With the exception of a few large pieces, the flow properties of the wood chip/coal blends was similar to junior pea stoker coal. The same held true for the flow properties of the tub-ground wood/coal mixture when properly mixed at relatively low wood percentages.

The critical bottleneck for handling fuel blends with a tub-ground wood content greater than approximately 33% occurred at the grizzly and feed pit. First, the fuel blend bridged the openings in the grizzly to the point that regular intervention was required to maintain flow. Intervention by the operators was acceptable to the manager of this plant. Second, transport of the fuel blend from the feed pit to the entrance of the bucket elevator was erratic and required occasional prodding to sustain flow.

In the initial stages of the first demonstration at PBC, a second problem with conveyance developed. The second, and more important, effect was on fines segregation in the bin. A mixture of wood and coal fines built up rapidly in the day bin. When the pile of fines slumped, a "plug" of fines passed down the chutes and eventually onto the grate, causing significant adverse shifts in burning characteristics, especially when the fuel was soaking wet.

Two adjustments to fuel preparation were made to limit this second problem. The tub-ground material received a second bottom screening to reduce fines, and the method of blending wood/coal mixture was altered. In early tests, the wood and coal were mixed on the ground with a front-end loader to ensure that homogeneous mixture would be delivered. However, this method crushed the coal somewhat and generated excess coal fines. After this problem was recognized, coal and wood were layered onto the truck without any mixing. It was then observed that conveyance through the PBC system components mixed the wood/coal sufficiently while reducing fines production.

At all wood/coal percentages, the green wood chips, when free of large pieces and "plates", flowed through the conveyance system in a manner similar to the stoker coal, with no observed change in fines segregation. However, the wood chips delivered to both PBC and the terminal did contain a small number of long, thin pieces (up to several feet long) and plate-like chips (up to eight inches across). The material delivered to PBC had to be hand-sorted before blending with coal to prepare a mixture that would pass through the grizzly and paddlewheel feeder. Such sorting was not possible in preparing fuel at Colona terminal. The grizzly acted as a screen for oversized pieces that required heavy manual effort for removal. The oversized pieces were attributed to operating problems with the chipper, which should be corrected with proper adjustment.

Fuel Conveyance: NIOSH Demonstration Just as in the PBC demonstration, the NIOSH demonstration showed that fuel conveyance plays the critical role in the ability of a stoker boilerplant to utilize a wood/coal fuel blend. The wood used was principally mulch-like. Long stringers had been screened out as planned, but the grinder had not yet been refitted to produce principally chip-like material, rather than mulch-like material. This led to a difference between expected and delivered processed wood to the project. The resulting wood/coal blend did flow reasonably well from the bunker to the boiler, and it burned well in the boiler, but it

needed considerable assistance to pass through the grate into the outside fuel-receiving hopper. Providing this assistance is unacceptable to this plant's superintendent.

Combustion Both at PBC and at NIOSH, once fed to the grate, properly prepared wood/coal mixtures of both ground pallets and green wood chips met the demonstration's goals for combustion characteristics. As expected, there were no occurrences of flame propagating back into the fresh fuel across the grate, or discharge of still-burning ash particles into the ash pit or out of the boiler during any test.

Compared to coal, wood is a high volatile, low heat content and low density fuel. The lower heat content of the wood can be compensated for by a higher rate of feed (on both a volumetric and weight basis) to achieve a satisfactory heat release rate. The heat content on a volume basis for a 33% tub-ground pallet/coal blend was 85% of that for the coal, while the 33% green wood chip/coal blend was 61% of that for the coal. This difference in volumetric heat contents required higher grate openings and faster grate and stoker speeds during wood/coal test burns relative to normal boiler operation on coal only.

Emissions/Opacity Flue gas emissions were continuously monitored during the PBC demonstrations with standard process gas analyzers that were installed by FETC. Emissions were low, with average levels of 685 ppm SO₂ and 333 ppm NO_x (corrected to 3% dry O₂) that correspond to about 1.1 lb SO₂/MMBtu and 0.4 lb NO_x/MMBtu. These results were consistent with the low sulfur content of the pallets, while NO_x levels were similar, if not slightly lower, than levels reported for other stoker boilers. A slight reduction in NO_x when firing a biomass/coal fuel is expected given the higher volatile and lower nitrogen content of the pallets as compared to the stoker coal. CO emissions were reasonable with an average 363 ppm (corrected to 3% dry O₂), which is indicative of good combustion, particularly given the load swings and other operational changes, and the fact that the boiler does not utilize any overfire air.

Opacity is monitored continuously by instrument at the NIOSH boilerplant and visually monitored at PBC. Opacity was normal during all the test burns at the NIOSH boiler and during the test burns of the tub-ground pallet fuel blend at the PBC. When a 50% by volume green wood chip blend was tested at the PBC, some smoking was observed, indicating an incomplete combustion of volatiles, perhaps due to high-moisture fuel pieces and/or an uneven distribution of air through the fuel bed. This may represent the upper limit to the percent of green wood that can be used.

WOOD FOR CO-FIRING IN STOKER BOILERS

Types, Sources There are numerous systems for categorizing the types of wood residues. Below is a listing for urban wood residues developed by C.T. Donovan and Associates, Inc.²

Urban wood residue is composed of highly heterogeneous woods. It is most simply defined as all the wood residue generated within a metropolitan area and may be sub-categorized into urban tree residues and post-consumer wood residue. Urban tree residue consists of residues from tree maintenance, utility right-of-way, and urban site conversion activities. This material is derived mainly from tops, limbs, and whole (small) trees. The material is composed of wood, needles, bark and leaves. Moisture content ranges from 35% to 50%.

Post-consumer wood residue consists of residues derived from secondary wood products. These residues may be further sub-categorized into:

- Pallet and Wooden Container residues – Each year, 16% to 18% of all the timber harvested in the US goes into the manufacture of pallets and wooden containers. Because of their number and bulk, pallets and wooden containers present significant disposal problems and are increasingly collected for reuse or repair. Pallets have a very low moisture content of 5% to 15% and are generally free of paints, stains or other treatments.
- Construction and Demolition (C/D) Wood residues – The wooden components of the debris generated during construction, renovation and demolition of buildings, roads and other structures. The amount of wood in the debris varies from 15% to 85%. 40% of new residential construction residue is believed to consist of wood and wood products. C/D residue wood can be treated or untreated. The wood may also contain laminates and have other waste (such as asphalt shingles, insulation and dry wall) attached. The average moisture content is 12% to 15%.
- Dunnage and Bracing Wood residues – Similar to pallet and wooden container wood residue.
- Urban Secondary Wood Products Manufacturing residues – The residues consist of chips, ends, sawdust, shavings and slabs. The moisture content ranges from 15% to 45%. The residues may contain preservatives, paint, glue and non-wood material such as plastic laminates. Also included are pallet recycling residues. Over 85 million pallets are received for recycling each year. 74% are repaired and reused (or reused without repair); 15% are dismantled for repairs; and the remaining go directly to disposal or are processed for mulch, fuel or fiber.
- Municipal Solid Waste (MSW) Wood residues – All types of urban wood, other than those types listed above, that are conveyed to a landfill for disposal. The average moisture content is 15% to 25%.

Characteristics Although the heat content for all hardwoods is approximately 8,500 Btu/lb on a moisture, ash-free basis (MAF) and MAF softwood has a heat content approaching 9,500, the physical and chemical

characteristics of wood residue varies widely depending on the type and source of the material. The most important characteristics of wood as it relates to its use as a fuel in stoker boilers are (i) moisture content, (ii) ash characteristics, (iii) post-harvest treatment/contamination, (iv) particle size/fuel blending, and (v) price/availability.

Moisture Content: The moisture content for freshly harvested "green" wood is approximately 50%. Over time the moisture content declines to between 5% and 15%. The high moisture content of green wood poses several problems related to its use as fuel: (1) It represents a weight with no caloric value that can increase the transportation and handling cost. (2) It will increase the volume of flue gas generated in combustion requiring an increase in draft fan output. (3) It will lower the furnace exit temperature, which will lower the heat transfer rate in the convective sections of the boiler. (4) It will lower the heating value of the fuel due to un-recovered energy in the flue gases that represents the heat used to vaporize the moisture in the fuel. Stoker boilers are designed for a given fuel moisture content (and fuel size distribution). Usually moisture content should be kept within 10% of design.

Ash characteristics: One of the major concerns associated with adding a biomass co-firing fuel to a boiler originally dedicated to coal firing is the possibility for a change in the ash fusion characteristics of the blended fuel. In a properly operating chain-grate stoker boiler, the individual ash particles fuse together in a porous mass that permits the passage of air and allows for uniform combustion across the bed. Adding wood to the coal has had a deleterious effect on the slagging and fouling characteristics with certain wood/coal fuel blends.

The clear stemwood of most species of trees contains very little ash, generally less than 1%. Stemwood is the inner wood from the trunk and larger branches. Actively growing portions of a tree such as the leaves and inner bark are higher in ash and the ash is high in "alkali" content. Alkali content refers to the sum of the potassium oxide (K_2O) and sodium oxide (Na_2O) in the ash. This high alkali content is the source of many of the problems with biomass ash.

Using indices originally developed to predict coal ash behavior, the elemental ash analyses of bottom and fly ashes from a stoker boiler burning Eastern Kentucky compliance coal, and published data on hardwood and urban wood residue ashes, mathematical predictions of the ash characteristics for two possible 20% wood / 80% coal fuel blends were calculated. The results of the comparisons indicate that the combustion on the grate of either urban wood residues or hardwood alone would likely cause severe fouling problems and a possible slagging problem. These calculations also indicate that slagging and fouling should not be a problem when co-firing urban wood residues at 25% mass input with compliance coal in stoker boilers. Slagging and fouling problems were not observed during any of the demonstration test burns.

Post-harvest treatment/contamination: Treatment may be as a (1) surface coating (paint, stain, etc.), (2) manufacturing agent such as resin, glue, or binder used as adhesive; or (3) impregnated preservative. The treatments which cause the greatest environmental concern in relation to their combustion are chromated copper arsenate (CCA) pressure treated lumber and lead-based paint. Wood with these treatments may be found in C/D wood, and makes the uses of C/D problematic. The most common type of contamination is dirt. Dirt will be found in the bark of harvested wood and urban wood residues. Dirt can have a negative impact on the slagging and/or fouling behavior of the ash. Much of the contaminating dirt can be removed by screening out the fines.

Particle size/fuel blending: Stoker boilers are designed for a given fuel size distribution. The wood provided to the first PBC and the NIOSH cofiring demonstration was refined tub-ground mulch. A tub grinder shatters the wood to produce a splinter material. This material is stringy with frayed ends and is subject to bridging at the delivery grill. When a wood chip produced from green whole-tree stems was tested at the PBC, no bridging was observed even when mixed to over 40% wood by volume. The superior behavior at the delivery grill of a wood chip is due to the chip's more cubic shape and sharp, knife-cut edges. Unfortunately, urban wood waste with nails and other hard contaminants causes rapid wear on a wood chipper's knife blades. Therefore, chippers cannot be used for primary size-reduction.

Three methods of fuel blending have been used in the demonstrations: mixing on the ground using a front-end loader, layering on the bed of the delivery truck and mixing in a FECON blender. Mixing with front-end loaders can produce a homogeneous fuel blend but the process generally creates excessive fines. Layering on the bed of truck can be sufficient to produce a reasonably uniform mixture on the grate if the layering is performed with care. In the first PBC demonstration, uniform layers several feet thick were found to pass through the delivery grill and reach the boiler grate mixed in a manner indistinguishable from the blends made on the ground. In the NIOSH demonstration, less care was used in layering the fuels in several deliveries and the wood formed large clumps on the delivery grill. These clumps interrupted the delivery and were never completely mixed into the coal by the boilerhouse conveyances. Wood and coal were simultaneously loaded into a FECON blender to produce a very uniform blend. The blend retained its consistency through the boilerhouse conveyances onto the boiler grate. However, the frayed ends of the tub-ground wood led to occasional interruptions of flow through the delivery grill of even the well-blended mixtures.

Price/availability. In order for a wood/coal fuel blend to gain commercial success it must be offered to the boilerplant at a cost equal to or below the plant's current cost of coal. Size reduction is the major cost in marketing urban wood residues as a boiler fuel. The processing costs for a commercial operation are expected to be approximately \$20 per ton. This is only marginally less than a wood processor can receive for the product from a coal vendor. In the current market in order to make wood to stoker boiler fuel processing profitable, the wood processor must capture a tipping fee for the waste residues that are collected. In 1996 at the beginning of the University's research program, wood processors in the Pittsburgh region were receiving a tipping fee for pallet wastes that they were tub grinding to produce a colored-mulch. Since then the highly profitable color-mulch market has expanded and all the readily available pallet residue is being collected for processing to colored-mulch without a tipping fee.

Nationally, it is estimated that 43.8 million tons of C/D waste are generated each year with 24.5 million tons available for cofiring⁴. This material is currently being landfilled with a tipping fee in the Pittsburgh region of approximately \$30 per ton. Regionally this amounts to more than 125,000 tons per year.

CONCLUSIONS /FUTURE PLANS

While working toward the introduction in western Pennsylvania of commercial cofiring fuel for stoker boilers, the University has learned much about the problems associated with seeking specific sources of urban waste wood and its processing into boiler fuel. The project team has concluded that use of a properly prepared blend of processed pallet residue and coal as stoker fuel with up to 12% wood by BTU content is technically feasible and environmentally desirable. Unfortunately in the Pittsburgh region pallet residue will not be available for processing to a stoker boiler cofuel. C/D wood residue will be required for the fuel blend.

In future planned demonstrations, the University will use C/D wood for the wood component of the fuel blend. ACHD has been supportive of the use of pallet residue as a cofiring fuel and has readily granted air quality variances for the demonstrations. Improperly source-segregated C/D wood has the potential of being contaminated with material that will cause toxic air emissions when combusted. The University and the wood processor plan to develop a quality assurance plan that will satisfy ACHD that the fuel is free of hazardous contamination. If a variance is granted to burn construction wood, then the University, through local builders organizations, will locate construction contractors that wish to supply source-segregated construction wood (and avoid a portion of their normal waste tipping fee for this material). The wood processor will locate a roll-off container at one or more of these sites. If a variance is also granted to burn demolition wood then wood processor will locate roll-offs at one or more demolition sites identified by the University with the aid of the Pennsylvania Department of Environmental Protection. The emissions from demolition waste combustion will be monitored for lead, arsenic and chromium.

Although standard tub-ground wood has been acceptable in the boiler as the wood component of the cofiring fuel at some boilerplants, the bridging it causes at the delivery grill will be unacceptable at most plants. For future demonstration the wood processor will develop two methods for producing a "chip" from urban wood waste. In the first method the processor will extend the work started for the second PBC demonstration on producing chip-like mulch from tub grinding. The processor will install a cut-off plate behind an over sized screen on the tub grinder that will shear off the long wood splinters to a more cubic wood fragment than is normally produced. The wood will be sized to 1 1/4 inch by 1/4 inch. In the second method, the wood will be very briefly tub ground to liberate the nails. Passing the wood through a standard knife-bladed chipper will follow this tub grinding. The wood will be sized to 1 1/2 inch by 1/4 inch.

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NO_x REDUCTION IN PULVERIZED COAL COMBUSTORS USING WASTE COAL AS COAL-WATER SLURRY

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INTRODUCTION

In order to comply with the regulations for nitrogen oxides emissions, various abatement strategies have been developed. These strategies can be divided into the following categories: 1) modification of the combustion configuration, 2) injection of reduction agents into the flue gases, and 3) treatment of the flue gas by post-combustion de-nitrification processes. A determination of the most effective and least expensive abatement technique depends on specific boiler firing conditions and the emission standards. A combination of techniques may be necessary to achieve certain mandated limits. Hence, the best NO_x control strategy for a certain unit is highly site dependent.

No definite rules exist to determine which nitrogen oxide formation mechanism dominates for a given stationary combustor configuration because of the complex interactions between burner aerodynamics, and both fuel oxidation and nitrogen species chemistry. But in general, fuel nitrogen has been shown to dominate pulverized coal fired boilers, although thermal NO is also important in the post-flame regions where over-fire air is used. Pershing and Wendt [1] showed that thermal NO contributions only become significant at temperatures above 2,500 °F in coal flames. Prompt NO_x is not a major source during coal combustion. Coal-water slurry (CWS) prepared from waste coal has a potential to reduce NO_x emissions [2, 3]. Reburning is proposed as a general mechanism for lower NO_x emissions when cofiring coal-water slurry with PC [3]. Coal-water slurry reburning is applicable to all types of coal-fired boilers and offers electric utilities a potential option to achieve significant NO_x emissions reduction [4].

OBJECTIVES

The main objective of this study was to gain insight into the mechanism by which NO_x emissions are lowered when cofiring coal and CWS as compared to coal firing by examining the extent of reburning in the gas phase, and understanding the heterogeneous char NO contribution to the reduction of NO_x.

EXPERIMENTAL

The study was conducted in the 0.5 MMBtu/h Down fired combustor (DFC) located at the Energy Institute of Penn State. Figure 1 provides a schematic diagram of the 0.5 MMBtu/h DFC. Detailed description of the facility can be found elsewhere [5]. Coal was fired through the central pipe of the burner, and slurry fuel was injected in Port 2 to simulate the reburn conditions. CWS was cofired with coal at 0, 10, 20, and 30 % of the total thermal input. A total of fifteen tests were performed in the DFC. Compositional analysis of the coal and CWS are provided in Table 1. Baseline flue gas concentration and temperature profile along the combustor was obtained when firing 100% coal. A continuous emission monitoring (CEM) system was used to measure O₂, NO, and CO at various Port levels. Axial oxygen concentration measurement was also obtained.

Table 1. Compositional analysis (wt%, dry basis) of PC and CWS

Fuel	Fixed Carbon	Volatile Matter	Ash	HHV (Btu/lb)	C	H	N	S	O
Coal	62.94	24.17	12.89	13,339	76.10	4.66	1.37	1.59	3.39
CWS	60.06	30.29	9.65	13,353	77.07	4.51	1.34	1.32	6.11

A nominal firing rate of approximately 0.5 MMBtu/hr was used in the study. Ports were installed as per EPA methods for stack gas sampling for the sulfur oxides evaluation. The coal-water slurry fuel atomization gun was placed at Port 2 for all tests. Combustion air for coal-water slurry fuel during all reburn tests was introduced in Port 3 of the DFC. An air pressure of 100 psig was used for atomizing the CWS.

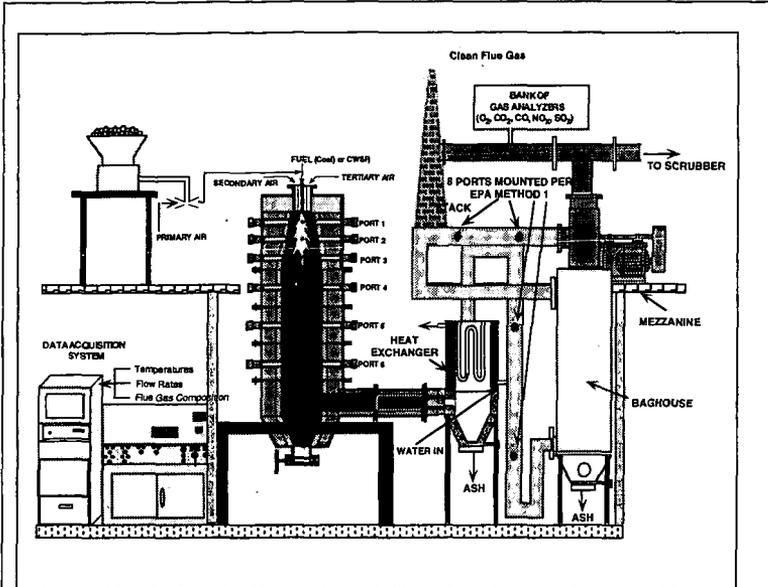


Figure 1. Schematic diagram of the down fired combustor (DFC).

Data on the gas temperatures using LAND suction pyrometer, and oxygen, CO, and NO_x concentration profiles using continuous emission monitoring system (CEM) in the combustor were also obtained during the tests. Char samples were collected from various Ports in the DFC using an isokinetic sampling probe. The char samples were collected in wet condition by washing the probe after each test and were analyzed for carbon, hydrogen, nitrogen, and carbon burnout.

RESULTS AND DISCUSSION

The gas composition (O₂, CO and NO_x) at various Port levels was measured at the center of the combustor, midway between the center and the wall (called "Mid") and at the wall. The results, when firing 100% PC with all the air through the burner (Figure 2), show that the NO_x concentration in the gas phase was maximum near the burner and as the flue gases pass down the combustor, the NO_x levels decrease. This suggests that the rate of destruction exceeded the rate

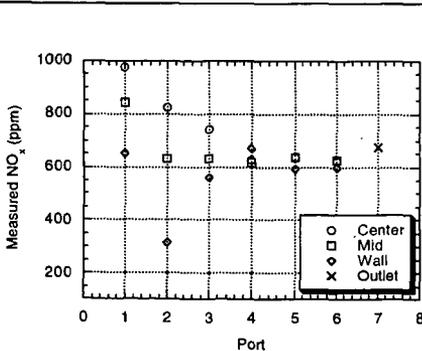


Figure 2. NO_x Profile in the DFC when firing 100% coal with all the air through the burner

of production of NO_x. This increase in the destruction is possibly accomplished by the reburn mechanism. Reburning can take place either by homogeneous gas phase reactions or by the NO_x - char reactions. Upon heating a coal particle, nitrogen is also distributed between the volatile and char phases. NH₃ and HCN species in the volatiles depending on the temperature, concentration and mixing can form NO_x or N₂. Simultaneously the char nitrogen will be released to form either NO_x or finally to N₂. Depending on the

net difference between the two processes, an increase or a decrease in the NO_x emissions occurs. It can be seen from Figure 3 that the initial NO_x levels when cofiring coal-water slurry are lower

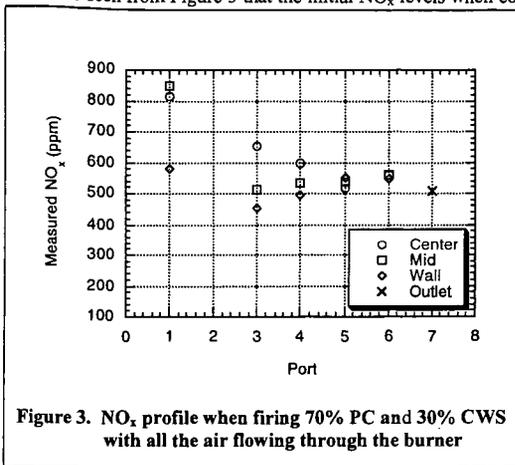


Figure 3. NO_x profile when firing 70% PC and 30% CWS with all the air flowing through the burner

than the values for 100% PC. This suggests that the formation of NO_x in the initial phases is lower. Subsequently there is a minor decrease in the NO_x concentration for the tests with CWS cofiring tests. These results indicate that the NO_x production and destruction rates after the primary zone are almost equal leading to no net increase in NO_x levels. Conceptually, the reburning process can be divided into three zones: a) Primary Combustion Zone: This is the main heat release zone which accounts for approximately 80 % of the total heat input to the system and is operated under fuel-lean

conditions. The level of NO_x exiting this zone is defined to be the input to the reburning process; b) Reburning Zone: The reburning fuel (10-30 % of the total fuel input) is injected downstream of the primary zone to create a fuel-rich, NO_x reduction zone. Reactive nitrogen enters this zone from two sources: the primary NO_x input and the fuel nitrogen in the reburning fuel. These reactive nitrogen species react with hydrocarbon radicals, primarily CH , from the reburning fuel, to produce intermediate species like NH_3 and HCN [6]. The HCN then decays through several reaction intermediates and ultimately reaches N_2 ; c) Burnout Zone: In this final zone, air is added to produce overall lean conditions and oxidize all remaining fuel fragments. The total fixed nitrogen species ($\text{TFN} = \text{NH}_3 + \text{HCN} + \text{NO} + \text{Char N}$) will either be oxidized to NO_x , or reduced to molecular nitrogen.

The amount of nitrogen from the fuel into volatiles and char will change as a function of temperature, nitrogen content and size of the coal particle. Figure 4 shows the wall temperature profiles for various cofiring configurations. A test was performed with 100% PC but water, equivalent to 30% CWS test, injected in Port 3 to separate the effect of NO_x changes due to temperature decrease and any reburning reactions. Since all the fuel and combustion air was

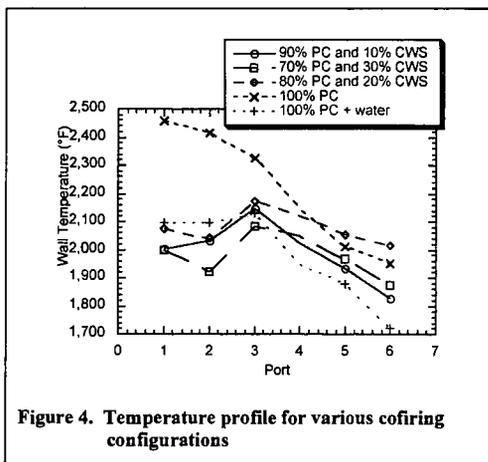


Figure 4. Temperature profile for various cofiring configurations

admitted through the burner the resulting temperature in the case of 100% PC was higher than the rest of the tests. This contributes to higher thermal and fuel NO_x during primary combustion zone. Partitioning of nitrogen between volatile and char phase is a function of temperature, heating rate and coal type and equipment used. It has been shown in the literature that total volatile and nitrogen yields are approximately proportional at comparatively low pyrolysis temperatures (1800 °F) and short heating times, but pyrolysis at temperatures > 2500 °F, results in the

evolution of significant amount of additional nitrogen [7]. Since the temperature for 100% PC in the Port 1 region is high (>2500 °F), it is likely that more nitrogen is released into gas phase which, with more air tends to form higher amounts of NO_x and thereby higher concentration of NO_x . However, there is a reduction in NO_x concentration between Ports 1 and 3. This is primarily due to gas phase reaction involving hydrocarbon species from the volatiles.

Carbon burnout data as a function of distance from the burner was obtained from the isokinetic char samples that were collected during the tests. The data show that the carbon burnout during cofiring runs was lower than that of 100% PC run. As a result, lesser amount of carbon was available in the form of HC radicals during the initial stages of cofiring than the 100% PC run. From Figure 5, it can be seen that the chars collected show higher amounts of carbon, and up to 18% of total nitrogen remaining in the char phase at Port 3. Wendt [8] has shown that under rich conditions, HCN plays a critical role in driving the nitrogen cycle to form N_2 and that one source of HCN formation is the destruction of NO by hydrocarbon radicals, which is the

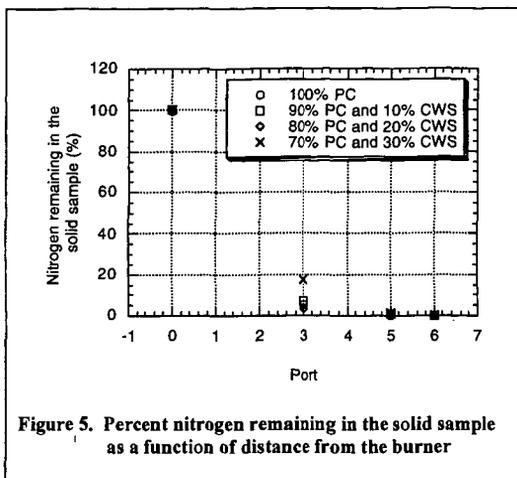


Figure 5. Percent nitrogen remaining in the solid sample as a function of distance from the burner

main reburning reaction destroying NO. In addition, it has been shown [6, 9] that the Fenimore N_2 fixation reaction also produces HCN, especially under natural gas reburning conditions. Mereb and Wendt [10] confirmed the fact that reburning with pulverized coal is also effective but less than with gas because natural gas produces more hydrocarbon species in the NO_x reduction zone and reactions between NO and hydrocarbons are important. Their data showed that with coal reburning, HCN was destroyed more rapidly than it was being formed and its values decayed to levels

below 20 ppm within 0.6 seconds. This result supported their hypothesis that it is important to maintain HCN formation rates during long time scales in order to keep N_2 formation mechanisms going, that this formation is mostly due to hydrocarbon reactions with NO or N_2 and that any slow release of nitrogen from the coal residue is a minor contributor to the process. The results in this study also confirm these observations since the residence time between Ports 1-4 is approximately 0.6-0.7 seconds. The gas phase reburning after this Port appears to be insignificant.

NO is expected to be the primary product of char nitrogen combustion [11]. However, the NO-carbon reaction can reduce the NO to N_2 . NO reduction is enhanced by the presence of CO [11]. From the CO measurements in the combustor in this study, no significant difference in the CO in the gas phase emissions was observed. In most of the tests the CO concentration was around 100-120 ppm. Therefore, it is likely that the NO produced from oxidation of char nitrogen reacts with the carbon in the pore structure. Char produced from the coal-water slurry is texturally different from the char from PC combustion [12]. Therefore, local NO-char reactions are believed to be responsible for the small reduction in NO above and beyond the reduction obtained due to temperature reduction caused by water addition.

It was also seen from the data that there was a significant difference between the NO_x concentrations measured at the center and the wall. This indicates the lack of mixing in the combustor up to about 7-8 feet in the combustor. If the NO_x molecules do not mix with hydrocarbon radicals, the reduction in NO_x will be reduced. It has been shown [9] that the reburning mechanisms occur in two regimes: one in which fast reactions between NO and hydrocarbons are usually limited by mixing; the other in which reactions have slowed and in which known gas phase chemistry controls.

CONCLUSIONS

The results of the study showed that NO_x formation occurs during initial phases in the pulverized coal flames. The NO_x concentration profile indicated that the concentration decreases rapidly by reburning in the gas phase by the radicals in the volatile phase. Excess air levels (air staging), and mixing appeared to be the most important parameters in reducing the NO_x in the primary zone. When coal-water slurry was cofired with coal the temperature in the upper part of the combustor was lower because of water addition. The NO_x concentration near the Port 1 region of the combustor was also lower. This reduction was attributed to the lower temperature and lower fuel nitrogen split into the gas phase. The reduction of NO_x due to reburn in the primary zone was not observed for coal-water slurry cofiring tests. The carbon burnout was lower for the CWS cofiring tests. Therefore, lower amount of carbon was available in the volatile phase to

reduce NO_x initially. It is believed that gas phase reactions did not play a significant role in the reduction of gas phase NO_x that was produced initially.

Char contained higher amounts of nitrogen because of the char structural differences, the nitrogen oxides that are formed are believed to react on the char surface on their way out through the pore structure.

ACKNOWLEDGEMENTS

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