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Controlled Oxidation Studies of Coal/Refuse Fuel Blends

Aiping Wu
Western Kentucky University

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CONTROLLED OXIDATION STUDIES OF COAL/REFUSE FUEL BLENDS

A Thesis
Presented to
the Faculty of the Department of Chemistry
Western Kentucky University
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In Partial Fulfillment
of the Requirements for the Degree
Master of Science

by
Aiping Wu
June 1994

CONTROLLED OXIDATION STUDIES OF COAL/REFUSE FUEL BLENDS

Date Recommended July 1, 1994

John T. Riley
Director of Thesis

John W Reasoner

Thomas K. Green

Date Approved 9/21/94

Elmer Gray
Dean of the Graduate College

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CONTROLLED OXIDATION STUDIES OF COAL/REFUSE FUEL BLENDS

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Directed by: John T. Riley, John Reasoner, and Thomas Green

Department of Chemistry Western Kentucky University

ABSTRACT

A study of the controlled combustion of blends of biomass materials and coals was conducted. Crushed limestone was added to the blends as an absorbent for sulfur oxides. The samples were combusted in quartz-fiber crucibles in a forced air furnace. Combustion at different times and temperatures were studied. The amount of carbon, hydrogen, and sulfur in the residues, as well as the amount of ash formed, were used as measures of combustion efficiency. The optimum temperature for combustion of most blends was found to be in the 700 - 800°C range.

A study of methods for determining the amounts of inorganic and organic carbon in combustion residues was performed. The American Society for Testing and Materials (ASTM) Method D 1756 for inorganic carbon yielded accurate results but is tedious and requires a great deal of skill. An

alternative method for determining inorganic carbon in combustion residues was developed.

I. INTRODUCTION

More than a 180 million tons of municipal solid waste (MSW) are generated in the United States each year.[1] The amount of waste generated and the rapidly declining availability of landfill space has forced most municipalities to evaluate alternative waste management technologies for reducing the volume of waste sent to landfills. Currently, about 16% of the municipal solid waste is processed in waste-to-energy facilities, and this fraction is expected to grow significantly by the year 2000, perhaps to 40%.[2]

The waste fuels burned in waste-to-energy plants are derived from a variety of sources, including residential and commercial refuse, urban demolition wastes, agricultural waste, wood waste from forestry operations and lumber mills, paper mill sludge, and other industrial wastes. Table 1 gives some typical analytical values and heating values for biomass wastes and fuels.[3] The information here shows that biomass wastes contain significant organic material which can be burned or processed in a manner similar to conventional fuels. The composition of waste is similar in many ways to such fuels as coal, except that wastes generally have higher oxygen and moisture contents. Direct combustion for heat, steam, and

Table 1. Typical Analytical values for Biomass Wastes and Coals

					Bituminous coal *	
	Wood (dried)	Wood bark (dried Douglas fir)	Municipal refuse (Altoona, Pennsylvania)	Paper mill sludge (dried)	West (Utah)	East (Pittsburgh seam)
Proximate Analysis (%)						
Moisture			43.3	23.2	5.0	3.0
Volatile matter	81.5	73.0	43.0		47.6	33.9
Fixed carbon	17.5	26.0	6.7		48.3	55.8
Ash	1.0	1.3	7.0	10.2	4.1	10.3
Ultimate analysis (%)						
Hydrogen	6.3	5.9	8.2	7.2	6.0	5.0
Carbon	52.0	56.2	27.2	30.9	77.9	75.5
Nitrogen	0.1		0.7	0.5	1.5	1.2
Oxygen	40.5	36.7	56.8	51.2	9.9	4.9
Sulfur		trace	0.1	0.2	0.6	3.1
Ash	1.0		7.0	10.2	4.1	10.3
Heating value (BTU/lb of refuse)						
Moist		3,000	4,830	5,350	13,470	13,250
Dried	9,000	9,500	8,519	6,966	14,170	13,650

* All values for the coals are given on a dry basis.

electric power generation is the most obvious route to energy from biomass and wastes.

The parameter used to measure the rate of burning of a fuel is the volatile matter. For refuse-derived fuel (RDF) or MSW, the volatile matter is 40% - 80% and wood waste is about 55% - 85% compared to the 36% - 47% volatile matter of bituminous coal.[4] Also, RDF and wood waste have heating values approximately 5,000 - 9,000 Btu/lb whereas bituminous coal, an energy rich fuel, contains about 12,500 - 13,500 Btu/lb. On the other hand, wastes generally have low sulfur contents and many have lower ash contents than typical coal. Due to their low sulfur contents, co-firing RDF or wood waste would reduce emissions of sulfur dioxide (SO_2) relative to those for coal firing.[5,6] Particularly, when some sorbent such as limestone was added to trap sulfur dioxide during coal combustion, sulfur capture efficiency was found to be in the range of 45 to 55% in the lab scale testing by H. N. Conkle and coworkers.[7] Sulfur contents, mainly in the form of pyrites and minerals in coal, will be converted to calcium sulfates by the reaction of sulfur oxides with calcium oxides decomposed from limestone during combustion.

With the current energy situation, the waste energy sources are becoming more valuable. Suitable combinations of these fuels, with limestone added as a sorbent for sulfur oxides, can be utilized as good and inexpensive fuels. The use of refuse fuels is also beneficial to the garbage industry.

A. Historical Perspectives

Beginning in the 1950's in Europe and in the 1960's in the United states, the technical community has had an increasing interest in the fuel value of urban solid wastes as a result of the energy crisis. Several short-duration, coal-RDF test burns have been done for a few basic types of solid waste fuels including RDF and wood wastes.[5] Up to the 1980's, direct combustion of these materials was used throughout the world at various levels of technological development and sophistication. Most waste-to-energy facilities use dedicated waste-to-energy technology designed to efficiently recover energy as steam or electricity while controlling environmental emissions. Several existing fuel combustion facilities have been retrofitted to burn waste fuels either alone or in combination with coal or oil, including industrial and utility boilers and cement kilns. Currently, RDF is co-fired with coal at one cyclone and three pulverized coal power plants,[8] co-firing with wood at two fluidized bed plants,[9,10] and firing alone at three converted utility stoker-fired plants[11] in the United States.

Waste fuel co-firing with coal can be expected to provide higher boiler and steam conversion efficiency than waste fuel firing in dedicated waste-to-energy plants, because coal-fired plants typically operate at higher steam pressures and temperatures and, therefore, higher steam-cycle and thermal efficiencies than dedicated plants. In addition, waste co-firing generally requires much lower incremental capital investment than waste firing in a dedicated waste-to-energy facility. Both factors can contribute to a lower break-even waste disposal cost.[2] McGown and Hughes reported the energy efficiency of waste energy recovery using an example of a 250 MW waste fuel/coal co-fired power plant (Figure 1).[12] Figure 1 compares the overall boiler efficiencies as functions of waste fuel heating input fractions for utility boilers co-firing RDF and wood with coal. As the waste fuel heat input fraction increases, the boiler efficiencies for RDF and wood co-firing decline significantly from 89% at 0% waste fuel input (100% coal firing) to 78 and 75%, respectively, at 100% waste fuel input. This decrease in efficiency results primarily from the high moisture contents and higher excess air requirements for the waste fuels, which increase the dry gas and moisture loss components of the boiler efficiency loss.

The principal waste-to-energy technologies under consideration include modular incineration, mass burning of unprocessed MSW, and preparation and firing of RDF. Fluidized bed combustion (FBC) is one of several technologies used to fire RDF. Others include semi-suspension stoker-fired boiler and co-firing in pulverized coal and cyclone-fired utility boilers.[13]

Gerald and coworkers did a field test using coal:dRDF (densified forms of refuse derived fuels) blends in spreader stoker-fired boilers.[5] The results indicated that coal:dRDF blends up to 1:2 can be handled and burned in conventional

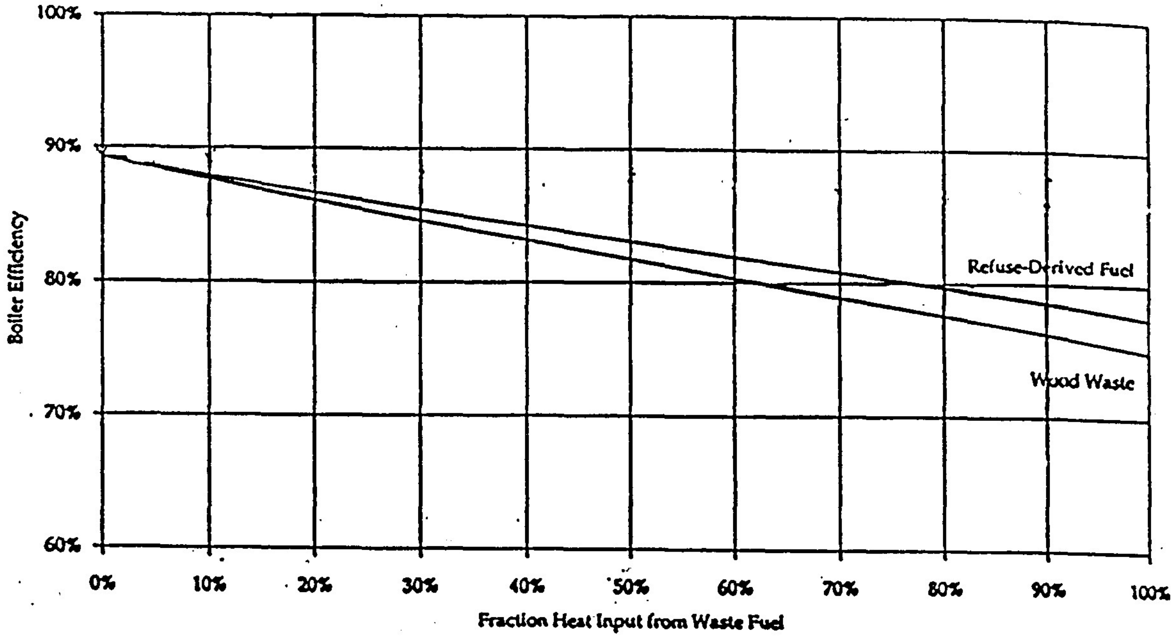


Figure 1. Boiler efficiency for waste fuel/coal co-firing.

spreader-type stoker-fired boilers without major equipment modification. The fuel blends handled satisfactorily, although some pellet deterioration (due to excessive handling and rain damage) caused much dusting and slightly impeded the pellet flow. After adjustments of the air controls, the spreader-feeders, and the grate pulse interval, the blends generally burned as well as coal alone. Moreover, as more dRDF was substituted for coal, the flame volume increased, the opacity decreased, the fly ash carbon burnout improved, and the turn-down ratio of boiler operation increased. Also as dRDF substitution increased, the SO_x emission from the blend firing decreased correspondingly.

V.J. Flanigan and coworkers conducted a study with a chain-grate stoker boiler with a blended coal and wood waste fuel.[6] In their research, the boiler performance was evaluated by plotting the boiler efficiency as a function of the wood percentage in the fuel and by plotting a performance index defined to be the pounds of steam produced per pound of fuel fired versus weight percent wood. The efficiency curve showed a slight increase with increasing wood content while the performance index naturally decreased due to the lower heating value of the wood. The results also indicated that sulfur dioxide emissions decreased with increased proportions of wood waste in the coal-wood mixture, whereas total hydrocarbon concentration increased when wood waste content was increased.

Hathaway and coworkers also co-fired densified RDF and coal mixed at a 1:1 volumetric ratio in a high-temperature hot water boiler at the Wright-Patterson Air Force Base, OH.[14] Their problem areas included deterioration of dRDF during transportation, lack of standard procedures to specify and analyze RDF, dust generation in receiving and handling operations, and difficulty in maintaining a uniform RDF:coal mixture at the feeder and within the furnace.

The co-firing of alternate fuels is not always technically feasible and the maximum waste fuel input fraction is often limited by practical or economic considerations. The degree of fuel processing, which affects fuel particle size and ash, moisture, and heat contents, can also determine the feasibility of co-firing waste fuels.[15] High ash, glass, and metal contents can lead to increased boiler slagging and fouling in pulverized coal boilers and plugging and jamming grates in stoker-fired boilers. Large particles can jam and plug fuel feeding and ash removal systems and cause poor combustion efficiency. Factors that need to be considered include the boiler type(cyclone-fired, stoker-fired, or fluidized bed), operating and performance limitations on coal, and required fuel specifications.

FBC systems are particularly suited for waste fuels firing because of their ability to burn low grade and variable fuels as well as absorb sulfur oxides through the use of sorbents.[16] It is a combustion technology in which burning takes place within a bed (usually sand and ash) which is kept turbulent by a passage of air, thus making the bed material behave like a liquid. This turbulence ensures a uniformity of temperature and gas flow over the bed. High heat transfer rates and more complete combustion is achieved at low temperatures of typically around 800 - 850°C. The bed's heat storage capacity helps smooth out any momentary changes in the calorific value of the feedstock material.

A typical FBC system has been described by Colin Parker and Tim Roberts.[16] FBC systems are very flexible units for combustion technology, able to accept low grade fuels in liquid, solid or gaseous form provided the fuel can be distributed within the bed satisfactorily. A more recent development is the circulating fluidized bed which has additional advantages including the ability to spread the feed material over a large bed area from a single feed point. The advantages of FBC systems offer a wider scope for solving most of the problems during co-firing RDF and wood wastes with coal than any other type of boiler.

Several FBC systems have been constructed in the U. S., Europe, and Japan for burning municipal waste alone or combined with wood waste.[17] However, there has been almost no experiences with municipal wastes and/or wood wastes co-fired with coal in FBC systems. Likewise, there is very little information available about adding limestone as a sorbent for sulfur oxides during co-firing RDF and wood wastes with coal. Therefore, in the current study of combusting mixtures of MSW, coal, and limestone, we tried to offer valuable information for combusting blends of these fuels in FBC systems. The optimum combustion temperature, the optimum amount of limestone to add and the optimum blends of coal and biomass materials were studied. We examined the quality of the fuels to be used, performing fundamental laboratory tests on the raw fuel mixtures, and collecting as much data as possible on fuels as useful information for testing the "best" fuel mixture in FBC systems. A test program to evaluate fuels derived from the combination of coal with biomass materials, including RDF and sawdust was carried out. The fuel combinations included crushed limestone as a sorbent for sulfur oxides. The test program included the following studies:

- Laboratory analysis and characterization of the coal, biomass materials, and limestone samples.
- Laboratory testing of the efficiency of absorption of sulfur oxides by various mixtures of refuse fuels with coal and limestone.
- Evaluation of the release and combustion of volatile matter followed by char combustion for the combination fuel mixture samples.
- Analysis of combustion residues for unburned carbon and sulfur oxides absorption.

B. Methods of Determining Carbon Dioxide in Combustion Residues

Another part of our work was to determine the forms of carbon in the combustion residues of RDF and coal. There is very little information available in this field. The American Society for Testing and Materials (ASTM) has developed a standard test method (D 1756) for carbon dioxide in coal.[18] In this method the determination of carbon dioxide is made by treating a weighed quantity of the sample in a closed system with acid and absorbing the carbon dioxide released on an absorbent. The increase in weight of the absorbent is a measure of the carbon dioxide in the sample used. Although the results can be used to calculate to the amount of inorganic carbon in the samples the method is tedious and requires a great deal of working skill to yield accurate results.

There are other different methods that have been used to determine total, organic and carbonate carbon in geologic materials. Larry L. Jackson and coworkers determined carbonate carbon by coulometric titration of acid-evolved CO_2.[19] Total carbon was determined by using a LECO model CR-12 instrument and combusting the sample at 1370°C in an oxygen atmosphere followed by detection of the evolved carbon dioxide with infrared spectrometry. The organic carbon was calculated as the difference between the total and carbonate carbon content. Saikkonen and Rautiainen[20] did this in a reverse way in which the total carbon was obtained by combusting samples at 1370°C in an oxygen flow, non-carbonate carbon was determined by leaching the sample with hydrochloric acid to remove carbonate carbon before combusting, and the concentration of carbonate carbon was calculated from the difference. In general, total carbon is best determined by combusting a sample and measuring the evolved carbon dioxide using infrared (IR) spectrometry,[21-23] a thermal conductivity detector,[24] coulometric titration,[25] or gravimetrically.[26-27] Organic carbon is determined as total carbon in a sample after removal of all carbonates by acid leaching,[28] or by direct oxidation,[29] or indirectly by difference between the total and carbonate carbon. Carbonate carbon is commonly determined by measuring the acid-evolved carbon dioxide gravimetrically,[30] volumetrically,[31] or by coulometric titration.[19,32,33] Nevertheless, as Terashima[23] points out, too little data has been collected for most geological reference materials to develop reliable consensus values.

In order to find out the "best" method to determine the forms of carbon in combustion residues of RDF and coal, we followed ASTM Method D 1756 using different acids and different apparatuses. We also modified other methods to test the carbon dioxide content in the residues. The residue samples used were the fly ashes from FBC systems in which RDF, wood wastes, rubber and coal, as well blends of these fuels, were combusted.

II. EXPERIMENTAL

Raw materials selected for the controlled combustion studies included coal from the Western Kentucky University reserve stockpile (#92050) and coal from the Kentucky #12 seam in Muhlenburg Co. KY (#85099), which are both high volatile B bituminous coal; a refuse-derived fuel from Robertson County, TN; a sawdust sample from the Tennessee Technological University; and agricultural limestone from Medusa Aggregates in Bowling Green, KY. Coal samples were prepared following ASTM procedure D 2013[34] for obtaining a representative analysis sample. The samples were pulverized to -60 mesh, split, and stored in a bottle filled with nitrogen and sealed with a heavy tape to help prevent the possible oxidation of pyrite by air. The coals were stored in a freezer until put in use. All raw materials were characterized by proximate analysis (moisture, volatile matter, ash analysis by ASTM Method D 5142[35]); ultimate analysis [carbon, hydrogen, nitrogen, sulfur, chlorine, and oxygen (by difference) analysis by ASTM Methods D 5373, D 4239, and D 4208[36]]; heating value tested by ASTM Method D 1989,[37] and mineral analysis of ash (13 major oxides including SO_3 by ASTM Method D 4326[38]).

A range of fuel mixtures were prepared, keeping in mind the heating values, the flammability/combustion properties, physical dimensions, and physical characteristics required of the fuels to be used in FBC systems. Specifically, combination fuels were prepared in a series as follows:

Materials	Ranges	Increments
coal	25% -- 100%	5% (16 total)
biomass	75% -- 0%	5% (16 total)
limestone	0% -- 10%	2% (6 total)

The -60 mesh (0.250 mm) coal was mixed with finely shredded paper (MSW) or sawdust and limestone, with all materials reduced to the same general partial size. The combinations of 16 increments of coal/biomass with 6 increments of limestone gave a total of 96 different compositions for each set of (coal + biomass + limestone mixtures). Since two types of biomass materials were used (RDF and sawdust), a total of 192 combination fuels were made. In further testing, blends of the sample materials were combined in series so that the amount of coal was between 50% and 94% in 10% increments, limestone added was 6%, and the amount of biomass materials made up the rest of the blend. In this way, there were 7 combinations of coal/biomass/limestone. Since two kinds of biomass were used, a total number of 14 samples were prepared.

All the combination fuels were subjected to carbon and sulfur analysis (ultimate analysis) which were used to compare with carbon and sulfur content in the residues of fuels blends. The proximate analysis of some fuel blends was performed using a LECO MAC-400 instrument for a comparison of normal ashing procedures.

A Fisher model 495A programmable temperature furnace was used to combust fuel blends and generate combustion residues for analysis. The furnace had the capacity for controlled heating and cooling in different atmospheres. Combustion of the fuel blends were carried out at temperatures of 600°, 750°, 800° and 900°C and at short time intervals of 0.5, 1, 2, 3, 5 minutes, and at long time intervals of 10, 15, 20, 25, 30 minutes. Gram size (2 grams) samples were used in porous (to air) quartz fiber crucibles with fiber sheets for covers.

The residues generated from furnace oxidations were analyzed for carbon, hydrogen, and nitrogen contents using a LECO CHN-1000 instrument and analyzed for sulfur contents using a LECO SC-432 instrument. The results from these analyses were used to evaluate suitable blends of coal + wood waste/RDF + limestone for combustion efficiency and sulfur trapping efficiency.

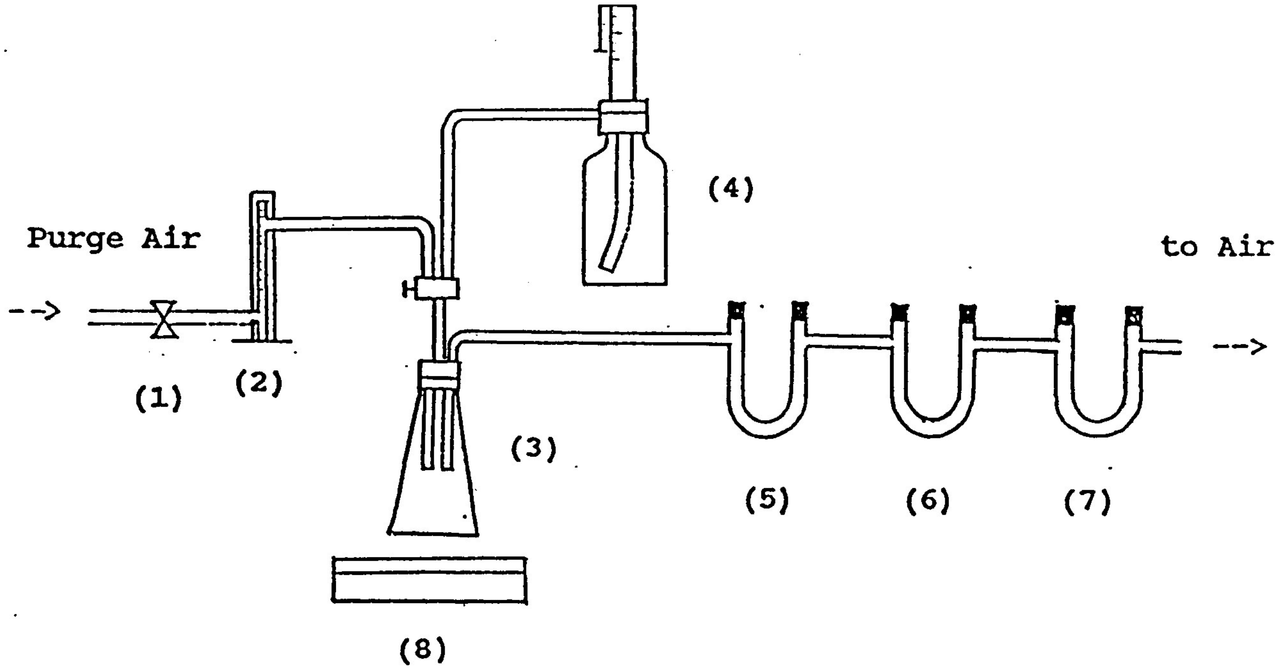
To determine forms of carbon in residues from the combustion of biomass wastes and coal, 15 fly ash samples were obtained from the FBC combustion facility studied by the Tennessee Technological University, in Cookeville, TN. These samples were subjected to proximate analysis, ultimate analysis and mineral analysis. Weighed quantities (2 grams) of fly ash samples were treated with phosphoric acid and the solution purged with air. The carbon dioxide released was absorbed by ascarite. The increase in weight of ascarite is a measure of the carbon dioxide in the sample used. The inorganic carbon can then be calculated. Total carbon was measured using a LECO model CHN-1000 instrument in which the sample is combusted at 1050°C in an oxygen atmosphere and the evolved carbon dioxide detected with a CO_2 infrared cell. The organic carbon is calculated as the difference between the total carbon and inorganic carbon.

The apparatus used in a modified method is shown in Figure 2. In this system, purging air is passed through air valve (1) and flow meter (2) into the reaction flask (3), which is also connected with a pipet-bottle of phosphoric acid (H_3PO_4)(4). The air flow carries the carbon dioxide through three U-shape glass tubes. In the three tubes there was anhydrous magnesium perchlorate [$Mg(ClO_4)_2$] for absorbing water (5), ascarite for absorbing carbon dioxide (6), and anhydrous calcium sulfate ($CaSO_4$) for absorbing water (7). A hot plate (8) was used to heat the flask with the sample and acid. The absorbents for carbon dioxide and water had a particle size of 8 - 45 mesh (2.36 - 0.36 mm). Reagents used included 50% phosphoric acid (H_3PO_4, sp. gr. 1.19) and 30% hydrogen peroxide (H_2O_2). In the apparatus all connections between the various components were assembled with flexible tubes, and the carbon dioxide adsorbent was filled with layers of the desiccant on each side of the absorbent.

The procedure for the modified method is as follows:

1. Introduce into the flask(3) 2.000 g of air-dried sample (passing a No. 200, 74 μm sieve), weighed to the nearest 0.1 mg. Add 50 mL of cold, carbon dioxide-free

Figure 2. The apparatus used in the modified method for the determination of carbon dioxide in combustion residues



distilled water, and 4 mL of hydrogen peroxide (30%). Heat the flask gently about 2-3 min, then cool.

2. Connect the flask to the assembly and allow air to flow into the apparatus at the rate of 13-15 mL/min for 15 minutes. Stop the air flow. Remove the absorber (6), wipe with a clean cloth and allow to come to room temperature. Weigh (6) to the nearest 0.2 mg, and then reconnect to absorbers (5) and (7). Start the air flow again.

3. Pipet 25 mL of phosphoric acid (1+1) from the pipet-bottle (4) into the flask (3). After the reaction subsides, heat the flask with a hot plate to slow boiling for 2-3 min. Remove the heat and continue the air flow for 20 min.

4. Stop the air flow, remove and wipe absorber (6) with a clean, dry cloth. After a few minutes of cooling, weigh absorber (6). The increase in weight is equivalent to the carbon dioxide in the sample.

The instrumentation used in these studies include a Fisher model 495A programmable temperature furnace, a LECO MAC-400 for proximate analysis, a LECO CHN-1000 for ultimate analysis, a LECO SC-432 for sulfur analysis, a selective ion electrode and meter for chlorine analysis, a LECO model AC-350 automatic calorimeter for heating value analysis, and an HNU TEFA X-ray fluorescence spectrometer for ash mineral analysis.

III. RESULTS AND DISCUSSION

A. Characterization of Refuse Fuels and Coals

The results of proximate analysis, ultimate analysis, heating value and miscellaneous analysis of two types of coal, two kinds of biomass (RDF, T-9B sawdust), and limestone are shown in Table 2. All the values in that table were on a dry basis. As can be seen from the data in the table, the volatile matter of both #92050 and #85099 coals are in the 32% - 36% range. Coal #92050 contains less sulfur than #85099 and has about half the amount of ash as #85099 coal. It also has a higher heating value. Therefore the quality of coal #92050 is better than #85099.

The biomass materials (RDF and T-9B sawdust) show very high volatile matter values (75% - 79%), thus their combustion rates are very fast. They can be utilized as valuable fuels since their heating values are above 8000 Btu/lb, which is approximately two-thirds of the heating value of bituminous coal, and they also have very low sulfur (0% - 0.1%) and ash contents (0.1% - 9%). The high ash content of RDF may be due to the presence of plastic, rubber and other miscellaneous materials.

During combustion, calcium carbonate in the limestone decomposes calcium oxide which will react with sulfur oxides.

Table 2. Characterization of Raw Fuels

Fuel Types	Coal		Biomass Materials		Sulfur Abs.
	#92050	#85099	RDF	T-9B Sawdust	Limestone
Ash	7.14	15.91	9.39	0.82	58.29
Vol. Matter	36.80	32.76	75.73	78.56	21.54
Btu/Pound	13408	12046	8012	8041	
Carbon	74.76	66.35	45.80	50.19	8.08
Hydrogen	4.80	4.4	6.19	5.99	0.03
Nitrogen	1.38	1.46	0.24	2.96	0.00
Sulfur	1.07	4.03	0.13	0.02	0.02
Oxygen	10.80	7.85	37.79	39.91	33.56
Chlorine(ppm)	458		4578	1180	202
Air Dry Loss	2.25	2.63	0.00	0.00	0.00

But limestone is a noncombustable substance and produces 58% ash in residues, which is a reason that the amount of limestone mixed in fuel blends cannot be too high.

B. Controlled Combustion of Coal/Refuse Fuel Blends

Three useful indices and calculations were chosen to help evaluate the combustion efficiency and sulfur trapping efficiency of fuel blends used in our study. They are Combustion Yield (Y), Carbon Retention Index (CRI) and Sulfur Retention Index (SRI).

The combustion yield is calculated as follows:

$$Y = \text{residue weight}/\text{sample weight} \times 100\% \qquad (1)$$

Combustion yield is the ratio of the amount of combustion residue to the amount of combination fuel used. It tells the percentages of residues generated from blends without the effects of different size of sample used and ash generated. It was used as a factor to eliminate the effect of sample and ash size when the amount of carbon retention and sulfur retention in residues were compared.

Carbon retention index (CRI) is calculated as follows:

$$\text{CRI} = (\text{carbon\% in residue}/\text{carbon\% in sample}) \times \text{yield} \qquad (2)$$

and sulfur retention index (SRI) is calculated as follows:

$$\text{SRI} = (\text{sulfur\% in residue}/\text{sulfur\% in sample}) \times \text{yield} \qquad (3)$$

Carbon retention index or sulfur retention index is a percent of carbon or sulfur in residues without any effect of residue or sample size. Thus making the comparison of combustion or sulfur trapping efficiency more obvious and accurate.

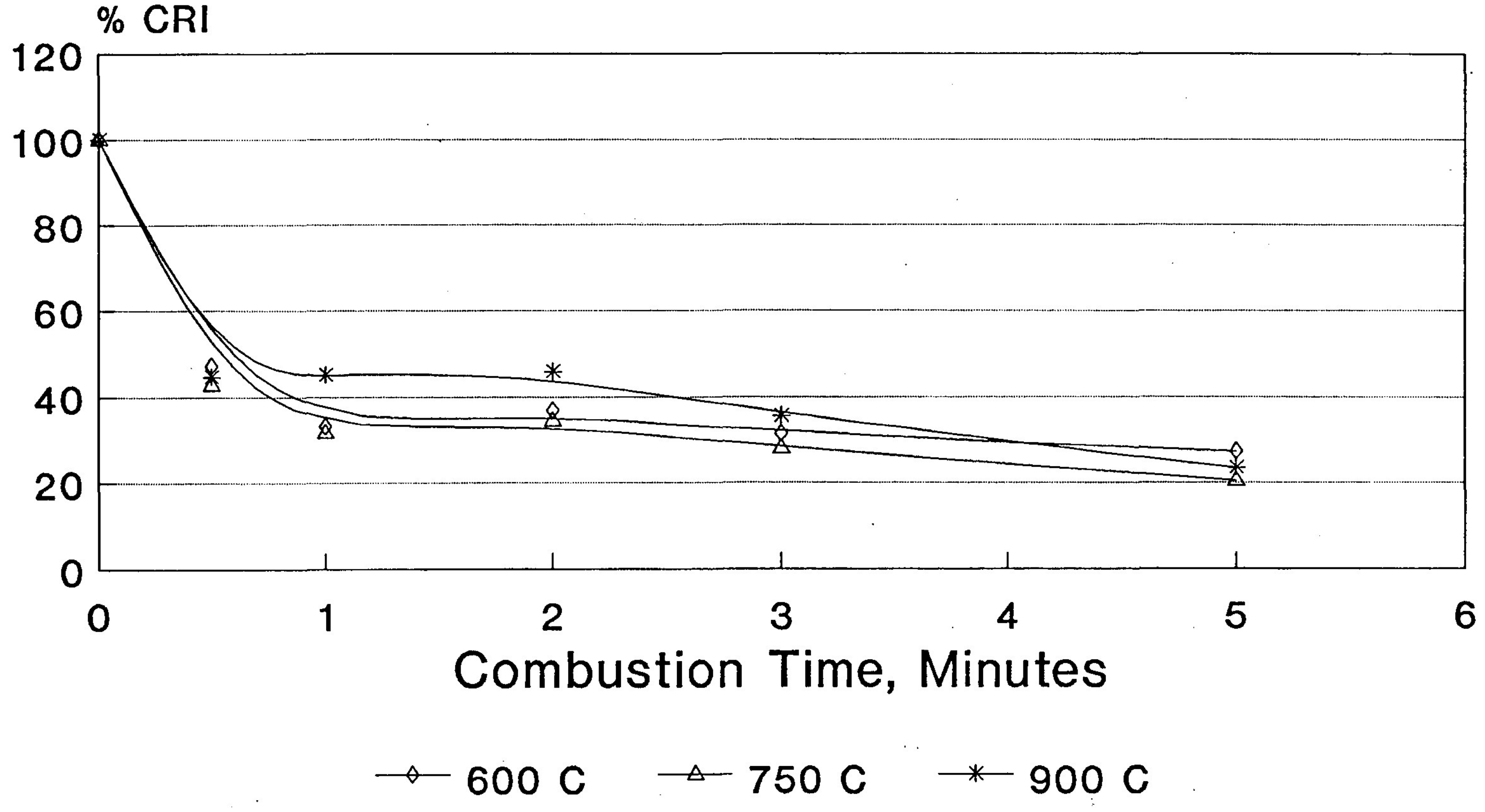
The evaluations of combustion efficiency of fuel blends includes three parts which are (1) the analysis of unburned carbon in residues at different temperature and time of combustion, (2) the analysis of sulfur trapped in residues at different temperature and time with different amounts of limestone added, (3) and the analysis of carbon and sulfur in residues at different composition of fuels at a certain temperature of combustion.

1. Analysis of Carbon Content in the Combustion Residues From Different Temperatures

Figure 3 shows the carbon retention index for fuel blend 50/44/6 (coal/RDF/ limestone) combusted at 600°, 750°, and 900°C over a short time range (0.5 - 5 minutes). The 44% RDF added in the blend is close to the highest amount recommended.[14] At 900°C, the CRI for the residue dropped very fast in the first 0.5 minutes, remained at the highest value for the three temperatures during the 0.5 - 4 minute period, and then decreased after 4 minutes combustion. At 750°C, the CRI dropped very fast in the first 1 minute and remained at the lowest value during the 5 minutes combustion. A value of 20% for the CRI was found after 5 minutes of combustion at 700°C, whereas a higher CRI (25% - 30%) was obtained for the residues at 900° and 600°C combustion. The value of CRI during 600°C combustion was between that of 750° and 900°C.

Because of volatile matter loss the CRI decreased about 70% in the first minute at all three combustion temperatures.

Figure 3. CRI vs. combustion time at different temperatures for combination fuel R50/44/6



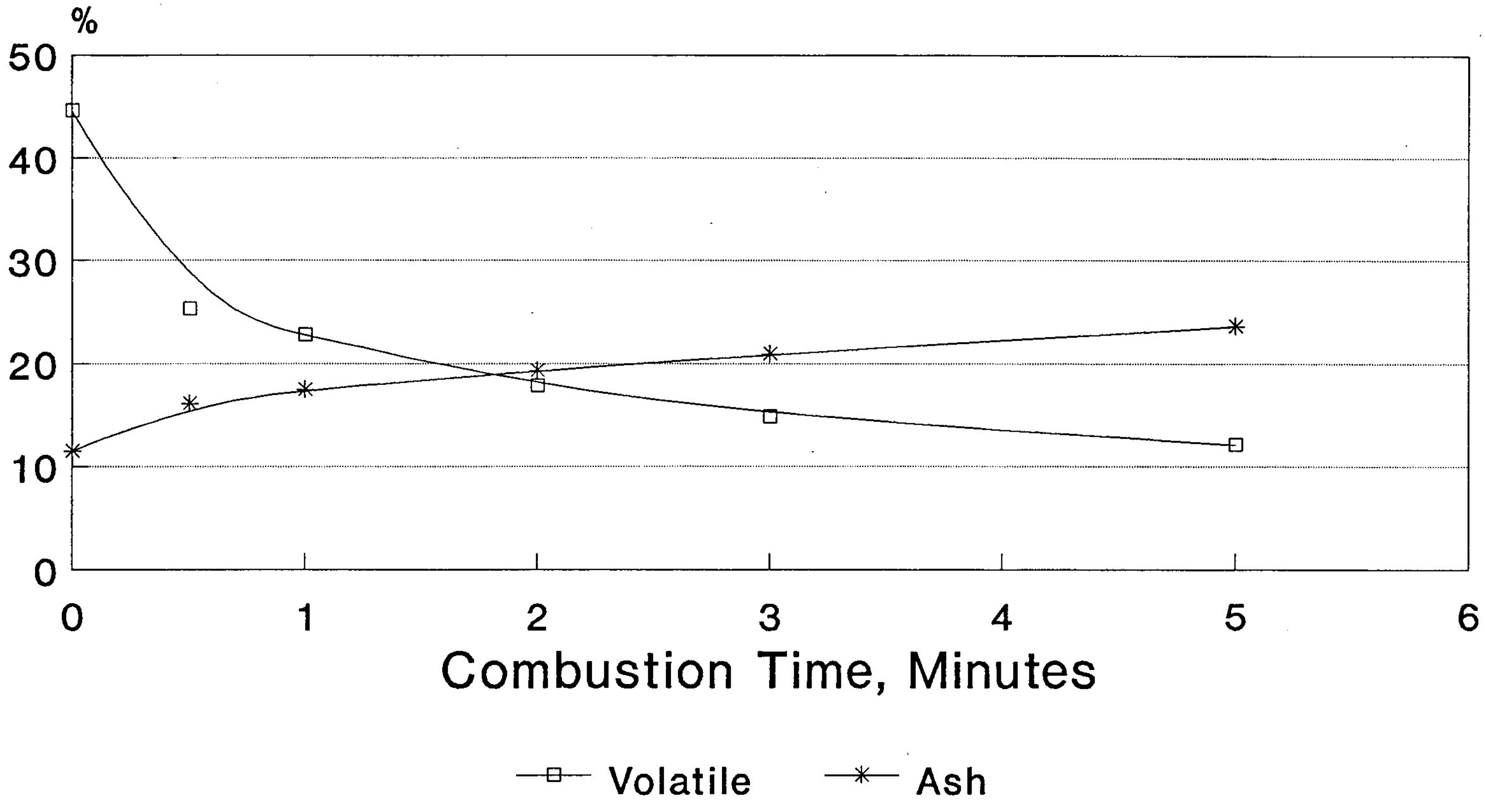
Coal 92050

The more volatile matter there is in the fuel blends, which means the more biomass in blends, the lower the CRI loss for the residues (illustrated in Figures 11 and 12). With the increase in combustion time, the weight loss tended to be stable because of "char" or "coke" formation, as well as ash formation, as shown more directly by the MAC-400 analysis illustrated in Figure 4. Sample 80/14/6 (coal/RDF/ limestone) was combusted at 750°C over a short time range, then the residues were analyzed with the MAC-400 instrument for the volatile matter and ash contents. The volatile matter curve shows the same trend as the curves of CRI in Figure 3. The ash curve goes up with the increasing combustion time.

Sample 79/15/6 (coal/RDF/limestone), with relatively low RDF content, was combusted at temperatures of 600 and 800°C (Figure 5). At 800°C, the carbon percent in the residue remained higher in the first 2.5 minutes because of incomplete burning, then dropped to about 34% carbon after 5 minutes of burning. Carbon percent remained almost unchanged in the residue for the 600°C combustion.

Figure 6 and Figure 7 represent data for blends of coal/RAF/limestone at the percentages of 75/25/0 (Figure 6) and 69/25/6 (Figure 7) combusted over long time periods (5 - 30 minutes). For the 600 and 900°C runs, the carbon contents in the residues were about 25% - 52% at 5 minutes, decreased about half within 5 - 10 minutes additional combustion, and approached zero as the combustion time reached 25 minutes. For the 750 or 800°C runs, with about 10% - 24% carbon after

Figure 4. MAC-400 analysis of residue of fuel blend R80/14/6 combusted at 750 C



Coal 92050

Figure 5. Carbon in residues vs. combustion time at different temperatures for fuel blend R79/15/6

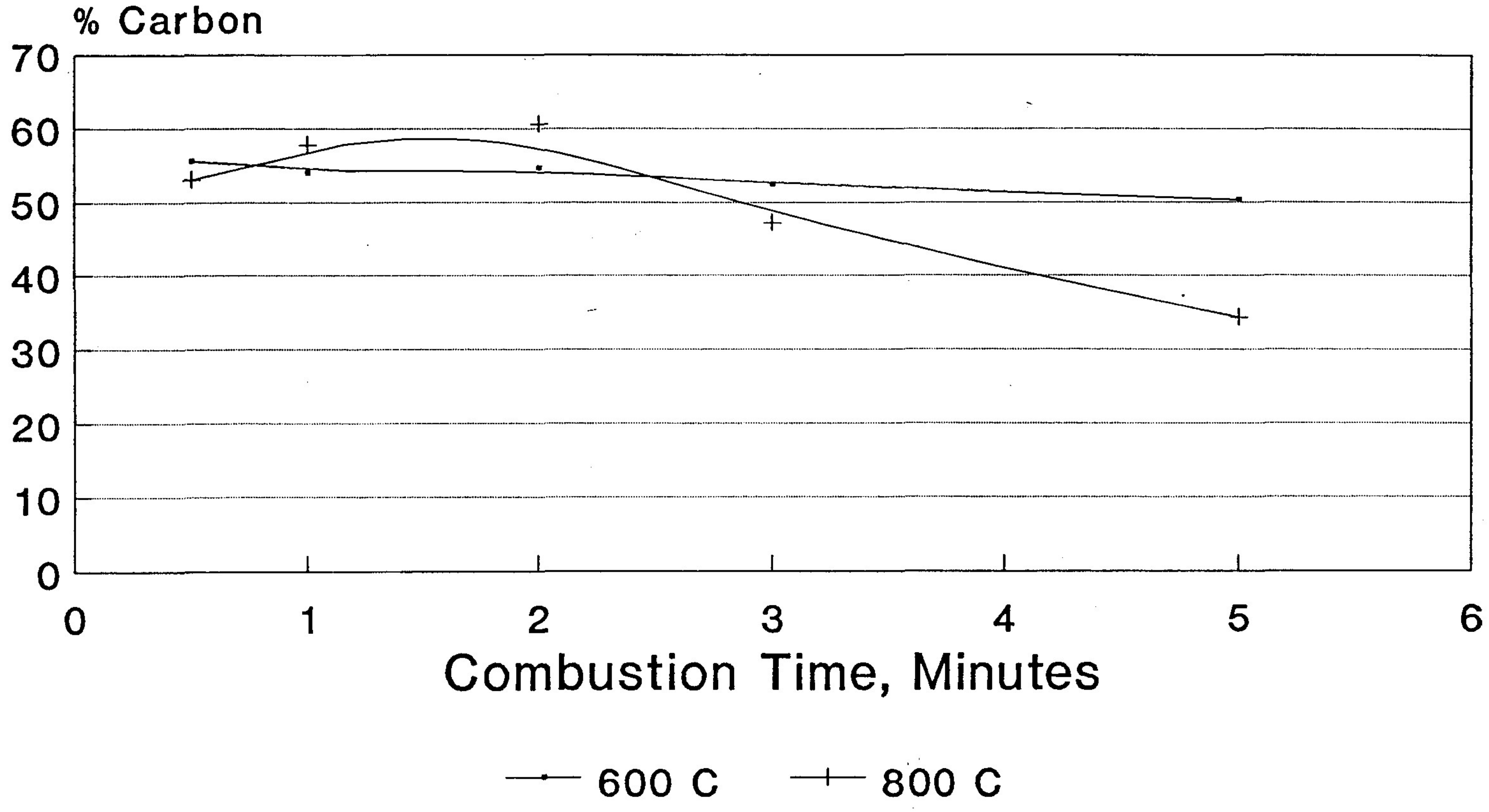
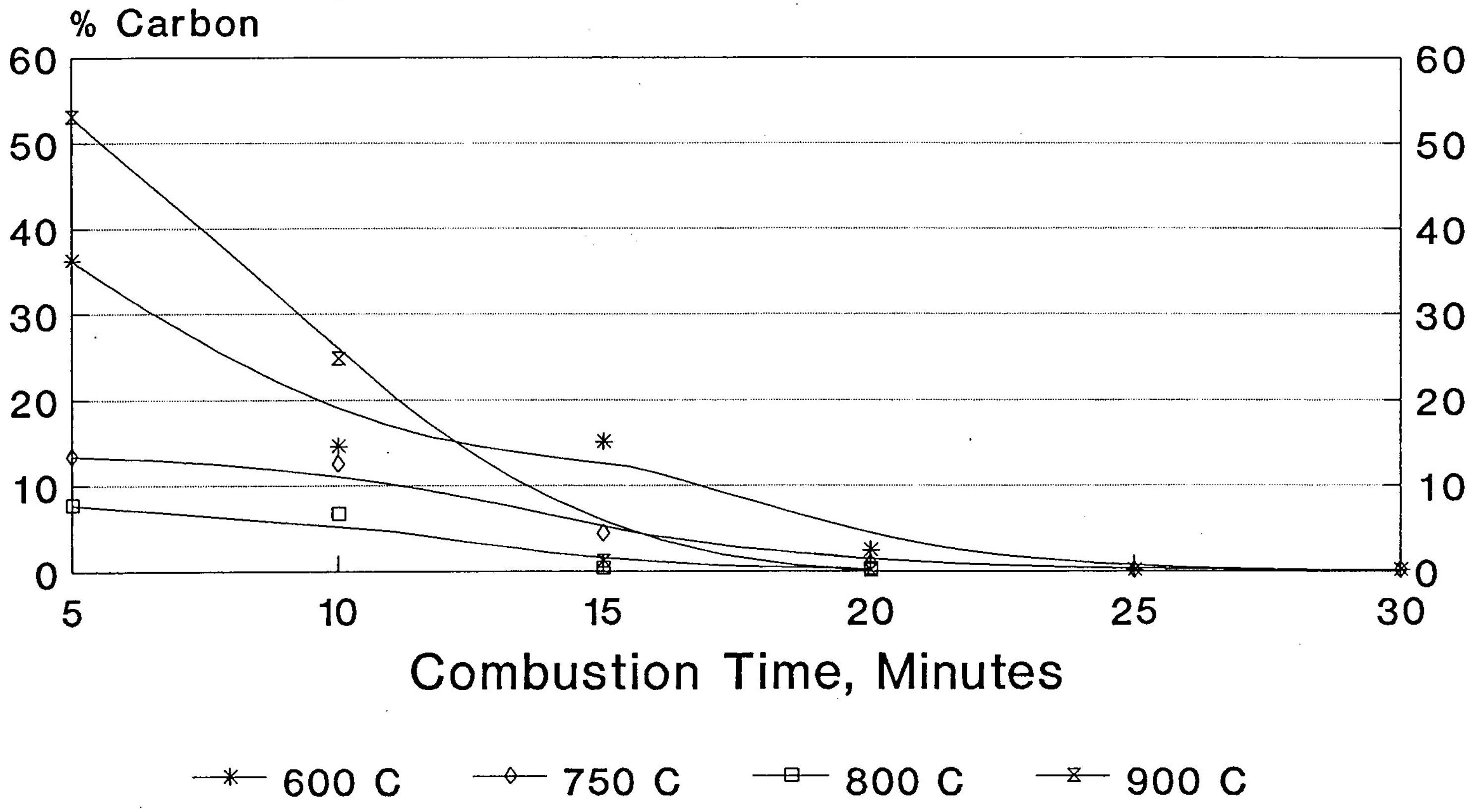
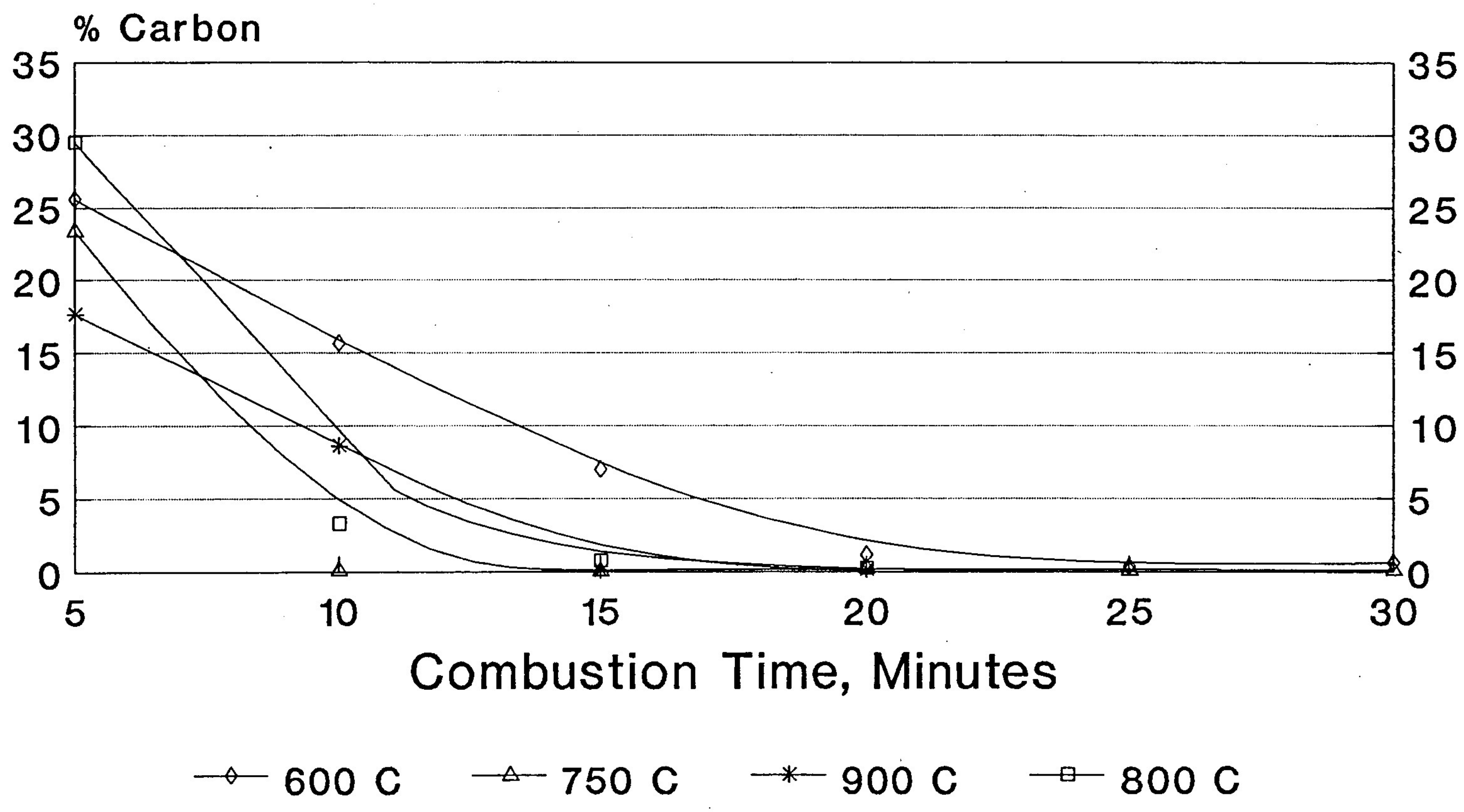


Figure 6. Carbon in residues vs. combustion time at different temperatures for fuel blend R75/25/0



Coal 85099

Figure 7. Carbon in residues vs. combustion time at different temperatures for fuel blend 69/25/6



Coal 85099

about 5 minutes, the blends burned faster and the carbon contents were the lowest in the residues.

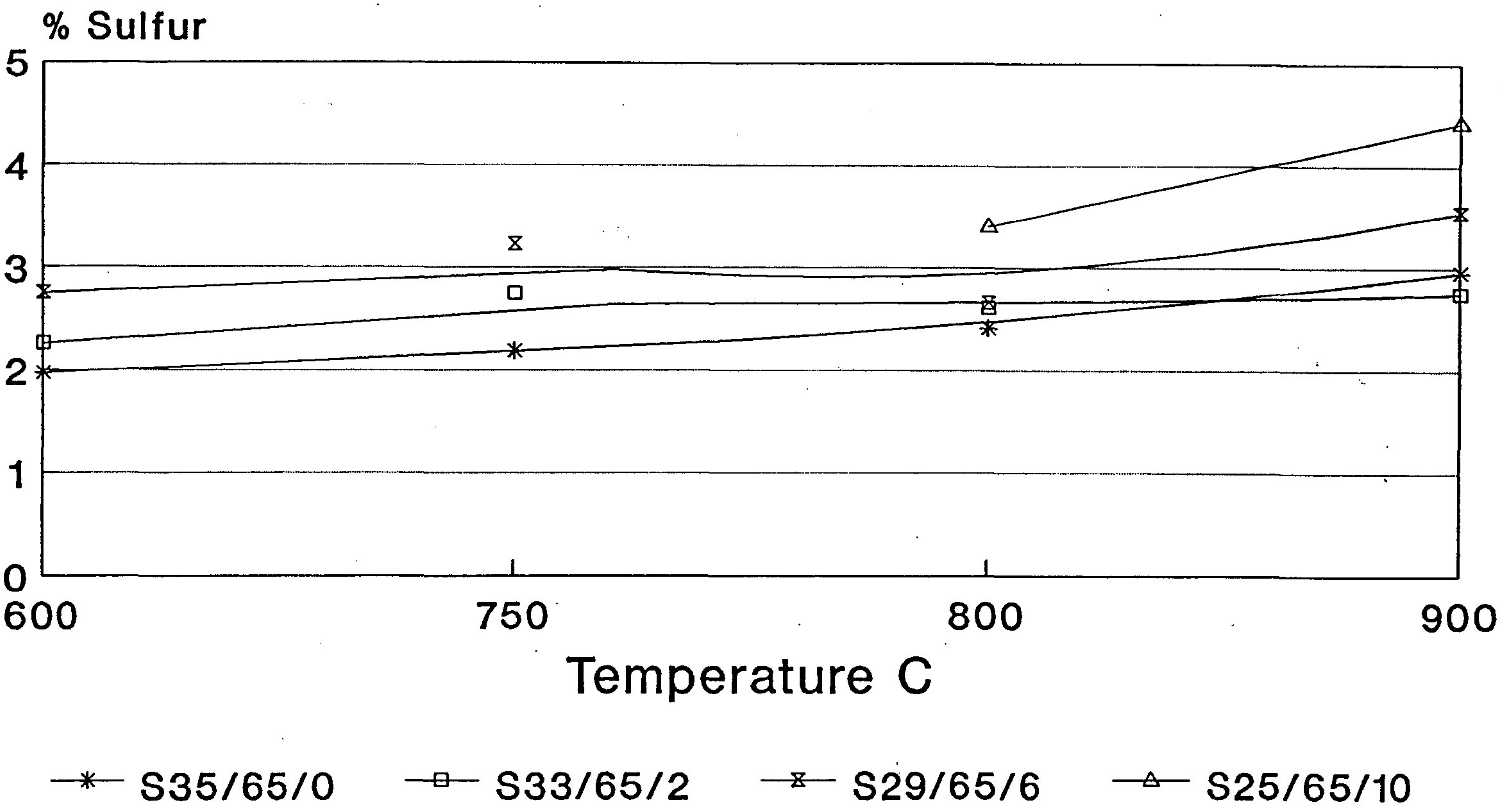
The reason that the 600°C run had the highest residual carbon values (Figures 6 and 7) is that at this temperature many combustion reactions were not completed, and considerable organic matter and carbon remained in the residues. At 900°C the samples pyrolyzed very quickly loosing volatile matter and formed a large amount of char. The char is harder to combust; therefore, these residues had large carbon contents.

Combustion efficiency was affected very little by limestone addition up to 6%. In general, analysis of the residues from the combustion of different combination fuels at different temperatures and times showed that the lowest carbon values or carbon retention indexes in residues was found for combustion at 750° - 800°C. In this temperature range the most complete combustion and the best combustion efficiency was achieved.

2. Analysis of Sulfur Contents in Combustion Residues

As discussed previously, sulfur contents in coal/refuse fuel blends will be less than those of coal. Desulfurization of combustion gases was accomplished when limestone was used as a sulfur oxides absorbent in our study. Figure 8 shows data for samples with 65% sawdust mixed with 0, 2, 6, and 10% limestone with the balance coal. The samples were burned at different temperatures for 10 minutes. The sulfur contents in the residues increased with an increase in the amount of

Figure 8. Sulfur in residues vs. temperature with different amounts of limestone combusted for 10 minutes



Coal 85099

limestone in the blends. Therefore, the more limestone used, the better the SO_2 trapping efficiency up to a point. Considering the overall combustibility of the sample, 6% limestone was chosen as the most efficient amount of limestone to be added in blends. Within the best combustion temperature range of 750 - 800°C, 6% limestone can trap more than 3% sulfur in residues of the blend 29/65/6 (coal/sawdust/limestone).

Figure 9 shows the SRI indices for coal/sawdust/limestone blends 59/35/6 and 79/15/6 versus the short combustion times at temperatures of 600 and 800°C. The curves show trends similar to the CRI curves. In the first minute the SRI decreased about 60% - 80% mainly because of weight loss. With increasing time, both samples show higher sulfur trapping at 800° than that at 600°C. The difference between 600° and 800° was not very much because of short combustion times.

Figure 10 shows the sulfur percent in residues of 69/25/6 (coal/RDF/ limestone) versus the combustion time at different temperatures. When combustion time increased from 5 minutes to 30 minutes, the sulfur in the residues increased. The most efficient sulfur trapping occurred at 750°C because the highest sulfur percents in ash were found, which were as high as 4.5% at 25 - 30 minutes combustion. At 600°C sulfur percents increased with an increase in combustion time, and up to about the same as that at 750°C in 30 minutes. From 5 to 20 minutes, the sulfur contents at 900°C remained at about 3%.

Figure 9. SRI vs. combustion time at different temperatures for blends S59/35/6 and S79/15/6

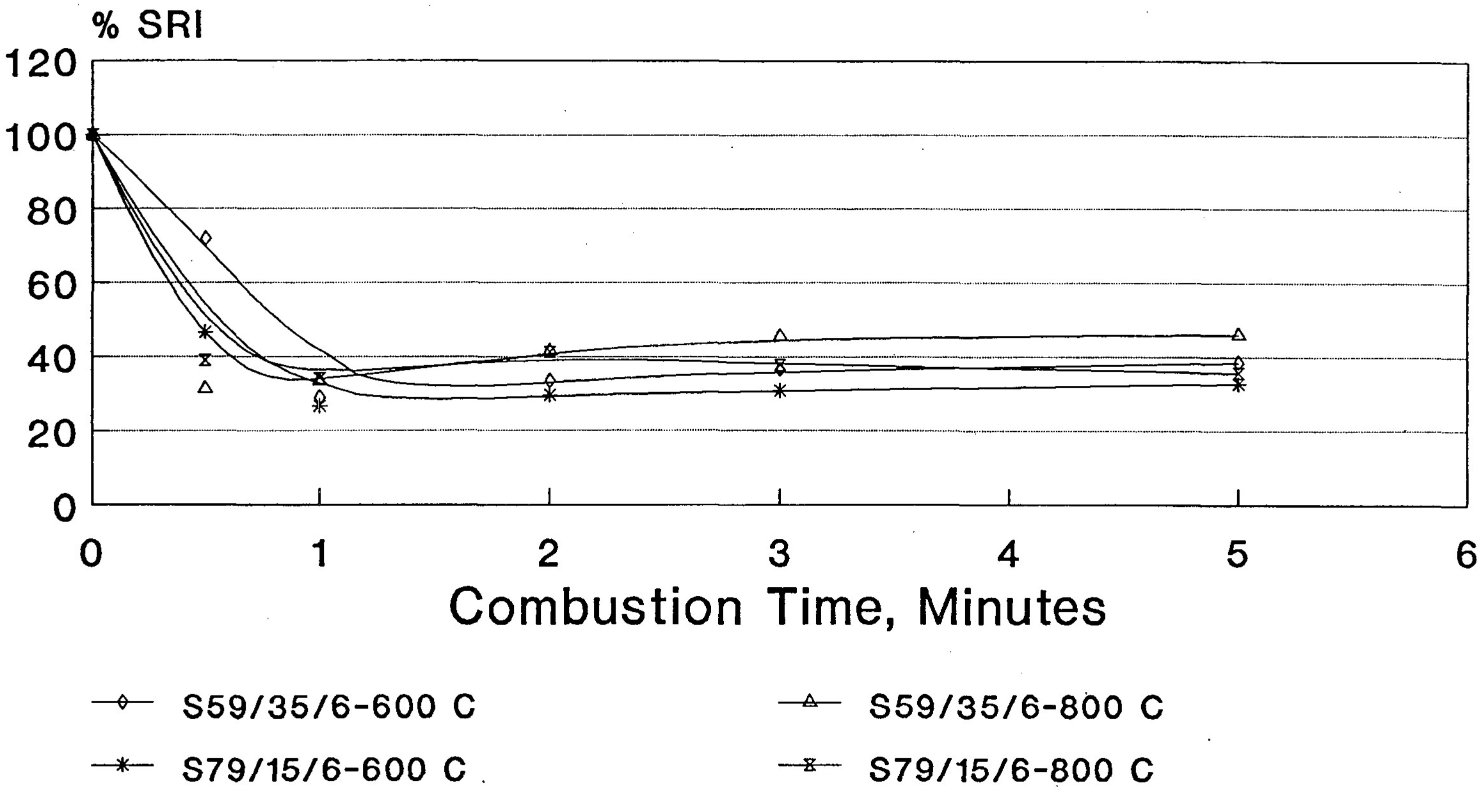
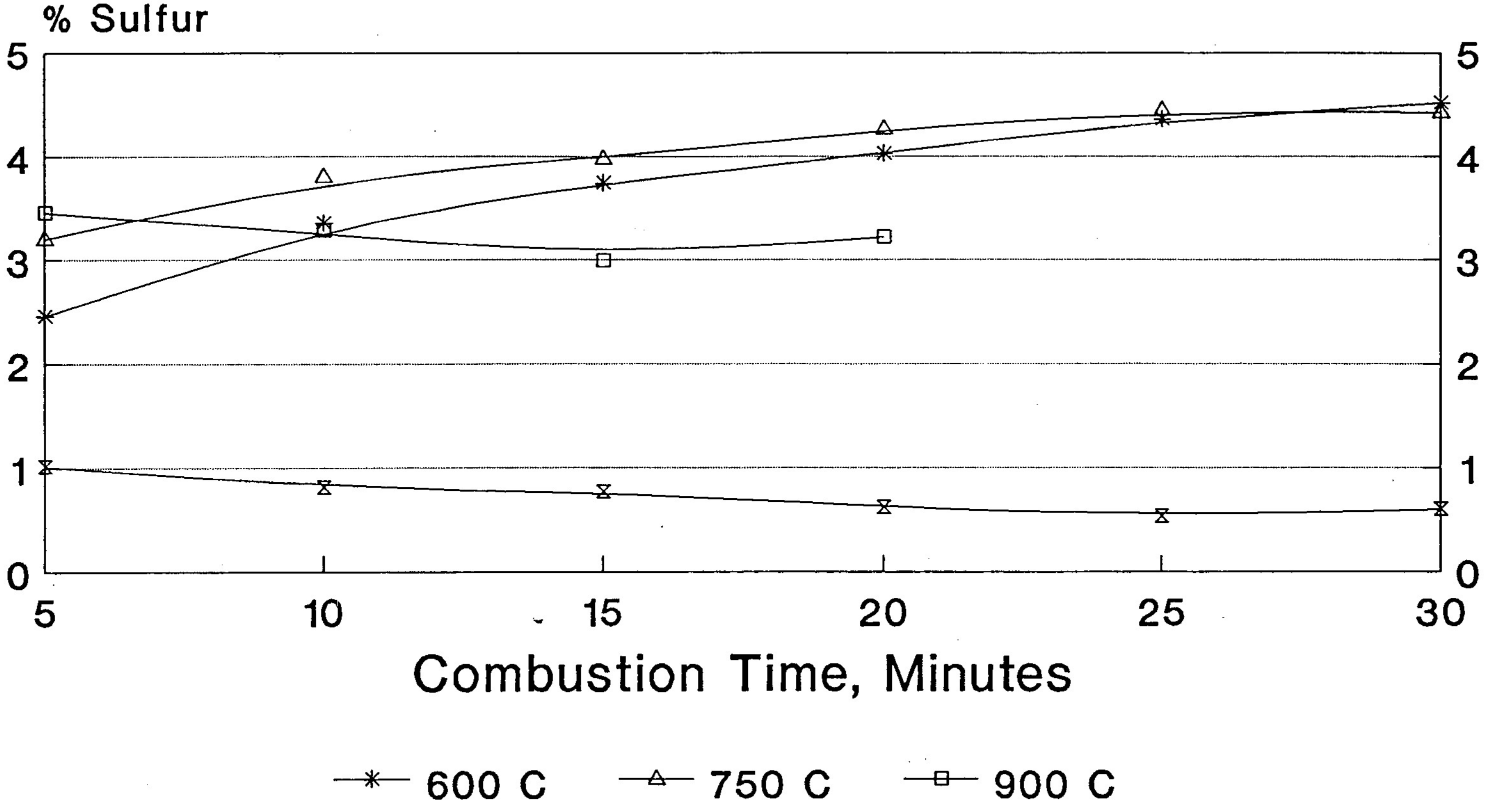


Figure 10. Sulfur in residues vs. combustion time at different temperatures for fuel blends R69/25/6



Sulfur in coal occurs in three forms: organic, sulfate, and pyritic. Organic sulfur, which is an integral part of the coal matrix and which comprises from 30% to 70% of the total sulfur of most coals, will be combusted and released as shown by the following equations:

$$RSH + 3/2\ O_3 \text{ ---> } RSO_2OH \tag{4}$$

$$2RSSR + 2H_2O + 5O_2 \text{ ---> } 4RSO_3H \tag{5}$$

Most organic sulfur compounds require temperatures of approximately 475°C.[39] RSO_2OH and RSO_3H will decompose to form SO_2 in the further combustion reactions.

Pyritic sulfur, FeS_2, can be oxidized to $FeSO_4$ during combustion:

$$FeS_2 + 3O_2 \text{ ---> } FeSO_4 + SO_2 \tag{6}$$

$$2FeS_2 + 11/2\ O_2 \text{ ---> } Fe_2O_3 + 4SO_2 \tag{7}$$

$$FeS_2 + 7/2\ O_2 \text{ ---> } 1/2\ Fe_2(SO_4)_3 + 1/2\ SO_2 \tag{8}$$

These reactions, beginning about 300°C, proceed through 400-500°C at a measurable rate.[40]

Limestone begins to decompose to lime and carbon dioxide at temperatures above 300°C during combustion:

$$CaCO_3(s) \text{ ---> } CaO(s) + CO_2(g) \tag{9}$$

Reaction (9) is the calcination step and is very quick. By converting calcium carbonate to calcium oxide, the product becomes more porous and more readily absorbs sulfur dioxide on its surface. Calcium oxide will react with the sulfur dioxide in the combustion system to form the intermediate calcium sulfite:

$$CaO(s) + SO_2(g) \text{ ---> } CaSO_3(g) \tag{10}$$

and then:

$$CaO(s) + SO_2(g) + 1/2O_2 \;\text{--->}\; CaSO_4(s) \qquad (11)$$

Reaction (10) occurs at temperatures above 330°C.[41] Below 640°C calcium sulfite dominates over the formation of calcium sulfate. At 720°C some of the calcium sulfite decomposes; as the temperature rises, calcium sulfite oxidizes to form calcium sulfate (11). This step is slow, and it is the rate determining step.[41] The optimum temperature for trapping sulfur oxides was found to be in the 750 to 800°C range, because all the reactions occur below these temperatures. At 900°C blends form char too fast and delay the combustion reactions as well as these sulfur decompositions and oxidizations. Therefore, the sulfur contents in ash are lower at this temperature than those at the optimum temperature.

3. Analysis of Carbon and Sulfur in Residues

Figure 11 shows the CRI's for different mixtures of coal, RDF and limestone combusted for short burning times. Figure 12 shows the CRI's of coal, sawdust and limestone mixtures combusted for short times. The CRI curves show trends similar to previous discussions. The CRI value decreases, which means the combustion rate increases with increasing amounts of RDF or sawdust in the blends -- due to the higher volatile matters in the blends with higher RDF or limestone. When only coal is mixed with limestone (94/0/6), the CRI shows the highest value in the residues and is about 50% after 5 minutes. With only RDF or sawdust mixed with limestone (0/94/6), the CRI drops to

Figure 11. CRI vs. combustion time at 750 C for different blends of coal/sawdust/limestone

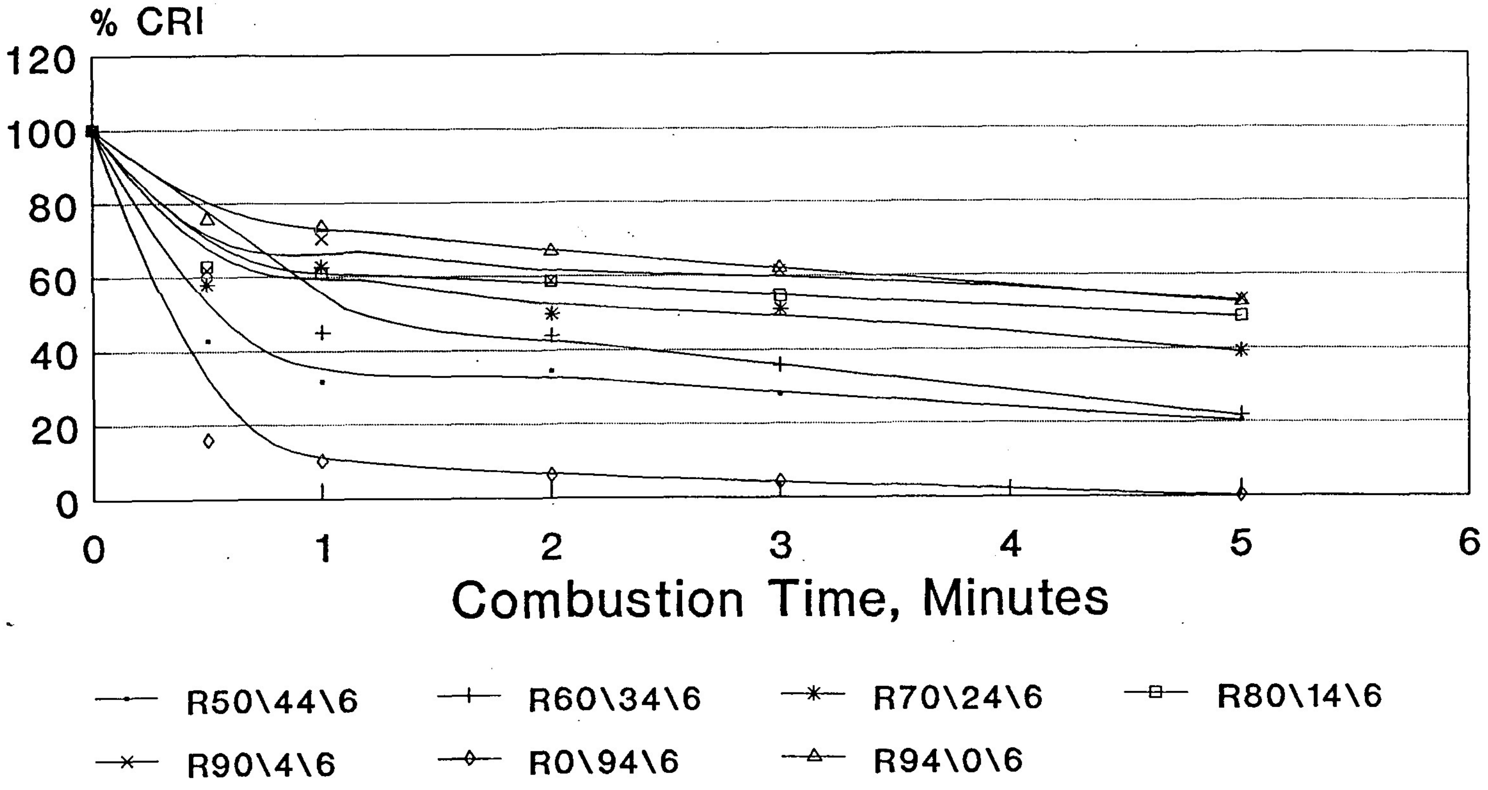
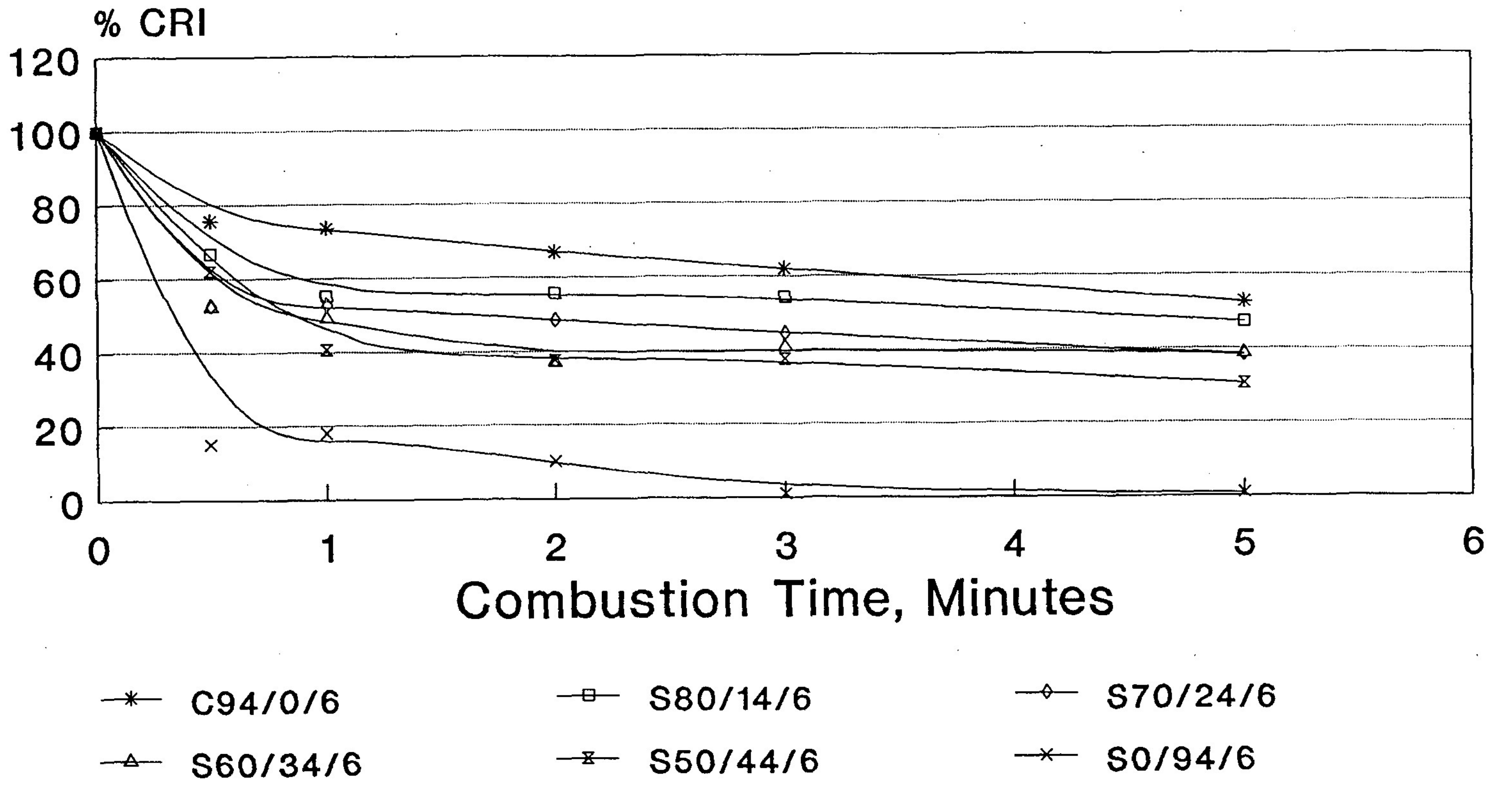


Figure 12. CRI vs. combustion time at 750 C for different blends of coal/RDF/limestone



Coal 92050

about 10% in the first minute and to near zero after 4 minutes. The other curves remain in the middle. With biomass increasing up to about 44%, the CRIs drop to 30% - 40%, which is still considered to be an efficient combustion rate.

The effect of desulfurization was also studied in the different fuel blends containing 6% limestone. Figure 13 shows one set of the results. Taking the sample 50/44/6 (coal/RDF/limestone) as an example, with the 1.8526 gram sample used, the sulfur in the sample was calculated to be 0.0110 gram. After 5 minutes combustion, the sulfur in the ash was about 1% in the 0.4764 gram of ash which is about 0.0048 gram of sulfur in the ash. Therefore, about 44% of the sulfur is trapped, an indication that very good sulfur trapping potential can be obtained with the biomass, coal and limestone blends.

C. Determination of Carbon Dioxide in Combustion Residues

To determine the forms of carbon in combustion residues, the fly ash samples used were characterized by ultimate analysis and mineral analysis (Table 3). When unsuitable combustion conditions were observed in the FBC, the waste fuels were incompletely combusted. Therefore, high carbon contents are contained in some of the fly ashes in Table 3. Because the hydrogen contents are near zero, the carbon in the fly ashes are in the form of incombustible "char."

During the beginning of the study, ASTM standard method D 1756 was followed so that hydrochloric acid was used to

Figure 13. Sulfur in residues vs. time at 750 C with 6% limestone mixed with RDF and coal

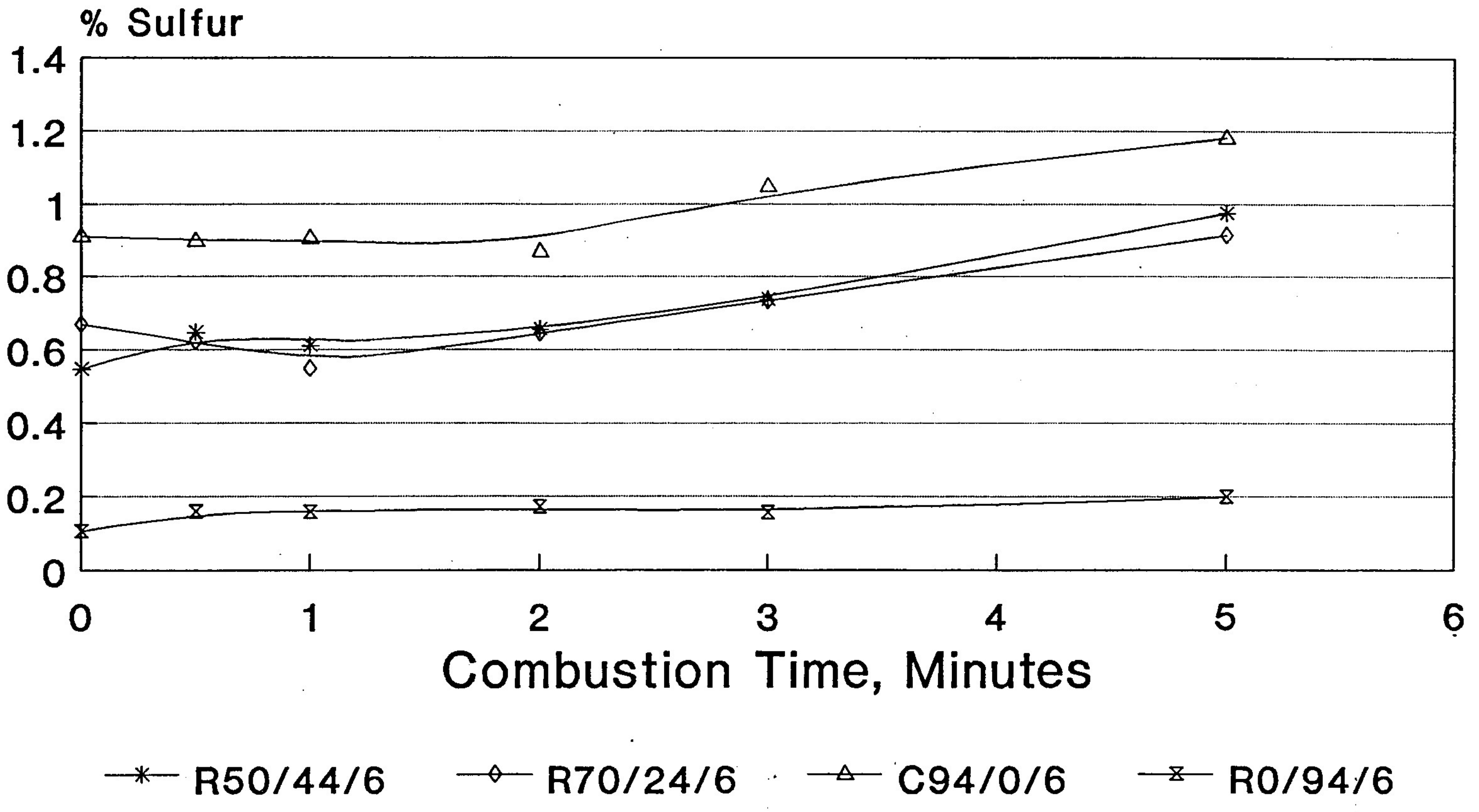


Table 3. Analysis of Fly Ash

	C	H	N	SiO2	P2O5	SO3	K2O	CaO	TiO2	Fe2O	Na2O	MgO	Al2O3	SrO	BaO	MnO2
7-3,	4.97	0.05	0.53	18.6	<0.01	0.48	0.01	53.72	0.33	0.89	1.55	10.32	14.4	0.06	0.36	0.03
8-19,	4.97	0.05	0.53	23.46	<0.01	3.38	<0.01	43.31	0.7	2.16	1.57	8.25	16.94	0.07	0.12	0.05
11-7,WC	4.02	0.06	0	25.36	<0.01	3.04	<0.01	42.95	0.72	2.1	1.53	7.85	16.07	0.06	0.29	0.04
T-1,Run	36.88	0.49	0.66	39.8	0.054	5.34	0.83	24.7	0.62	4.73	1.3	7.95	14.4	0.058	0.16	0.58
Test 2-B	28.4	<0.01	0.7	28.2	1.89	28.6	1.79	31.1	0.56	14.1	1.27	5.22	4.52			<0.01
Test-5	22.93	-0.04	0.38	49	1.78	12.4	2.76	23.7	0.9	11.5	1.13	3.76	12.4			<0.01
T-9,WC	35.57	0.24	0.62	14.8	2.74	14.6	1.63	42.9	0.8	9.04	1.34	6.93	5.12			
T-10,1800	16.62	0.14	0.26	36.5	0.65	5.77	1.6	23.9	1.38	4.98	1.08	4.14	19.9	0.05	<0.01	0.02
T-11	4.05	0.09	0	27.1	2.37	6.23	0.9	29.7	1.52	3.58	0.97	5.02	17.8	0.06	<0.01	0.004
T-15	30.21	0.28	0.5	17.5	<0.01	18.7	1.83	30	0.35	9.11	2.36	9.03	7.13	0.05	4.26	0.07
RDF,T-16	10.87	0.09	0	22.3	3.05	4.65	1.85	43.2	1.67	6.18	0.81	4.78	11.2			0.02
T-17	38.63	0.26	0.56	23.2	1.63	7.05	1.35	37.8	0.91	14.5	0.84	4.53	7.59			0.5
T-18 Rubber	22.91	0.16	0.09	19.4	1.58	17.4	1.97	32.3	1.24	11.1	1.49	7.28	6.14			0.43
T-22	5.97	0.16	0.22	38.57	<0.01	2.84	0.2	24.54	1.72	1.92	1.21	3.56	25.19			0.02
3-11,	5.42	0.09	0	28.77	0.98	11.36	0.33	28.88	0.48	5.62	1.25	5.88	15.99	0.09	0.33	0.05
T-23	2.46	0.1	0.28	21.95	<0.01	1.41	<0.01	50.93	0.38	1.31	1.57	8.93	13.14	0.06	0.28	0.04

react with calcium carbonate and release carbon dioxide. The results from this method varied over a wide range, and some of values were unreasonable (Table 4). The reason is that hydrochloric acid vapor generated in the heating process was also absorbed in the absorbent, causing erroneous results. Therefore, phosphoric acid was then chosen; the fly ash samples were analyzed again (Table 5). The results were much better but still show some variations.

If there were mixtures of calcium carbonate and calcium sulfite in the samples, each would react with acid and release carbon dioxide as well as sulfur dioxide. Both gases would be absorbed by ascarite and give incorrect values. For this reason the samples were pretreated with hydrogen peroxide. The relative reactions are as follows:

Calcium carbonate and calcium sulfite mixtures react with acid:

$$3CaSO_3(s) + 2H_3PO_4(aq) \text{ ---> } Ca_3(PO)_4(s) + 3H_2SO_3(aq) \quad (12)$$

$$H_2SO_3(aq) \text{ ---> } H_2O(aq) + SO_2(g) \quad (13)$$

$$3CaCO_3(s) + 2H_3PO_4(aq) \text{ ---> } Ca_3(PO)_4(s) + 3H_2CO_3(aq) \quad (14)$$

$$H_2CO_3(aq) \text{ ---> } H_2O(aq) + CO_2(g) \quad (15)$$

Pretreating with hydrogen peroxide causes the following:

$$CaSO_3(s) + H_2O_2(aq) \text{ ---> } CaSO_4(aq) + H_2O(aq) \quad (16)$$

Table 4. Analysis of Carbon Dioxide in Fly Ashes by ASTM Method D 1756

Fly Ash	Run 1	Run 2	Run 3	Average
#1	0.04	0.035	0.025	0.033
#2	<0.001	<0.001		<0.001
#3	0.035	0.01		0.023
#4	0.04	0.011	<0.001	0.017
#5	0.01	0.13	0.035	0.058

Table 5. Analysis of Carbon Dioxide in Fly Ashes by Reacting with H_3PO_4

Fly Ash	Run 1	Run 2	Run 3	Run 4	Average
#1	0.234	0.115	0.181		0.18
#2	0.06	<0.001	<0.001	<0.001	0.005
#3	0.065	0.22	0.13		0.138
#4	0.12	0.35			0.24
#5	0.055	0.065	0.043		0.061
#6	0.06	2.14	0.51		0.9
#7	0.34	0.23			0.29
#8	0.16	0.24			0.20

$CaCO_3(s) + H_2O_2(aq) \dashrightarrow$ No reaction in basic solution

To modify the ASTM method, we also changed the aspiration system to the air flow system and simplified apparatus system. The standard deviations for the results given in Table 6 show that this method is reliable and assumed to be accurate.

Table 6 also shows the results of carbon dioxide and inorganic carbon in the fly ash samples tested by the modified method. Calculation of the percentages of carbon dioxide in residues is shown as follows:

$$CO_2\% = (A/B) \times 100 \tag{17}$$

where: A = increase in weight of absorber, in grams.

B = grams of sample used.

The value of carbon dioxide in fly ash can be used to estimate mineral matter content, particularly $CaCO_3$ and $MgCO_3$. Conversion of carbon dioxide to inorganic carbon is as follows:

$$C\% = CO\% \times 12/44 \tag{18}$$

Organic carbon is calculated by subtracting the inorganic carbon from the total carbon (in Table 3).

Table 6. Analysis of the Forms of Carbon in Fly Ashes

	CO2 % 1	CO2% 2	CO2 % 3	CO2 %Avg	Sdv.	Inorg.C%	Org. C%
Spl #1 91016	2.39	2.45		2.42	0.04	0.66	
7-3, 8-19	4.16	4.94	4.18	4.43	0.44	1.21	3.76
11-7, W.C.	4.09	3.69	3.93	3.9	0.2	1.06	2.96
T-1, Run	1.31		1.91	1.61	0.42	0.44	36.44
Test 2-B	1.27	1.57	1.64	1.44	0.2	0.39	28.01
Test-5	1.54	1.62		1.58	0.06	0.43	22.5
T-9 W.C.	<0.001	0.46	0.21	0.22	0.23	0.06	35.51
T-10, 1800	0.21	0.36		0.29	0.11	0.08	16.54
T-11	0.82	1.42	0.61	0.95	0.42	0.26	3.79
T-15	0.59	0.3		0.45	0.17	0.12	30.09
RDF (T-16)	1.67	1.3	1.89	1.62	0.3	0.44	10.43
T-17	0.55	0.47		0.51	0.06	0.14	38.49
Jates Rubber	1.42	1.53		1.48	0.08	0.4	22.51
T-22	0.41	0.31		0.36	0.07	0.098	5.87
3-11, T-23	0.99	1.48		1.24	0.35	0.34	5.08

IV. CONCLUSIONS

The following conclusions can be drawn from this study:

1. The optimum temperature for combustion of most coal/refuse fuel blends was found to be 750° - 800°C.
2. The percentages of biomass materials to be mixed with coal in the fuel blends may as high as 44% for refuse derived fuels and sawdust.
3. The optimum amount of limestone to be used as an absorbent for sulfur oxides in the fuel blends is 6% in the 750° - 800°C temperature range.
4. The method of determination of carbon dioxide in residues has been developed from ASTM Method D 1756 and showed an accuracy of 0.04 to 0.4%.
5. A method for the determination of forms of carbon has been developed for the fly ash residues from the fluidized bed combustion of waste fuels.

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