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THE EFFECT OF LIMESTONE ON THE COMBUSTION OF FUEL BLENDS

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Combustion profiles of coal-limestone-paper blends were studied using thermogravimetric/Fourier transform infrared spectroscopy (TG/FTIR). The role of limestone in promoting the initial combustion of coal-paper blends and its ability to absorb sulphur oxides were examined.

Keywords: coal-paper blends, combustion, fuel blends, limestone, TG/FTIR

Introduction

More than 180 million tons of municipal solid waste (MSW) is generated in the United States each year. This excessive amount of waste, combined with decreasing landfill space and tougher regulations on waste disposal, has created major environmental concerns. Programs are now being initiated for reducing the volume of waste being deposited in present-day landfills. Such programs include recycling, composting, and waste-to-energy projects. It has been estimated that these programs will involve 30–40% of generated waste by the year 2000 [1].

This paper describes investigations into blending coal fines with refuse-derived fuels (RDF) to produce fuels suitable for use in fluidized-bed combustion systems. Coal fines provide a cheap, rich source of energy, while burning RDF provides a means of reducing the volume of waste deposited in landfills. Fluidized-bed combustion systems are particularly well suited for burning variable low-grade fuels and have the capacity of absorbing sulphur oxide emissions through the use of sorbents such as lime and limestone. Compared to other types of combustion systems the formation of nitrogen oxide species is minimized due to lower furnace operating temperatures.

Thermal analytical techniques were employed for this investigation. Using a coupled TG/FTIR technique one can study the volatile matter evolved along with

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the thermal degradation characteristics of various fuel blends. From the experimental results, the combustion behaviour and sulphur oxide absorbing capacity of fuel blends can be predicted.

Experimental

Materials used in the investigation included an Illinois #6 coal, a Kentucky agriculture limestone, and a sample of newspaper. Analytical data for the samples are given in Table 1. Samples of –60 mesh (250 μm) coal were thoroughly mixed with –200 mesh (75 μm) limestone and shredded paper to prepare samples for investigation. The paper was shredded in a bench-top Wiley mill.

Table 1 Samples used

Parameter	Coal	Paper	Limestone
Moisture	8.62	7.37	0.19
Ash	10.71	0.43	57.93
Volatile matter	40.95	75.56	18.90
Fixed carbon	39.72	16.64	22.98
Carbon	62.53	45.32	11.18
Hydrogen	5.68	6.54	0.16
Nitrogen	1.12	0.00	0.00
Oxygen	16.51	47.65	30.73
Sulfur	3.41	0.07	0.00

The TG/FTIR analyses were run on a DuPont Model 951 TGA interfaced to a Perkin-Elmer Model 1650 FTIR spectrometer. Analysis conditions were an air atmosphere with a flow rate of 50 ml/min, sample size of 10–30 mg, and a heating rate of 20 deg·min^{-1}.

Results and discussion

Thermogravimetric (TG) curves for coal, paper and limestone blends have been described previously [2, 3]. The thermal decomposition of agricultural limestone involves one major weight loss (calcination) beginning at 600°C. Total weight loss is 43% and represents the conversion of limestone to calcium oxide and carbon dioxide. The decomposition of paper occurs in three weight loss stages. The initial weight loss represents moisture loss, with the second stage due to oxidative pyrolysis of the paper, and the final stage attributed to char gasification. The thermal decomposition of coal also occurs in three weight loss stages. The first weight loss is due to moisture loss by the coal, with the second stage characterized by two DTG peaks. The first (377°C) is the result of the combustion of aliphatic materials in the coal, while the second (471°C) is attributed to the combustion of aromatic materials.

From earlier investigations by Roth and coworkers [4], the addition of large amounts of paper (≥30%) to coal had no effect on the initial and last stages of combustion of the paper. However, in a 9%/91% paper/coal blend all DTG peak maxima for the paper were shifted to higher values. Results from this earlier investigation suggest the optimum concentration of paper to blend with coal is 25% or less.

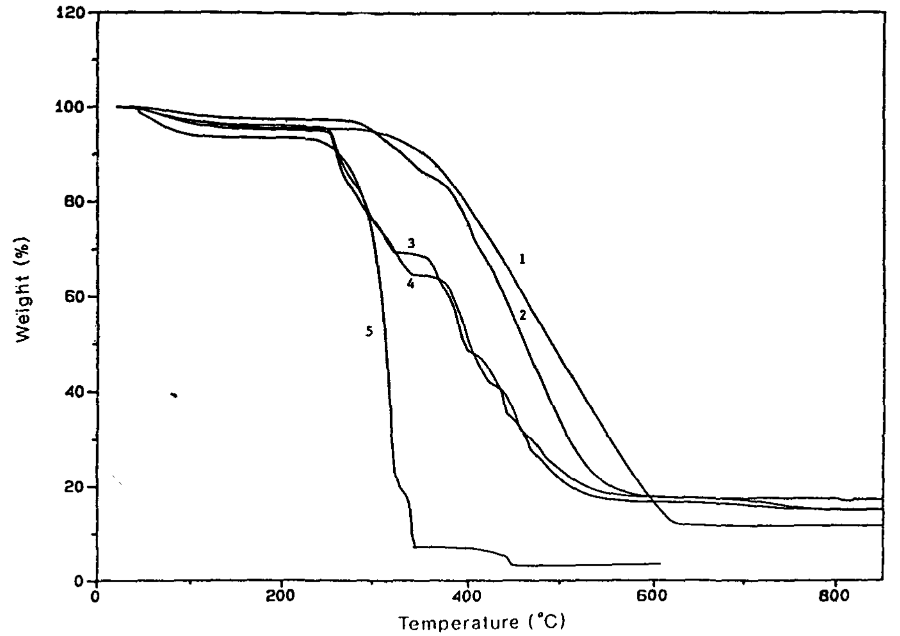

Fig. 1 TG curves for: (1) raw coal; (2) 7% limestone, 85% coal, 8% paper; (3) 5% limestone, 88% coal, 7% paper; (4) 2% limestone, 90% coal, 8% paper; (5) raw paper

Addition of limestone retards the combustion of paper, while small amounts of limestone (1–5%) promote combustion of coal [4]. TG curves of blends of paper and coal with various amounts of limestone (2, 5 and 7%) are given in Fig. 1. The TG curves for each blend contain four thermal decomposition stages with T_{max} at 283°, 384°, 450° and 489°C, respectively. The first and second stages may be due to the combustion of cellulose and lignin materials found in paper. The third and fourth stages may be attributed to the combustion of coal. The TG curves shown in Fig. 1 illustrate the shift to lower temperature (roughly 70°C) for fuel blends containing 2 and 5% limestone only.

To examine the catalytic effect of limestone on the combustion of coal/paper blends, we calculated the observed weight loss to theoretical weight loss ratios for each fuel blend studied. Three stages of decomposition were arbitrarily chosen: the first stage between 200°–400°C, the second stage between 400°–600°C, and the final stage between 600°–850°C. Percent weight loss in the three temperature ranges for each individual component of the fuel blends were determined. These values were then used to calculate the theoretical weight loss for fuel blends for the specified temperature range using the following equation:

Theoretical weight loss=% limestone*(RLWL)+% coal*(RCWL)+%paper*(RPWL)

where: RLWL, RCWL and RPWL are the weight losses for raw limestone, raw coal and raw paper, respectively.

The observed weight loss values were determined from TG curves for each fuel blend during each stage. To illustrate the apparent catalytic effect of added limestone, the observed weight loss values were divided by their corresponding calculated theoretical weight loss values for each fuel blend. Ratios greater than one indicate the presence of catalytic behaviour within the blend. Data generated from these calculations are listed in Table 2.

Fuel blends containing 2% and 5% limestone illustrate an increase in the observed/theoretical (O/T) weight loss ratio with increasing percentage of coal within their respected series. In general, those fuel blends containing roughly 90%, 80% and 70% coal (with the balance paper) had calculated O/T weight loss ratios of 1.9, 1.6 and 1.5, respectively. As reported earlier, calcium promotes the thermal decomposition of coal, while inhibiting the devolatilization of paper. Therefore, one would expect a greater catalytic effect with increasing percentage of coal. This hypothesis is verified by the calculated O/T ratios presented in Table 2.

For fuel blends containing 7% limestone, O/T weight loss ratios were calculated to be near one for the second and third weight loss stages. This suggests there is no catalytic effect from limestone in blends containing 7% limestone under the experimental conditions chosen for this investigation.

In the second thermal decomposition stage, O/T weight loss ratios were roughly 0.6 for all fuel blends consisting of 2 and 5% limestone. Although values less than one were expected, due to the catalytic shift during the first stage, calculated O/T weight loss ratios of 0.6 was not expected for all fuel blends experiencing catalytic effects. Fuel blends which experienced greater catalytic effects were expected to have lesser O/T weight loss ratios in the second thermal decomposition stage compared to those fuel blends experiencing lesser or no catalytic effects.

Table 2 Observed/theoretical weight loss ratios for fuel blends

Composition of blend[a]	1st stage 200°–400°C	2nd stage 400°–600°C	3rd stage 600°–850°C
7L–85C–8P	1.0	1.0	0.88
7L–75C–18P	1.0	1.0	0.97
7L–65C–28P	1.1	0.9	0.75
5L–88C–7P	1.9	0.6	0.8
5L–78C–17P	1.6	0.6	0.7
5L–68C–27P	1.5	0.6	0.8
2L–90C–8P	1.9	0.6	0.3
2L–80C–18P	1.7	0.5	0.3
2L–70C–28P	1.5	0.6	0.3

[a] L = limestone, C = coal and P = paper

Fuel blends with O/T weight loss ratios calculated to be near one for the third thermal decomposition stage indicates that the limestone failed to calcine in the first two stages, thus inhibiting the calcium oxide to act as a sorbent for sulphur oxide emissions. Fuel blends with O/T weight loss ratios less than one indicate the opposite effect. Fuel blends containing 7% limestone failed to utilize the majority of added limestone as a sorbent, whereas fuel blends containing 2% limestone utilized it most efficiently.

Employing coupled TG/FTIR, evolved gases detected and profiled from the combustion of Illinois # 6 coal were CH_4, H_2O, SO_2, CO_2, COS and CO, while those detected for paper were CO_2, CO, CH_4, H_2O, acetic acid, formic acid and methanol. The shift to lower combustion temperatures by fuel blends containing low percentages of limestone is also illustrated by evolved gas profiles. From the evolved gas profile for SO_2 shown in Fig. 2, the production of SO_2 is shifted to lower temperatures with the addition of 5% or less limestone. Fuel blends containing 7% limestone illustrate similar evolved gas profiles when compared to raw coal. Integrating the area underneath the evolved gas profile for SO_2 and dividing it by the corresponding area from raw coal, one can obtain a relative estimate of the percentage of SO_2 emissions absorbed by added limestone. In general, 2%, 5%, and 7% limestone reduced the percentages of evolved SO_2 roughly by 25%, 32% and 33%, respectively. All fuel blends had a pronounced effect in lowering the amount of SO_2 evolved. Blends containing 7% limestone were the least efficient in capturing evolved SO_2 during combustion.

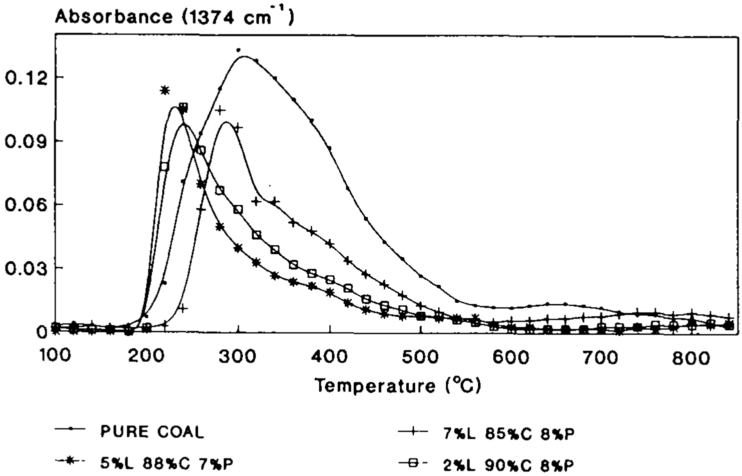

Fig. 2 Evolution of sulphur dioxide from fuel blends containing 7, 5, and 2% limestone compared to that of raw coal during combustion

Conclusions

Based on studies thus far, the following conclusions can be made.

1. As indicated by TG studies, addition of 1–5% limestone promotes the combustion of coal blended with paper; addition of 7% limestone has no increased effect on similar blends.

2. Blending of paper with coal results in the evolution of SO_2 at lower temperatures.

3. Recommended percentages of coal, paper and limestone to use as a blend is roughly 70% coal, 25% paper and 5% (or less) limestone.

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References

1 C. R. McGowin, E. M. Petrill, M. A. Perna and D. R. Rowly, 'Fluidized Bed Combustion Testing of Coal/Refuse-Derived Fuel Mixtures', Report from EPRI Project RP 718-2 (1989).

2 W. P. Pan, M. Campbell, J. T. Riley and M. Zhang, Amer. Chem. Soc., Div. Fuel Chem., 36 (1991) 830.
3 T. Roth, M. Zhang, J. T. Riley and W. P. Pan, 'Thermogravimetric-Fourier Transform Infrared Analysis (TG/FTIR) Studies of Combination Fuels', Proc., 9th International Coal Testing Conf., Lexington, KY, 1992, pp. 46–49.
4 T. Roth, M. Zhang, S. Burris, J. T. Riley and W. P. Pan, 'Combustion of Blends of Refuse Derived Fuels and Coal', Proc., 9th Internat. Pittsburgh Coal Conference, Pitsburgh, PA, 1992 pp. 799-807.

Zusammenfassung — Mittels TG/FTIR-Spektroskopie wurden die Verbrennungsprofile von Kohle-Kalkstein-Papier-Gemischen untersucht. Dabei wurde die Rolle von Kalkstein bei der Förderung des Verbrennungsbeginnes von Kohle-Papier-Gemischen und bei ihrer Fähigkeit, Schwefeloxide zu absorbieren, geprüft.