



# TG-FTIR characterization of coal and biomass single fuels and blends under slow heating rate conditions: Partitioning of the fuel-bound nitrogen

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## ARTICLE INFO

### Article history:

Received 28 October 2008

Received in revised form 31 August 2009

Accepted 4 September 2009

### Keywords:

Coal

Biomass

Thermogravimetry

FTIR analysis

Fuel-bound nitrogen partitioning

## ABSTRACT

The devolatilization behavior of a bituminous coal and different biomass fuels currently applied in the Dutch power sector for co-firing was experimentally investigated. The volatile composition during single fuel pyrolysis as well as during co-pyrolysis was studied using TG-FTIR characterization with the focus on the release patterns and quantitative analysis of the gaseous bound nitrogen species. It was shown that all investigated biomass fuels present more or less similar pyrolysis behavior, with a maximum weight loss between 300 and 380 °C. Woody and agricultural biomass materials show higher devolatilization rates than animal waste. When comparing different fuels, the percentage of fuel-bound nitrogen converted to volatile bound-N species (NH<sub>3</sub>, HCN, HNCO) does not correlate with the initial fuel-N content. Biomass pyrolysis resulted in higher volatile-N yields than coal, which potentially indicates that NO<sub>x</sub> control during co-firing might be favored. No significant interactions occurred during the pyrolysis of coal/biomass blends at conditions typical of TG analysis (slow heating rate). Evolved gas analysis of volatile species confirmed the absence of mutual interactions during woody biomass co-pyrolysis. However, non-additive behavior of selected gas species was found during slaughter and poultry litter co-pyrolysis. Higher CH<sub>4</sub> yields between 450 and 750 °C and higher ammonia and CO yields between 550 and 900 °C were measured. Such a result is likely to be attributed to catalytic effects of alkali and alkaline earth metals present in high quantity in animal waste ash. The fact that the co-pyrolysis of woody and agricultural biomass is well modeled by simple addition of the individual behavior of its components permits to predict the mixture's behavior based on experimental data available for single fuels. On the other hand, animal waste co-pyrolysis presented in some cases synergistic effects in gas products although additive behavior occurred for the solid phase.

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## 1. Introduction

The application of biomass and other cheap secondary fuels, like poultry waste and meat and bone meal (MBM), in power generation has become more attractive in recent years as a consequence of concerns for the climate (global warming) and increased fossil fuel prices against facing decreased easy availability. Co-firing of these novel fuels is already used to mitigate CO<sub>2</sub> emissions in an economically attractive way. For an overview of the technology see e.g. [1,2]. This use of such waste biomaterials is considered as an acceptable way to dispose them while they are thus even exploited as energy source. MBM was banned by the EU as cattle feed since 1994 to prevent the spread of BSE (bovine spongiform encephalopathy).

In order to further improve the co-firing process with the aim to reduce harmful emissions, more detailed insight is needed into combustion (sub)processes, especially in the initial pyrolysis stage of particle conversion. Also more advanced applications like co-gasification for IGCC or syngas production purpose can benefit from this. An improved understanding is particularly needed for the formation of NO<sub>x</sub> precursors. NO<sub>x</sub> emission is one of the major concerns for co-firing technology, as the co-fired fuels often contain substantial amounts of fuel-bound nitrogen. The release of the related nitrogen species during the initial particle pyrolysis stage has not been completely elucidated yet. Especially the interaction between old fuels and diverse younger co-fired materials has got less research attention in this respect. A number of researchers have studied the co-pyrolysis using a wide range of pyrolysis conditions, reactor types and coal/biomass fuels. Given such a wide range of variables involved, the results obtained by different groups are sometimes conflicting, some reporting significant synergies, others additive behaviors. An overview of the existing literature is summarized in Table 1.

The aim of the research described in this paper is to characterize the pyrolysis behavior of single biomass fuels and to study whether coal–biomass mixtures follow their parent fuel behavior during

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**Table 1**  
Co-pyrolysis studies of coal/biomass blends.

1st author	Exp. <sup>d</sup>	HR/temp [°C/min/°C]	Fuels <sup>b,c</sup>	Blending [w/w]	Gas analysis	Ref
Rüdiger	DTF	~800–1100	Coal-ss-st	25–50–75	GC	[4]
Pan	TGA	100/900	Bl-lq-pc	20–80	None	[5]
Moliner	Pyr	n.r. <sup>a</sup> /900	lv-hsb-pr	30	GC-MS	[6]
Collot	FB-FDB	10/850–1000	Dm-bw	50	None	[7]
Suelves	Pyr	n.r. <sup>a</sup> /900	lv-hsb-pr	30–40–60	GC-MS	[8]
Biagini	TGA	20/900	hv-lv-sd-ss	15 to 60	None	[9]
Kastanaki	TGA	10/850	Li-oc-fr-cr	5–10–20	None	[10]
Meesri	HF	10–30–50/1000	Coal-sd	5–75	GC	[11]
Meesri	DTF	~10 <sup>4</sup> /900–1400	Coal-sd	5–10	GC	[11]
Moghtaderi	HF	10–30–50/1000	Coal-sd	5–75	GC	[12]
Moghtaderi	DTF	~10 <sup>4</sup> /900–1400	Coal-sd	5–10	GC	[12]
Vamvuka	TGA	10–100/850	Li-oc-fr-cr	5–10–20	none	[13]
Vuthaluru	TGA	20/1250	Sub-ww-ws	10–50	none	[14]
Jones	Py-GC-MS	1/600	Bit-hvb-li-sd	25–50–75	GC-MS	[15]
Jones	TGA	25/900	Bit-hvb-li-sd	25–50–75	GC-MS	[15]

<sup>a</sup> Not reported.

<sup>b</sup> Coals: bit, Bituminous; bl, Black; dm, Daw Mill; hsb, High vol. sub-bituminous; hvb, High vol. bituminous; hv, High volatile; li, Lignite; lq, Low quality; pr, Petroleum residue; sub, Sub-bituminous.

<sup>c</sup> Biomass: cr, Cotton residue; fr, Forest residue; oc, Olive cake; pc, Pine chips; pr, Palm kernel; sd, Saw dust; ss, Sewage sludge; st, Straw; ws, Wheat straw; ww, Waste wood.

<sup>d</sup> Equipment: DTF, Drop tube furnace; FB, Fixed Bed reactor; FDB, Fluidized-Bed reactor; HF, Horizontal furnace; Pyr, Pyrolyzer; TGA, Thermogravimetric analyser.

decomposition at well controlled slow heating rates, or that synergistic effects take place. Especially, nitrogen species quantification and concerning fuels, coal and slaughter residues have been scarcely addressed in this respect.

## 2. Experimental

### 2.1. Materials

Several biomass materials, ranging from woody and agricultural biomass to slaughter and poultry residues, and a coal blend have been selected for analysis of their devolatilization behavior in this work. They were supplied by Dutch power operators (E.ON Benelux, Essent Energie), currently employing them on commercial projects in their power stations. Table 2 summarizes the standard fuel analyses. Ash analyses for both coal and biomass fuels are reported in Table 3. In a deposition directed characterization study, Tortosa et al. reported the particle size distribution for these fuels [3].

Coal/biomass blends pyrolysis experiments have subsequently been carried out at 10 °C/min. The procedure that was followed during the thermogravimetric experiments is similar to that used for the single fuels. The influence of the biofuel share on the mixture was analyzed, from 5 to 20% share on thermal basis. Table 4 gives the

overview of the conversion from thermal to mass basis for the biomass fuels. Depending on the calorific value of the biomass fuel, values span between 6.5 and 47.8% on mass basis.

### 2.2. Apparatus

A thermobalance (TGA) of the type SDT 2960 was used and coupled with an FTIR spectrometer in order to identify and quantify relevant gas species. A scheme of the TG-FTIR setup is shown elsewhere [16]. The coupling was realized via a heated transfer line, kept isothermal at 150 °C. Heating rates of 10, 30, and 100 °C/min were chosen in the current work, which facilitates future kinetics parameter derivation which is out of the scope of this paper. FTIR gas analysis was carried out using a resolution of 0.25 cm<sup>-1</sup>, 12 scans per sampling, for a sampling interval of 33 s. Details on the FTIR calibration have also been described in [16].

### 2.3. Methods

A quantity of 5 ± 0.5 mg of sample was used for every experiment. The balance was continuously purged with 100 ml/min of Helium (chosen for its excellent heat transfer properties to reduce temperature inhomogeneities in the reaction zone [17]) to sweep the pyrolysis gases and prevent secondary reactions and tar redeposition

**Table 2**  
Proximate, ultimate<sup>a</sup> analyses (on wt. % dry basis) and lower heating values of the fuels.

	Coal	CL <sup>b</sup>	MBM <sup>b</sup>	B-wood	Corn residue	Olive cake	Palm kernel
Moisture <sup>c</sup>	9.15	8.7	2.74	9.08	7.44	7.3	7.01
Ash	12.5	24.3	17.1	1.8	7.6	7.7	5.5
Volatiles	35.4	71.0	80.1	76.5	73.1	70.9	76.9
Fixed C	52.1	4.6	2.8	21.6	19.3	21.5	17.6
C	71.0	37.1	43.1	50.3	44.7	50.2	47.6
H	4.9	4.2	6.0	8.0	5.9	8.0	6.9
N	1.5	3.8	9.2	1.0	0.6	1.3	2.7
S	0.7	0.7	1.2	–	0.1	–	–
O <sup>d</sup>	9.5	29.4	22.5	39.9	41.1	33.7	38.1
Cl	0.001	0.5	0.8	–	–	–	–
LHV <sup>c,e</sup>	25.03	8.78	16.1	16.7	15.0	18.9	17.9

<sup>a</sup> Performed at ECN on a CE CHNO analyzer Flash EA 1112.

<sup>b</sup> Biofuels were received in dried and sterilized form; MBM = meat and bone meal; CL = Chicken Litter.

<sup>c</sup> As received basis.

<sup>d</sup> Calculated by difference.

<sup>e</sup> Expressed in (MJ/kg).

**Table 3**  
Ash analysis of the biomass fuels (in wt. %, dry basis).

	Coal	CL	MBM	B-wood	Corn	Olive	Palm
SiO <sub>2</sub>	53.49	4.5	<0.02	22.8	43.4	17.9	18.0
Al <sub>2</sub> O <sub>3</sub>	33.92	0.79	2.4	3.7	4.4	3.3	6.1
Fe <sub>2</sub> O <sub>3</sub>	3.53	0.35	0.25	3.6	2.2	1.6	9.1
CaO	2.65	44.3	41.8	24.2	12.8	10.4	9.2
MgO	0.42	3.2	1.4	5.1	3.9	4.7	6.5
Na <sub>2</sub> O	0.51	0.47	6.5	2.7	0.14	0.1	0.14
K <sub>2</sub> O	0.46	9.5	3.2	10.4	16.1	34.4	16.3
TiO <sub>2</sub>	1.93	0.02	0.01	1.6	0.25	0.12	0.12
Mn <sub>3</sub> O <sub>4</sub>	n.a.	0.11	0.01	0.24	0.08	0.04	0.59
P <sub>2</sub> O <sub>5</sub>	0.65	12.0	41.5	10.2	2.1	4.9	30.6
SO <sub>3</sub>	n.a.	2.8	4.3	5.3	1.6	3.0	2.5
SrO	n.a.	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01
BaO	n.a.	<0.01	<0.01	0.32	0.03	0.01	<0.01
ZnO	n.a.	0.08	0.05	0.23	0.03	0.02	0.06
V <sub>2</sub> O <sub>5</sub>	n.a.	<0.01	<0.01	0.01	<0.01	<0.01	<0.01
Cr <sub>2</sub> O <sub>3</sub>	n.a.	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01
LOI	25.1	n.a.	8.2	14.7	21.8		

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