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EVOLVED GAS ANALYSIS OF SOME SOLID FUELS BY TG-FTIR

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Abstract

FTIR spectrometry combined with TG provides information regarding mass changes in a sample and permits qualitative identification of the gases evolved during thermal degradation. Various fuels were studied: coal, peat, wood chips, bark, reed canary grass and municipal solid waste. The gases evolved in a TG analyser were transferred to the FTIR via a heated teflon line. The spectra and thermoanalytical curves indicated that the major gases evolved were carbon dioxide and water, while there were many minor gases, e.g. carbon monoxide, methane, ethane, methanol, ethanol, formic acid, acetic acid and formaldehyde. Separate evolved gas spectra also revealed the release of ammonia from biomasses and peat. Sulphur dioxide and nitric oxide were found in some cases. The evolution of the minor gases and water paralleled the first step in the TG curve. Solid fuels dried at 100°C mainly lost water and a little ammonia.

Keywords: EGA, fuel, TG-FTIR

Introduction

Solid fuels are classified as fossil fuels and biomass. Great amounts of biomass are formed as by-products or waste in agriculture, industry and the community. It is possible to produce chemicals from these sources by hydrolysis and fermentation, to burn gases and liquids obtained from solid fuels by pyrolysis, and to receive energy by direct burning [1–3]. Thermal properties of fuels are an integral part of their value. These properties provide information on how to use fuels in order to achieve the best possible benefits. Thermogravimetry is a very useful method for predicting the thermal behaviour of fuels. It yields information on water content, volatile matter content, and fixed carbon and ash contents [4–8].

In the present investigation, our aims were the continuous and qualitative measurement of the gases emitted during the thermal treatment solid fuel of samples and the testing of the suitability of a commercial combined TG-FTIR system for EGA [9–13].

The moisture content of a fuel sample is usually determined by keeping the sample at 105°C for 24 h and determining the mass change during heating. One of the purposes of this study was to determine what gases are evolved during moisture measurements in the laboratory [7, 14].

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Experimental

Samples

The samples used were coal (commercial origin, bituminous, low sulphur content), peat (S H3 from Central Finland, S=sphagnum peat; H3=von Post degree of humidification), wood chips (softwood from Central Finland), bark (softwood from Central Finland), reed canary grass (*Phalaris arundinacea*, from Southern Finland) and municipal solid waste (MSW, source-separated, from Jyväskylä). Fuel samples were obtained from VTT Energy. The samples were first air-dried at room temperature, milled and dried (105°C, 24 h) for elemental analyses. The milled samples were preserved in a silica gel desiccator for thermal analysis. For isothermal measurements, milled samples were kept at constant (44%) relative humidity at 20°C. Fuel mass analysis was carried out with a Perkin Elmer CHN-2400 elemental analyser, and sulphur analysis with a LECO SC-132 sulphur analyser, and calorific values were determined with a LECO AC-300 calorimeter according to the standard method ASTM D 1989.

Measuring system

The thermal analysis and EGA measurement system consisted of a Perkin Elmer Thermogravimetric Analyser TG7, coupled to the Perkin Elmer System 2000 FTIR by a transfer line. A teflon tube (1.1 m length, 1.2 mm ID) was placed inside the transfer line. The gas cell was 10 cm in length with KBr windows. The detector used was DTGS. To minimize secondary reactions and condensation, the transfer line and the gas cell could be heated from room temperature to 250°C.

Thermogravimetric measurements and EGA

The temperature range for thermal analysis was 30–800°C, the heating rate was 10°C min^{-1} and the sample mass was 7–14 mg. The purge gas was synthetic air at a flow rate of 83 ml min^{-1}. FTIR measurements were made with a resolution of 8 cm^{-1} and 4 scans per slice. The temperature in the gas cell was adjusted to 190°C and that in the teflon tube to 180°C.

For the presentation of FTIR spectra and the identification of evolved gases, the TR-IR (Time-Resolved Infrared Spectra), Spectrum and search programs of Perkin-Elmer were used. The search program uses PSU (possible structure units), a select enhanced EPA Vapour Phase Database (code: 4602) and the Inorganic Database (code: 4359) of BIO-RAD (Sadtler). Additionally, the Aldrich Library of FTIR Spectra, Vapour Phase was used. The frequency values of peaks given later in the text were taken from these FTIR databases.

Isothermal measurements were made at 100°C for 30 min in a TG analyser. Sample masses were 24–35 mg. The purge gas was pure nitrogen at a flow rate of 89 ml min^{-1}. The temperatures in the gas cell and in the teflon tube were adjusted to 100°C.

Results and discussion

Fuel analysis

Table 1 presents data on the fuel analysis of the studied samples. They clearly differed in composition. One equation utilized to calculate the heat contents of fuels from their compositions [2] is

$$HHV_v = 0.475C - 2.38$$

where HHV_v is the higher heating value in MJ kg^{-1} for dry matter, and C is the percentage of carbon. Use of this equation yielded the following values: coal 30.1, peat 24.3, wood chips 21.6, bark 22.5, reed canary grass 19.9 and MSW 20.8 MJ kg^{-1}. CO_2 is a greenhouse gas, formed in the production of energy from fuels. The energy produced from these samples is 510–530 kJ mol^{-1} CO_2. The heat contents can also be calculated via the basic combustion equations [2]:

$$C + O_2 \rightarrow CO_2 \qquad \Delta H = 33.9\ \text{MJ kg}^{-1}$$

$$H_2 + 0.5O_2 \rightarrow H_2O \qquad \Delta H = 142.9\ \text{MJ kg}^{-1}$$

Table 1 Fuel analysis of coal, peat and biomasses

Sample	Ash%	Volatile matter%	C%	H%	N%	S%
Coal	17.7	29.2	68.3	4.36	1.97	0.88
Peat	3.88	70.3	56.1	6.10	2.24	0.16
Wood chips	0.39	85.3	50.5	5.96	0.25	0.11
Bark	3.84	75.2	52.3	5.91	0.57	0.06
Reed canary grass	6.21	78.3	47.0	5.54	1.02	0.01
MSW	18.9	69.1	48.8	6.58	1.54	0.16

The approximate total heat contents and the experimental caloric heat contents (in parentheses) were as follows: coal 29.4 (27.4), peat 27.7 (23.0), wood chips 25.6 (20.9), bark 26.1 (21.0), reed canary grass 23.8 (19.1) and MSW 25.9 (21.2) MJ kg^{-1}. The heat contents per mole CO_2 were coal 516 (481), peat 606 (503), wood chips 623 (509), bark 614 (494), reed canary grass 624 (601) and MSW 655 (536) kJ mol^{-1}.

The biomass and MSW in particular are as good as or even better than coal as a fuel in relation to the formation of CO_2. CH_4, which is considered to be the best fuel from the aspect of air pollution, gives a value of 980 from the equation, while the experimental caloric value for combustion to one mole of CO_2 is 890 kJ mol^{-1} [15].

TG results

The TG curves obtained on heating illustrate the loss of water and the decomposition of the samples. The water contents, the decomposition temperature ranges and

Table 2 Mass losses and peaks of DTG curves for coal, peat and biomasses in air at a heating rate of 10°C $\min^{-1}$

Sample	Water%	Temp. range/°C	Mass loss/%	DTG peak/°C	Temp. range/°C	Mass loss/%	DTG peak/°C	Ash%
Coal	1.0	–	–	–	314–596	82.6	483	16.6
Peat	3.3	187–312	84.3	274	312–503	9.1	385	3.9
Wood chips	1.1	212–339	71.4	322 335	339–467	26.0	443	0.6
Bark	2.5	175–333	58.2	316	333–401	27.3	400	3.4
Reed canary grass	1.5	202–336	61.4	322	336–515	29.5	449	6.4
MSW	3.4	177–360	52.0	305	360–535	28.9	460	13.7

the mass losses as the DTG peaks are shown in Table 2. The mass loss between 25 and 150°C is mainly due to water. After the water loss, the samples decomposed in two steps, except for the coal sample, which decomposed in one step. Biomasses normally consist of cellulose, hemicellulose and lignin. MSW, in addition to these, also contains plastic, rubber, leather, stone material from paper, etc. [3, 6, 17]. According to the literature, the mass losses in the first step (150–350°C) of degradation basically correspond to the loss of the volatile species resulting from the decomposition of cellulose and hemicellulose. The second step is connected with the lignin content and the burning of carbon [3]. Lignin starts to decompose in the same temperature range as cellulose, but the decomposition curve is broad [3].

The TG curve indicates that the peat contains very small amount of lignin. After lignin degradation, bark burns slowly in the temperature range 401–668°C. Obviously, tar and carbon burn to CO_2.

FTIR results

The detected peaks of the total evolved gases in FTIR parallel the DTG curves very well. For example, the DTG peaks for peat were at 274 and 385°C, while the detected gas peaks were at 283°C (25.3 min) and 385°C (35.5 min); the analogous peaks for wood chips were at 322 and 443°C, and at 326°C (29.6 min) and 443°C (41.3 min), respectively.

The evolved gases mostly consist of CO_2 and water. CO_2 gives two strong absorption peaks, at 2362 and 667 cm^{-1}. CO absorbs at 2180 and 2114 cm^{-1}. Water vapour has many absorption bands arising from the rotation-vibration frequencies of the gas state, at 1900–1300 and 3900–3500 cm^{-1}. CO_2 was evolved throughout the degradation of all the samples. CO was found in the interval of the fastest decomposition in both steps, except for peat, where it was observed only in the first step. Water was found in the first step for biomasses and peat. During the second step, water was evolved in only minute amounts. This means that the second step in the TG curves arises from the burning of carbon. The lignin decomposed mainly during the first step and produced the greatest part of the elemental carbon, which burned in the second step. Figure 1a presents TG and DTG curves for wood chips, and Fig. 1b illustrates thermoanalytical curves of the total gases (Gram-Schmidt), CO_2, CO and H_2O evolved from wood chips.

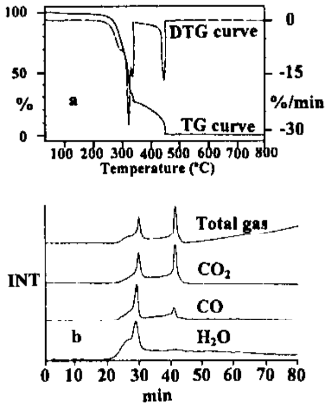

Fig. 1 TG-FTIR analysis of wood chips. a) – TG and DTG curves; b) – thermoanalytical curves of total gas, CO_2, H_2O and CO

Water is easy to recognize, but it may overlap peaks of other gas species. For the identification of gases, we recognized functional groups, compared spectra with literature spectra and analyzed the shapes and positions of peaks. Identification is laborious, but it is possible in most cases. Figure 2a presents a stacked plot diagram, and Fig. 2b the four IR spectra obtained at different times of the TG curve for wood chips.

CH_3 and CH_2 groups absorb in the range 3100–2700 cm^{-1}, and were observed during the first decomposition steps and in minor contents in the second steps. Closer examination of the spectra reveals a peak at 3014 cm^{-1}, due to CH_4 or C_2H_4. The other strong peak of CH_4 is at 1298 cm^{-1}. CH_4 appeared mainly at the end of the first step and at the beginning of the second step for peat and all the biosamples. C_2H_6 gives strong peaks at 3000–2880 cm^{-1} and medium peaks at 1457 and 829 cm^{-1}. These peaks were resolved as weak in the fastest decomposition range of the first step. Peaks of other compounds overlap the peaks of C_2H_2 and C_2H_4.

Alcohols were found in the first step. Methanol (3720–3680, 2980–2920, 1351, 1061, 1032, 1003 cm^{-1}) and ethanol (3680–3670, 2980–2920, 1394, 1244, 1056, 901 cm^{-1}) were confidently recognized. Formic acid (3584–3550, 2961–2927, 1786–1747, 1133, 1104, 1075, 640 cm^{-1}) and acetic acid (3594–3565, 1800, 1777, 1394, 1273, 1178, 988, 655, 582 cm^{-1}) were observed in the first decomposition step. Carbonyl compounds give rise to a strong band at 1900–1550 cm^{-1}. In this range, many peaks were found in the spectra. Some of these peaks are due to carboxylic acids. Ketones are best characterized by the strong C=O stretching frequency absorption near 1715 cm^{-1}. A CH_3 group next to the carbonyl yields a strong band due to a CH_3 deformation at 1370–1350 cm^{-1}, while a CH_2 group furnishes a strong band at 1440–1405 cm^{-1}. Methyl alkyl ketones have C–C–C stretching vibrations at 1170 cm^{-1} [17]. All the peak ranges were detected during the first step. Aliphatic al-

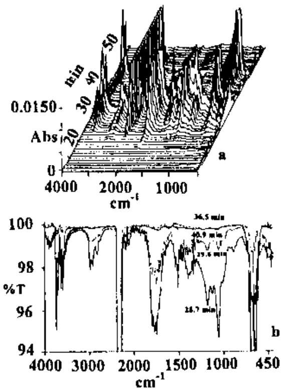

Fig. 2 a) – Stacked plot diagram of evolved gases; b) – Four IR spectra obtained after different times of degradation of wood chips in air

dehydes give bands at 2830–2810 cm^{-1} and 2720–2695 cm^{-1} for the CH stretching vibrations and at 1390 cm^{-1} for the bending vibration. Acetaldehyde has peaks at 2825 (medium), 2733 (medium), 1762 (strong), 1414 (medium), 1365 (medium) and 1114 (medium) cm^{-1}. Formaldehyde affords the strongest peaks at 2801 and 1747 cm^{-1} and medium peaks at 2998, 2869, 1776, 1704 and 1506 cm^{-1}. Formaldehyde appeared in the evolved gases of all samples. Peaks of acetaldehyde were also observed, but the peaks of other gases overlap these peaks. It is possible but not certain that acetaldehyde was present.

Gaseous sulphur and nitrogen compounds are harmful to the atmosphere. Obviously, organic nitrogen decomposes to NH_3 and HCN. The two strongest peaks of NH_3 are at 964 and 935 cm^{-1}. These peaks were found for peat between 250 and 280°C. A small amount of NO (1902, 1849 cm^{-1}) was found in the spectra of coal, peat, MSW and reed canary grass. Traces of SO_2 (1351, 1149 and 517 cm^{-1}) were found in coal and peat. The elemental analyses on the other samples indicated that they contain very small amounts of sulphur. H_2S and COS were not found in the gases evolved from the biosamples or peat.

Most of the detected gases follow the first step of the DTG curves or total gas evolution. CH_4 appeared some time after the first step and a small amount of CO was evolved in the second decomposition step.

In general, the biosamples were dried at 105°C for 24 h before elemental analysis. Other readily volatile compounds were possibly released together with the water. Minor amounts of NH_3 were found in all the samples except coal.

Conclusions

The measuring system used proved useful and flexible enough to analyse gases evolved from solid fuels. The total evolved gas contents of the samples followed the DTG curves very well. The greatest weakness was contamination of the teflon tube and gas cell. Water peaks partly overlapped peaks of other gases in the FTIR spectra.

Fuel analyses gave ash, volatile matter, C, H, N and S contents. The ratios of hydrogen to carbon and the approximate calculated heats of combustion showed the biomasses to be as good as or even better than coal in energy production from the aspect of air pollution.

The major gases evolved were CO_2 and H_2O. The following compounds were recognized in medium or minor amounts: CO, CH_4, C_2H_6, HCO_2H, CH_3CO_2H, CH_3OH, CH_3CH_2OH, HCHO and ketones.

Small amounts of NO were to be observed in the spectra of coal, peat, reed canary grass and MSW. NH_3 was found in peat. Traces of SO_2 were evolved from coal and peat. Most of the detected gases followed the DTG peaks or total gas evolution. Isothermally dried samples (except for coal) released not only water, but also a small amount of NH_3.

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