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Professor Stan Kolaczkowski 10 Dec 2015

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Using quadrupole mass spectrometry for on-line gas analysis – gasification of biomass and refuse derived fuel

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ABSTRACT

A quantitative method of on-line gas analysis was developed, using quadrupole mass spectrometry to measure gas composition when charcoal, wood, straw, and refuse derived fuel were gasified. Despite overlapping between some of the species, the method was demonstrated on small-scale laboratory gasifiers, recording the main components (e.g. N2 ~ 54-67 vol.%; H2 ~ 5-13 vol.%; CO2 ~ 15-17 vol.%; CO ~ 10-17 vol.%), and lower levels of CH4 (~ 1-2 vol.% and O2 (~ 0.1-1 vol.% in the gas. Trace levels of H2S (~ 100-300 ppmv) and COS (~ 10-30 ppmv) were also measured (important for gas clean-up strategies). On-line measurements were performed on a commercial pilot-scale down-draft gasifier (using waste wood), and the concentrations of H2S varied from 200 to 700 ppmv, and COS from 7 to 17 ppmv. The ratio of H2S:COS was higher than in the laboratory trials - probably because of COS hydrolysis reactions taking place in the wet scrubbing systems.

Key words: Biomass gasification; gasifier; down-draft; on-line gas analysis; quadrupole mass spectrometry (QMS).

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1. Introduction

Because the supply of oil and natural gas resources is finite, biomass is considered as a potential feedstock for the supply of energy and chemicals in the future.

There are three main ways to convert biomass into energy, namely: pyrolysis, combustion and gasification, in which pyrolysis and gasification technologies are attractive, as the gas produced (producer gas) is in a suitable form for either energy conversion or as a chemical feedstock [1]. The pyrolysis process generally produces three products (gas, bio-oil, and char), whereas in the gasification process, biomass is almost completely converted into gaseous products (except for the ash in the feed).

Therefore, biomass gasification is considered to be an important technology to supply cleaner gases for many end-use applications such as combined heat and power using a gas engine or fuel cells, and in chemical synthesis.

Depending on the way in which the gas is used [2], different restrictions apply on the concentrations of the contaminants in the gas produced. In addition, final emissions from the plant need to conform to environmental regulations that apply where

List of Abbreviations

<table>
<thead>
<tr>
<th>Abbreviation</th>
<th>Description</th>
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<tr>
<td>GC</td>
<td>Gas Chromatography</td>
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<tr>
<td>HESS</td>
<td>High Efficiency Water Scrubber</td>
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<tr>
<td>IR</td>
<td>Infrared</td>
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<tr>
<td>NDIR</td>
<td>Non-Dispersive Infrared Analyzer</td>
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<tr>
<td>QMS</td>
<td>Quadrupole Mass Spectrometry</td>
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<tr>
<td>RDF</td>
<td>Refuse Derived Fuel</td>
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<tr>
<td>RS</td>
<td>Relative Sensitivity</td>
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<tr>
<td>SEM</td>
<td>Secondary Electron Multiplier</td>
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<tr>
<td>TCD</td>
<td>Thermal Conductivity Detector</td>
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the plant is operated. For example, in Europe, if a refuse derived fuel is used, then the
Waste Incineration Directive [3] applies, and in such a situation in order to design the
gas clean-up system, it is important to know the concentration of contaminants such as
H₂S and COS [4]. Thus, the ability to perform on-line analysis is beneficial for
monitoring the quality of the gas produced, both at an industrial and an experimental
scale of operation.

To analyze the gas produced from a biomass gasification system, discrete samples of
gas may be taken and then analyzed by a specialist laboratory. Such analysis can be
done using gas chromatography (GC), or with an infrared (IR) system, and these two
methods of measurement are often used. The main advantage of GC is that it can
provide a quantitative analysis of complex gas mixtures, whereas its main drawback is
the long measuring time. Therefore, it is not a suitable method for on-line analysis
during transient operating conditions encountered in a gasification process. Also, even if
a set of discrete samples were to be taken for subsequent analysis, then problems can
often be encountered either, with possible leakage of species (e.g. hydrogen) from the
sample container, or difficulties in the sampling process, both resulting in incorrect
results.

Although IR spectroscopy could be used to perform measurements on-line, its main
disadvantage arises from the fact that, in general, it measures a single gas species, and
hence information on the other key components in the gas mixture is missing. It is
therefore not unusual to find in the literature that a combination of GC and IR
techniques is used. For example, Craig [5] reports the use of both methods, using a non-
dispersive infrared analyzer (NDIR) to monitor continuously levels of CO and CO₂.
The concentrations of the other gases e.g. H₂, CH₄, NOₓ, O₂ were obtained from
measurements on samples taken every 15 minutes, and the GC was one of the analytical instruments used. Ntshengedzeni and Edson [6] used an NDIR technique to measure the composition of the gas produced from an Imbert downdraft gasifier. However, only five gases were analyzed (CO, H2, CO2, CH4, N2), providing information on gas composition at one minute intervals.

In the literature, there is evidence of an interest (and hence need) to perform on-line analysis of the gas produced. Examples include work done by Karellas and Karl [7], where the producer gas stream from a fluidized-bed gasifier was analyzed on-line by means of laser spectroscopy; however, only the concentrations of the main constituents (H2, CH4, CO, CO2, H2O) and some heavier hydrocarbons were reported. In Karlegärd et al. [8], the use of quadrupole mass spectrometry (QMS) for on-line analysis of gas (from gasification process) was reported. Nevertheless, this method was limited due to its complexity, and it was only tested for a very narrow range of concentrations of species in the gas.

Although QMS is already used in many industries, its use for the analysis of fuel gas streams is not so widespread [8, 9]. In addition, despite being a well-established technique, there are still some technical difficulties in using it for the on-line analysis of multi-component gas mixtures. For example, Turner et al. [10] reported that the accuracy of measurements using QMS was questionable due to the non-linearity and instability of this method. Furthermore, overlapping fragments at similar m/z values can make the identification of individual species difficult.

In this paper, a methodology is developed to illustrate how QMS may be used for on-line analysis of gas species. There were challenges that had to be overcome, as
there were overlaps in the signals from some of the species (e.g. N$_2$ with CO), and the magnitude of the concentration of the species also varied. The technique is developed and illustrated by first performing some measurements on a relatively clean gas (from the gasification of charcoal with steam), and then on a more challenging system when wood, straw and refuse derived fuel (RDF) pellets are gasified (partial oxidation with air) in a laboratory-scale gasifier. Finally, it is applied to measure in real-time, the composition of the gas produced from a commercial pilot-scale plant, using waste-wood as a fuel.

2. Material and methods

2.1. Gas chromatography

To help validate the measurements using QMS, measurements were also performed using gas chromatography (GC). This method is often used for quantitative analysis even of very complex gas mixtures. However, its main drawback is the time it takes to obtain a measurement, as this depends on the retention time in the column. If real-time analysis is required (e.g. to follow a transient), then this method is unsuitable. The gas chromatograph used was a Chrompack CP9001, fitted with one pre-column and one molecular sieve column (connected in series), and a thermal conductivity detector. The chromatograph was calibrated using calibration gas mixtures with argon as the carrier gas.

To check the repeatability of measurements using GC, a bag-sample of gas was taken during a steam gasification of char experiment, which was run at 800 °C over a
period of 45 minutes. To this bag a quantity of air was added from a gas cylinder, so
that O₂ was also present. The gas was then injected into the column 10 times, and the
average gas composition (vol.%) was: H₂ = 28.68 (± 0.56); CO₂ = 7.60 (± 0.50); O₂ =
7.51 (± 0.35); N₂ = 48.01 (± 0.73); CO = 7.79 (± 0.82); CH₄ = 0.56 (± 0.09).

2.2. Quadrupole mass spectrometry (QMS)

Mass spectrometry identifies the species by using the difference in mass-to-
charge ratio (m/z) of ionized atoms or molecules. It is very useful to quantify atoms or
molecules, and to determine chemical and structural information about molecules. Each
molecule has its own distinctive fragmentation patterns that help to identify its structure.
Further information can be found in the literature [11]. In this study, a standard Hiden
HPR-20 Quadrupole Mass Spectrometer was used, which made use of Hiden’s MASsoft
software. This enables data to be reviewed, and it had export facilities that were
compatible with the Windows™ operating systems.

2.2.1. Setting the operating parameters

Before a methodology can be developed, the operating parameters for QMS
need to be set. The resolution and sensitivity of QMS depends on these conditions. After
calibration, any changes in these parameters will result in adverse effects on
repeatability [10].

Detector selection: Either a Faraday cup, or an Electron multiplier (SEM
detector) may be selected depending on the concentrations of the species in the gas. To
detect a trace level of gas, an SEM detector with a detectable pressure range from 1×10⁻
to 1×10^{-13} \text{ torr (1.3332×10^{-10} to 1.3332×10^{-16} bar)} could be selected, whereas, the Faraday detector would be more suitable for a gas with a detectable pressure range from 1×10^{-5} to 1×10^{-10} \text{ torr (1.3332×10^{-8} to 1.3332×10^{-13} bar)} [12].

In preliminary experiments, it was found that the selection of a suitable detector (or a combination of both SEM and Faraday) for a particular gas mixture affects not only the sensitivities, but also the measuring time. If the SEM detector is selected, it is necessary to calibrate the voltage applied so that it gives an equivalent signal to that of the Faraday detector. This voltage value changes slightly depending on the mass number and helps to increase the sensitivity when measuring trace levels of gases.

**Electron emission:** This maximizes the sensitivity for a particular gas. The value of this parameter is selected for a particular gas mixture by using a calibration facility in MASsoft, in which the highest concentration of gas in the mixture should give approximately 1×10^{-5} \text{ torr (1.3332×10^{-8} bar)} [12]. Above this value, the signal becomes non-linear, leading to inaccurate results.

**Electron energy:** This is normally set at 70 eV [10], and this will singly and doubly ionize most species. However, to minimize second ionization (producing a signal at ½ mass) electron energy can be adjusted to optimize the signal without double ionization.

**Measuring time:** For on-line analysis, measuring time is important and depends on a number of operating parameters such as: the detector used, acquisition range, dwell and settle times. It was found that by reducing both the dwell and settle times, and also narrowing the acquisition range, then this helped to increase the number of measurements per minute. However, these values need to be optimized to avoid an undue reduction in accuracy.
Operating Pressure: During experiments, it was noticed that any change in the
base pressure (the vacuum operating pressure), had a strong negative effect on the
accuracy of the measurement. This is consistent with findings in Turner et al. [10].
Thus, during an experiment, this operating pressure must be carefully monitored and
adjusted (by using the sample by-pass control valve).

General operating procedure: This is an important factor, and was also found
to affect the accuracy of the measurements (also discussed in Turner et al. [10]). In this
paper, both the Faraday and the SEM detectors were used to analyze gas mixtures
containing: N₂, CO, H₂, CO₂, CH₄, and trace gases of O₂, H₂S and COS. The values of:
SEM detector’s voltage, electron emission, and electron energy, were all optimized and
set at: 910 V, 250 uA and 70 eV, respectively. The analysis frequency was up to 10
samples per minute, which was considered adequate for the planned set of experiments.
The mass spectrometer was started-up and left running for at least two days to
obtain ultimate base pressure and stability prior to measurement. Then, the filaments
were also switched on and left running for 24 hours (to warm-up) prior to measurement.
A final base pressure of 1.6 × 10⁻⁶ torr was achieved.

2.2.2. Method development

Challenges: Turner et al. [10] reported that mathematical methods are important
to provide both qualitative and quantitative information from mass spectra. Basically,
these methods are based on the assumption that the measured spectrum is linear for each
pure component [13, 14]. However, if the sample was a complex mixture, then
considerable errors were noted [8, 14]. In attempts to solve this problem, some other
methods have been developed [9, 14], in which normalization methods are frequently
employed.
When using QMS to measure a mixture consisting of different species, it is often difficult to separate some of the species in the mixture due to spectral interference and the extensive fragmentation of the ions produced [14], particularly for organic species, which because of their characteristic have complex fragmentation patterns. In theory, this problem may be solved by the selection of non-interfering peaks. However, in practice, this is not always easy to do.

The gas stream to be analyzed may consist of H\textsubscript{2}, CO, N\textsubscript{2}, O\textsubscript{2}, CO\textsubscript{2}, CH\textsubscript{4}, H\textsubscript{2}O, C\textsubscript{2} & C\textsubscript{3} hydrocarbons, argon, longer chain hydrocarbons such as tars, and other contaminants such as sulphur and nitrogen compounds. In this study, a method was developed to measure the concentrations of the main gases (H\textsubscript{2}, CO, N\textsubscript{2}, CO\textsubscript{2}, CH\textsubscript{4}) and the trace gases (O\textsubscript{2}, H\textsubscript{2}S and COS) in a dried gas stream. In this case, three gases consisting of N\textsubscript{2}, CO and CO\textsubscript{2} exhibit similar fragmentation patterns in the mass spectra. This can be problematic to even the experienced mass spectrometrists. Karlegärd et al. [8] also reported that the quantification of N\textsubscript{2} and CO in gas mixtures (biomass gasification) was a problem for QMS analysis. According to Cook et al. [9], “in normal operation, a Quadrupole Mass Spectrometer does not have sufficient resolution to distinguish ‘isobars’ (ions of different elemental composition but the same nominal mass; e.g., CO at 27.99491 Da and N\textsubscript{2} at 28.006 Da both have nominal mass ‘28’).”

It can be said that, for building an on-line analysis method using QMS, it is beneficial to deal with as few mass fragments as possible. This helps to reduce the complexity of the method, leading to an increase in the measuring time of measurements. However, for a complex gas mixture, the use of more fragments could improve the accuracy of measurements. For example, Karlegärd et al. [8] failed in analyzing the gas produced from gasification of biofuel when they selected mass
fragments of m/z(12), m/z(14), m/z(28) and m/z(44) to separate N₂, CO and CO₂. In that study, the authors used an external method that attempted to determine absolute analyte concentrations from absolute signal intensities. This method, according to Cook et al. [9] and Hoffmann and Stroobant [14], is considered not to give good measurement repeatability due to the difficulty of controlling operating parameters, such as electron emission from the hot filament, in a precise manner.

Therefore, in the present study, with the aim of improving the speed and accuracy of the analysis method, fewer mass fragments would be used. Normalizing to the total ion current (estimated by summing the peaks) was selected to build the method. This method (called internal standard) is based on a comparison of the intensities of the signal, corresponding to the product that has to be quantified, with the signal of a reference compound. It provides the smallest sum of the squares of the difference between the calculated and experimentally measured mixture spectra – this is known as least-squares analysis [9].

**Building the method:** In order to quantify the individual components in the gas mixtures (from the experiments), the method consisted of:

- The identification of all molecular ions / significant peaks.
- The identification of peaks due to known components.
- The assignment of remaining peaks noting the general appearance of the spectrum, checking for peak clusters from isotope patterns and low-mass neutral fragment loss.
- The comparison of results with reference spectra on the database [13].

Then, a number of spectra were selected to create the mathematical method for quantification. Table 1 shows the mass fragments used in the analysis.
In general, the ion-molecule fragment of a species is often chosen, as it is the most intensive signal (the base peak) compared to the other spectra. However, for CH$_4$, because there is an overlap with oxygen at a value of m/z(16), the spectra of CH$_4$ at m/z(15) was selected. For H$_2$, CH$_4$, and CO$_2$, the values obtained did not need to be corrected. The partial pressures of H$_2$, CH$_4$ and CO$_2$ were derived from peaks corresponding to values at m/z(2), m/z(15) and m/z(44), respectively. Therefore:

\[
\begin{align*}
P_{H_2} &= P_{m/z(2)} \\
P_{CH_4} &= P_{m/z(15)} \\
P_{CO_2} &= P_{m/z(44)}
\end{align*}
\]

(1)

where: $P_i$ and $P_{m/z(j)}$ are the corrected partial pressure of component $i$, and the raw partial pressure recorded by the QMS at peak m/z(j), respectively.

For N$_2$ and CO, because there are overlaps with some of the species:

- the partial pressure of N$_2$ was derived from the m/z(14) N$_2$ spectra, which was corrected for CH$_4$, and also CO overlaps (possibly from a second ionization peak at $\frac{1}{2}$ mass), while
- that of CO was derived from the m/z(28) peak, corrected for N$_2$ and CO overlaps.

The following two equations were applied to separate N$_2$ and CO, and these featured in the iterative mathematical method used.

The partial pressure of N$_2$, after being corrected for CH$_4$ and CO overlaps:

\[
P_{N_2} = P_{m/z(14)} - P_{CH_4} \frac{C_{CH_4(14)}}{C_{CH_4(15)}} - P_{CO} \times C_{CO(14)}
\]

(2)

The partial pressure of CO, after being corrected for N$_2$ and CO$_2$ overlaps:
\[ P_{CO} = P_{m/z(28)} - P_{N_2} \times \frac{1}{C_{N_2(14)}} - P_{CO_2} \times C_{CO_2(28)} \] (3)

where: \( C_{i(j)} \) is the ratio of partial pressure of component \( i \), at peak \( m/z(j) \) to that of component \( i \), at the main peak (the highest peak of component \( i \)), and can be collected from the software’s library. However, these ratios change, depending on the operating parameters. Thus, in this study, they were calculated from a calibration at operating conditions.

For the species, \( H_2S \) and \( COS \), very careful checks were performed to avoid spectral interference with other species (e.g. main gases, tars, and other contaminants).

Thus, the non-interfering peak of \( m/z(60) \) was chosen for \( COS \), whereas \( H_2S \) partial pressure was derived from the \( m/z(34) \) peak, corrected for \( O_2 \) overlap. Similarly, partial pressure of \( O_2 \) was derived from the \( m/z(32) \) peak, corrected for \( H_2S \) overlap.

The partial pressure of \( COS \):

\[ P_{COS} = P_{m/z(60)} \] (4)

The partial pressure of \( H_2S \), after being corrected for \( O_2 \) overlap:

\[ P_{H_2S} = P_{m/z(34)} - P_{O_2} \times C_{O_2(34)} \] (5)

The partial pressure of \( O_2 \), after being corrected for \( H_2S \) overlap:

\[ P_{O_2} = P_{m/z(32)} - P_{H_2S} \times C_{H_2S(32)} \] (6)

Finally, the concentrations of the species were calculated from:

\[ x_i = \frac{(P_i / RS_i)}{\sum_i (P_i / RS_i)} \] (7)

where: \( x_i \) and \( RS_i \) are the calculated concentration and relative sensitivity (RS value) of component \( i \), respectively.
2.2.3. Calibration

To quantify the gases in a mixture, it is necessary to calibrate for RS values. RS is a factor which takes into account the sensitivity of different species dependent on the efficiency of the quadrupole. It is best to determine these for the specific quadrupole mass spectrometer used, at its particular set of operating conditions. The calibration requires a known gas mixture, and the highest concentration of gas is assigned a sensitivity of 1 (in this study, N\textsubscript{2} was selected and became the reference gas).

\[ RS_i = \frac{P_i}{P_{N_2}} \times \frac{x_{N_2}}{x_i} \] (8)

where: \( x_{N_2} \) and \( x_i \) are the known concentrations of reference gas N\textsubscript{2} and component i, respectively.

The gas mixture used to test the gas chromatograph (see Section 2.1), was then used to calibrate the mass spectrometer, for the main components in the gas. For the trace gases, the RS values of H\textsubscript{2}S and COS with N\textsubscript{2} as the reference gas were calculated by calibration with 2000 ppmv H\textsubscript{2}S in N\textsubscript{2}, and 200 ppmv COS in N\textsubscript{2}.

2.3. Experimental

2.3.1. Laboratory-scale gasifier

Gasification experiments were performed in a small laboratory-scale quartz-tube gasifier, in which in earlier work [15], it was shown that it can produce a gas stream similar in composition to a pilot-scale gasifier. An outline schematic of the gas sampling scheme is shown in Figure 1.
The gas flowed from the bottom of the gasifier, then through a cooler, and any condensate was trapped in the first plastic vessel. The gas then passed through a cooling coil, where more of the liquid was condensed. The gas was then passed through a glass wool filter, and then discharged into the vent from the fume cupboard. Samples of gas were drawn from the exhaust line, and passed through another glass wool filter and a filter coalescer before going to a gas chromatograph and the mass spectrometer for analysis. This system of filters helped to remove the majority of tars and particulates in the gas stream (so as not to damage the analytical equipment). Further details on this experimental set-up are available in earlier work [15].

2.3.2. Measurements on a pilot-scale plant

Gas analysis measurements were also taken on a commercial pilot-scale plant operated by Refgas Ltd at a test site in Sandycroft (near Chester, UK). A ‘waste-wood’ was used as a fuel. The term ‘waste-wood’ is used to describe a material that has been mainly produced from recycled wood, but may also contain a small amount of other contaminants (e.g. plastic, paper).

In its present configuration, this pilot-plant had a nominal capacity of 150 to 250 kg/h, depending on the material fed into the gasifier and the choice of operating conditions. The potential electrical output from the gas produced from this plant could vary from 150 to 250 kW. A simplified schematic of the process flow diagram is shown in Figure 2.

The waste-wood chips were fed from a hopper into the gasifier. The down-draft gasifier operates under a negative pressure, and the gases are drawn from the gasifier by the centrifugal gas blower. Because of the negative pressure in the gasifier, air is drawn into
the gasifier, and this supports the combustion and partial oxidation reactions that take place inside this unit. Some of this air is preheated in the outer jacket around the two cyclones. Another quantity of air is fed at ambient temperature directly into the gasifier along the central shaft.

The gas leaves the reactor at the bottom of the unit, at a temperature of about 550 °C. Char is discharged from the base of the gasifier, and char fines/ash are also trapped in the two cyclones. The dirty gas from the cyclones is quenched with water, and then passes through a HESS unit (which is a high efficiency water scrubber). The gas then passes through a heat exchanger (chiller), where additional residual water/tars are condensed. The blower draws the gas from the gasifier, and then blows it (under positive pressure) through the filters, into the storage tank, and then to the gas engine, and/or to the gas flare. The gas engine has the capacity to produce electrical energy.

During the course of measurements on the plant, the gas was discharged to flare.

The gas sample to the mass spectrometer was drawn from the line, at the point where the gas was sent to flare (see Figure 2). At this point, the gas was at positive pressure. The gas sample then flowed through a glass wool filter and a filter coalescer, (same procedure as shown in Figure 1), before going to the mass spectrometer for analysis.

3. Results and discussion

3.1. Experiments in laboratory-scale gasifier
A series of experiments was performed to generate gases that had different compositions, but at the same time reflected compositions which could be encountered in real applications.

3.1.1. Proximate analysis of fuels

Table 2 shows the proximate analysis of fuels used for the gasification experiments that were done in the laboratory. Experiments were performed with charcoal, wood, straw and refuse derived fuel (RDF) in the form of pellets.

3.1.2. Reliability check of the developed QMS method

A gas stream was generated by the use of a steam in nitrogen mixture to gasify charcoal. The molar ratio H₂O:N₂ was 2:1, and N₂ and H₂O flows were 0.1 litre/min and 0.196 g/min, respectively, passing through a 9.5 mm i.d. tube reactor, packed with charcoal (4 mm in diameter). The gas composition was measured on-line using QMS over a period of 45 min, while the temperature of the furnace was gradually increased from 600 to 900 °C, see Figure 3. At 5½ min intervals, gas samples were taken and analyzed using GC equipped with a thermal conductivity detector (TCD). The data from QMS is presented as a continuous curve (because measurements are frequent), and the data using GC is in the form of discrete data points. From these results it is clear that:

- a very good match was obtained between QMS and GC,

- as the gas composition was measured over a wide range of concentrations (which arose as a result of the experiment), the match between QMS and GC remained very good. For example:

  - For N₂ in the range of 21 to 100 vol.% (it was within ± 2.1 % of the value).
For H\textsubscript{2} in the range of 0 to 44 vol.% (it was within ±2.7 % of the value).

For CO in the range of 1.2 to 29 vol.% (it was within ±3.7 % of the value).

For CO\textsubscript{2} in the range of 2 to 14 vol.% (it was within ±2.1 % of the value).

For CH\textsubscript{4} in the range of 0.45 to 1 vol.% (it was within ±12.7 % of the value).

Big differences only occurred at low concentrations of CO, CO\textsubscript{2}, and CH\textsubscript{4}.

To check on the accuracy of the method for H\textsubscript{2}S, COS, and O\textsubscript{2} detection, some experiments were done using 2000 ppmv H\textsubscript{2}S in N\textsubscript{2}, 200 ppmv COS in N\textsubscript{2}, and air, respectively. These were tested in ‘as supplied form’, and they were also diluted with nitrogen (using rotameters). The results show that there was a good match between the measured values and those calculated from gas flows using rotameters (e.g. H\textsubscript{2}S in the range of 0 to 2000 ppmv (it was within ±1.1 %); COS in the range of 0 to 200 ppmv (it was within ±2.0 %); and O\textsubscript{2} in the range of 0 to 21 vol.% (it was within ±9.5 %)).

In general, these results were most satisfying, as the methodology was shown to work and produce good results.

3.1.3. The composition of the producer gas from gasification of wood pellets

Having established that the QMS method worked well for a relatively clean gas, a more complex gas mixture was used. This was produced by the gasification of wood pellets (using partial oxidation). These experiments were performed in a small scale, 21 mm i.d. quartz tube gasifier filled with wood pellets (5 mm diameter, and 13 mm long), to a depth of about 400 mm. The air flow was kept constant at 3 litre/min, and
temperatures in the hot zone were in the region of 912 to 1046 °C. Further information on that experimental facility is available in Kolaczkowski et al. [15].

An example of measurements on dry gas is shown in Figure 4. In this example, the average trace gas concentrations were: O$_2$ = 1510 ppmv; H$_2$S = 99 ppmv, and COS = 10 ppmv.

To check the repeatability of measurements with QMS, a bag-sample of gas was taken during this wood gasification experiment. The gas was then connected to the sampling line to the mass spectrometer. The repeatability was checked over a 10-minute period, during which it was found that the average composition of the species was: N$_2$ = 58.34 (± 0.28) vol.%; CO = 15.62 (± 0.16) vol.%; H$_2$ = 9.1 (± 0.16) vol.%; CO$_2$ = 14.31 (± 0.09) vol.%; CH$_4$ = 1.48 (± 0.01) vol.%; O$_2$ = 9987 (± 80) ppmv; H$_2$S = 83 (± 5) ppmv; COS = 6.55 (± 0.11) ppmv.

3.1.4. The composition of the producer gas from gasification of straw and RDF pellets

The same experimental procedures were repeated, this time using various compositions of the producer gas from gasification of straw and RDF pellets. The average values of concentration of components are presented in Table 3.

As can be seen in Table 3, there are obvious differences in the composition of the gas streams generated by gasification of different biomass sources. The straw pellets produce a slightly higher H$_2$S gas concentration, and the COS concentration is very similar. According to Little [16], the typical sulphur content in straw pellets was about 0.1 wt.%, which was higher than those of wood pellets made from heather (0.07 wt.%), gorse (0.08 wt.%), and rhododendron (0.02 wt.%).
The concentration of H$_2$S and COS produced from RDF pellets is about three
times higher than values from the wood and straw pellets. This is not surprising, as the
RDF was expected to have higher sulphur content. Depending on the source of RDF, its
sulphur content will vary. As an example, based on information from one supplier [17],
sulphur levels generally vary from 0.12 to 0.17 wt.%., yet can even be as low as 0.09
wt.%, or peak as high as 0.3 wt.%.

There is also consistency in the molar ratio of the concentration of H$_2$S to COS
(around 10:1) for gasification of wood, straw and RDF pellets, in which the temperature
in the hot zone was observed as high as 1084 °C. This information will also be very
useful when gas clean-up strategies need to be developed for commercial plants.

The results also show that there is a certain amount of O$_2$ in the gas stream, and
this can vary. This clearly depends on the design of the gasifier and operating
parameters. For example, the concentration of O$_2$ in the gas from the RDF pellets was
higher, because the pellets were large relative to the i.d. of the tube (higher void fraction
and wall channelling). The presence of O$_2$ in the producer gas streams is also reported in
the literature [18].

The concentration of the main components in the gas is also compared with
earlier experiments [15], using GC (with a TCD) for gas analysis. Although there are
slight differences, the comparison in general is very good. Slight differences probably
arise from slight variations in operating conditions/composition of pellets used.

Thus, it can be concluded that the developed QMS methodology had been
upgraded successfully to measure up to 8 species, including the main gases (N$_2$, H$_2$,
CO$_2$, CO, CH$_4$) and other trace gases (O$_2$, H$_2$S and COS). It was also shown that an
acceptable level of repeatability can be achieved. Also, provided that gas pre-cleaning
was effective, the mass spectrometer was stable for months without needing to be re-
calibrated.

3.2. Measurements on a pilot-scale plant

3.2.1. The actual waste-wood processed

Samples were taken of the waste-wood that was processed, and this is illustrated
in Figure 5. This clearly shows that the sample consists of wood from a variety of
different sources (e.g. bark, used wood, painted wood), and that it also contains small
quantities of cardboard, brown paper, and even plastics.

Samples of the waste-wood and waste-wood-derived char, were analyzed, and
their key properties (proximate analysis on a wt.% wet basis), are: moisture = 9.97;
voltiles = 70.57; fixed carbon = 19.13; ash = 0.33).

3.2.2. The composition of the gas produced from the pilot-plant

Initiation of reactions in the gasifier: At the start of each run, reactions in the
gasifier are initiated by starting the blower, which draws air through the gasifier. An
ignited lance (through which propane flows) is then inserted into the throat of the
gasifier, which sustains a flame to initiate reactions in the gasifier. When temperatures
start to rise in the throat of the gasifier, and gas temperatures from the gasifier also rise,
the supply of propane is turned-off, and the lance is withdrawn.

By selecting the following key parameters: (a) temperatures at the top and
bottom of the throat (in the gasifier, but measured near the wall of the throat); (b)
producer gas flow; (c) producer gas composition (N₂, CO, CO₂, H₂, CH₄ and O₂); and
(d) the sulphur species, H$_2$S and COS, in the gas, the results of one test run are summarized in Figure 6. In general, during this run, temperatures fluctuated at the top and the bottom of the throat, and gas flow varied depending on the choice of operating conditions.

Looking at the data, the following general observations can be made:

- As the blower speed was increased, the flow of air into the gasifier increased, and temperatures in the gasifier increased. The flow of gas from the gasifier also increased, as more gas was drawn by the centrifugal blower.

- As the unit was started-up, the composition of the gas changed (see Figure 6 (b)), providing a very clear indication of the point at which H$_2$ and CO started to be produced, and O$_2$ was consumed.

- In general, as temperatures in the gasifier increase (above and below the throat), the concentration of CO decreases (from 23 to 16 vol.%), whereas that of H$_2$ increases (from 10 to 15 vol.%).

- At various fixed operating speeds of the blower, the gas composition fluctuates (for example, see Figure 6 (b)), and this most probably arises from the nature of the gasification process (and composition of waste-wood) that is taking place in the throat of the gasifier. Although some gas back-mixing will occur in the pipework and process units before the gas sampling point, the fact that these fluctuations still remain indicates the presence of far bigger variations in gas composition at the base of the actual gasifier.

However, considering the nature of the waste-wood feedstock, and the variations in size of the feedstock (Figure 5), this is not surprising. For example, for a fixed operating speed of the blower at 40 %, it is interesting
to see that these variations are approximately: $\text{CO} = 16.0 (\pm 1.8) \text{ vol.\%}$, $\text{H}_2 = 11.9 (\pm 2.9) \text{ vol.\%}$, $\text{CO}_2 = 15.8 (\pm 1.4) \text{ vol.\%}$, $\text{N}_2 = 54.1 (\pm 3.3) \text{ vol.\%}$, $\text{CH}_4 = 1.9 (\pm 0.7) \text{ vol.\%}$, $\text{O}_2 = 0.3 (\pm 0.2) \text{ vol.\%}$.

- In Figure 6(c), the changes in $\text{H}_2\text{S}$ and COS levels are shown. The concentration of $\text{H}_2\text{S}$ varies from about 200 to 700 ppmv. This is not surprising as this will vary depending on the composition of the waste-wood that is being gasified at a particular moment.

- The COS concentrations were in the region of 6 to 17 ppmv, which are ~30 times smaller than the concentrations of $\text{H}_2\text{S}$. This is different from the findings in the laboratory, where the molar ratio of $\text{H}_2\text{S}$:COS was around 10:1 for all three types of biomass (wood, straw and RDF pellets). This difference might arise from the possibility of COS hydrolysis reactions taking place in the water quench and HESS units with the presence of ash particles as a catalyst - if it occurred, this would lead to the conversion of COS into $\text{H}_2\text{S}$.

In a recent patent, McDaniel [19] reported a method and apparatus for removing COS from a producer gas stream via wet scrubbing in the presence of ash particles. The ash particles contained alumina oxide, which could exhibit catalytic properties for the reaction.

$$H_2O + COS \underset{\text{catalyst}}{\leftrightarrow} CO_2 + H_2S$$  \hspace{1cm} (9)

McDaniel [19] found that if the producer gas stream from the gasifier went directly into a wet scrubber (without passing through any other particulate removal devices), then up to a 30 % drop in the COS occurred across the
scrubber. This depended on the design of the scrubber and its operating conditions, and flooding conditions were preferred.

4. Conclusions

Using QMS, a quantitative method of on-line gas analysis was developed to measure gas composition when a range of fuels was gasified. The method is informative and the data provides an indication of gas composition, especially on the trace components $\text{H}_2\text{S}$ and COS for which there is relatively little data. From measurements on a commercial scale down-draft pilot-scale gasifier (with waste wood as fuel), valuable data was obtained during the start-up phase. In addition it was found that the $\text{H}_2\text{S}:\text{COS}$ ratios were higher than obtained in laboratory experiments, and this has important implications for the choice of gas clean-up equipment to remove sulphur compounds.

Acknowledgements

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References


Figure Captions

Figure 1. Outline schematic of the gasification experiment, focusing on gas analysis.

Figure 2. Simplified process flow diagram of the commercial pilot-scale plant.

Figure 3. Comparison between QMS and GC measurements (data points correspond to GC measurements).

Figure 4. Composition of dry gas from gasification of wood pellets: (a) main gases and (b) trace gases.

Figure 5. Photograph of a sample of waste-wood used.

Figure 6. The results of a test run performed on the pilot-plant: (a) temperature and gas flow, (b) dry gas composition, and (c) concentration of H₂S and COS in dry gas.
Figure 1
Figure 2
Figure 3
Figure 4
Figure 6
Table 1. Analysis matrix for the gas produced from biomass gasification.

<table>
<thead>
<tr>
<th>Component</th>
<th>Mass</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>2</td>
</tr>
<tr>
<td>H₂</td>
<td>x</td>
</tr>
<tr>
<td>CH₄</td>
<td></td>
</tr>
<tr>
<td>CO₂</td>
<td></td>
</tr>
<tr>
<td>N₂</td>
<td></td>
</tr>
<tr>
<td>CO</td>
<td></td>
</tr>
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<td>O₂</td>
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<tr>
<td>H₂S</td>
<td></td>
</tr>
<tr>
<td>COS</td>
<td></td>
</tr>
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</table>
Table 2. Properties of the fuels used with proximate analysis.

<table>
<thead>
<tr>
<th>Properties</th>
<th>Wood Charcoal (1)</th>
<th>Wood pellets (2)</th>
<th>Straw pellets (3)</th>
<th>RDF pellets (4)</th>
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<tbody>
<tr>
<td>Dimensions:</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Diameter, mm</td>
<td>4</td>
<td>5</td>
<td>6</td>
<td>14</td>
</tr>
<tr>
<td>Length, mm</td>
<td>4</td>
<td>5 - 17</td>
<td>5 - 17</td>
<td>30 - 80</td>
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<tr>
<td>Moisture (wt.% in wet basic)</td>
<td>4.7</td>
<td>7.4</td>
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<td>Volatiles (wt.% in wet basic)</td>
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<tr>
<td>Fixed carbon (wt.% in wet basic)</td>
<td>82.8</td>
<td>18.8</td>
<td>21.7</td>
<td>29.2</td>
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<tr>
<td>Ash (wt.% in wet basic)</td>
<td>1.2</td>
<td>1.3</td>
<td>1.4</td>
<td>23.9</td>
</tr>
</tbody>
</table>

(1) Obtained from an actual pilot-plant that has used wood pellets as fuel.
(2) Supplied by Treenergy Ltd, Monmouth.
(3) Supplied by Agripellets Ltd, Evesham.
(4) Supplied by Refgas Ltd, Sandycroft.
Table 3. Comparison of gas compositions produced from different biomass sources.

<table>
<thead>
<tr>
<th>Component</th>
<th>Previous study (Kolaczkowski et al., 2011b), GC used for analysis</th>
<th>Current study, QMS used for analysis</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Wood pellets</td>
<td>Straw pellets</td>
</tr>
<tr>
<td>CO, vol.%</td>
<td>15.8</td>
<td>14.7</td>
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<tr>
<td>H₂, vol.%</td>
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<td>CH₄, vol.%</td>
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<td>2.0</td>
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<tr>
<td>CO₂, vol.%</td>
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<tr>
<td>N₂, vol.%</td>
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<td>56.5</td>
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<td>O₂, ppmv</td>
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<td>-</td>
</tr>
<tr>
<td>H₂S, ppmv</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>COS, ppmv</td>
<td>-</td>
<td>-</td>
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