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1 **Using quadrupole mass spectrometry for on-line gas analysis – gasification of**

2 **biomass and refuse derived fuel**

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8

9 **ABSTRACT**

10 A quantitative method of on-line gas analysis was developed, using quadrupole mass

11 spectrometry to measure gas composition when charcoal, wood, straw, and refuse

12 derived fuel were gasified. Despite overlapping between some of the species, the

13 method was demonstrated on small-scale laboratory gasifiers, recording the main

14 components (e.g. $N_2 \sim$ 54-67 vol.%; $H_2 \sim$ 5-13 vol.%; $CO_2 \sim$ 15-17 vol.%; CO ~ 10-17

15 vol.%), and lower levels of CH_4 (~ 1-2 vol.%) and O_2 (~ 0.1-1 vol.%) in the gas. Trace

16 levels of H_2S (~ 100-300 ppmv) and COS (~ 10-30 ppmv) were also measured

17 (important for gas clean-up strategies). On-line measurements were performed on a

18 commercial pilot-scale down-draft gasifier (using waste wood), and the concentrations

19 of H_2S varied from 200 to 700 ppmv, and COS from 7 to 17 ppmv. The ratio of H_2S:

20 COS was higher than in the laboratory trials - probably because of COS hydrolysis

21 reactions taking place in the wet scrubbing systems.

22 *Key words:* Biomass gasification; gasifier; down-draft; on-line gas analysis; quadrupole

23 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

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List of Abbreviations

GC	Gas Chromatography
HESS	High Efficiency Water Scrubber
IR	Infrared
NDIR	Non-Dispersive Infrared Analyzer
QMS	Quadrupole Mass Spectrometry
RDF	Refuse Derived Fuel
RS	Relative Sensitivity
SEM	Secondary Electron Multiplier
TCD	Thermal Conductivity Detector

40   the plant is operated. For example, in Europe, if a refuse derived fuel is used, then the

41   Waste Incineration Directive [3] applies, and in such a situation in order to design the

42   gas clean-up system, it is important to know the concentration of contaminants such as

43   H_2S and COS [4]. Thus, the ability to perform on-line analysis is beneficial for

44   monitoring the quality of the gas produced, both at an industrial and an experimental

45   scale of operation.

46   To analyze the gas produced from a biomass gasification system, discrete samples of

47   gas may be taken and then analyzed by a specialist laboratory. Such analysis can be

48   done using gas chromatography (GC), or with an infrared (IR) system, and these two

49   methods of measurement are often used. The main advantage of GC is that it can

50   provide a quantitative analysis of complex gas mixtures, whereas its main drawback is

51   the long measuring time. Therefore, it is not a suitable method for on-line analysis

52   during transient operating conditions encountered in a gasification process. Also, even if

53   a set of discrete samples were to be taken for subsequent analysis, then problems can

54   often be encountered either, with possible leakage of species (e.g. hydrogen) from the

55   sample container, or difficulties in the sampling process, both resulting in incorrect

56   results.

57   Although IR spectroscopy could be used to perform measurements on-line, its main

58   disadvantage arises from the fact that, in general, it measures a single gas species, and

59   hence information on the other key components in the gas mixture is missing. It is

60   therefore not unusual to find in the literature that a combination of GC and IR

61   techniques is used. For example, Craig [5] reports the use of both methods, using a non-

62   dispersive infrared analyzer (NDIR) to monitor continuously levels of CO and CO_2 .

63   The concentrations of the other gases e.g. H_2, CH_4, NO_x, O_2 were obtained from

64   measurements on samples taken every 15 minutes, and the GC was one of the analytical

65   instruments used. Ntshengedzeni and Edson [6] used an NDIR technique to measure the

66   composition of the gas produced from an Imbert downdraft gasifier. However, only five

67   gases were analyzed (CO, H_2, CO_2, CH_4, N_2), providing information on gas

68   composition at one minute intervals.

69

70   In the literature, there is evidence of an interest (and hence need) to perform on-

71   line analysis of the gas produced. Examples include work done by Karellas end Karl [7],

72   where the producer gas stream from a fluidized-bed gasifier was analyzed on-line by

73   means of laser spectroscopy; however, only the concentrations of the main constituents

74   (H_2, CH_4, CO, CO_2, H_2O) and some heavier hydrocarbons were reported. In Karlegärd

75   *et al*. [8], the use of quadrupole mass spectrometry (QMS) for on-line analysis of gas

76   (from gasification process) was reported. Nevertheless, this method was limited due to

77   its complexity, and it was only tested for a very narrow range of concentrations of

78   species in the gas.

79   Although QMS is already used in many industries, its use for the analysis of fuel

80   gas streams is not so widespread [8, 9]. In addition, despite being a well-established

81   technique, there are still some technical difficulties in using it for the on-line analysis of

82   multi-component gas mixtures. For example, Turner *et al*. [10] reported that the

83   accuracy of measurements using QMS was questionable due to the non-linearity and

84   instability of this method. Furthermore, overlapping fragments at similar m/z values can

85   make the identification of individual species difficult.

86   In this paper, a methodology is developed to illustrate how QMS may be used

87   for on-line analysis of gas species. There were challenges that had to be overcome, as

88   there were overlaps in the signals from some of the species (e.g. N_2 with CO), and the

89   magnitude of the concentration of the species also varied. The technique is developed

90   and illustrated by first performing some measurements on a relatively clean gas (from

91   the gasification of charcoal with steam), and then on a more challenging system when

92   wood, straw and refuse derived fuel (RDF) pellets are gasified (partial oxidation with

93   air) in a laboratory-scale gasifier. Finally, it is applied to measure in real-time, the

94   composition of the gas produced from a commercial pilot-scale plant, using waste-wood

95   as a fuel.

96

97   **2. Material and methods**

98

99   *2.1. Gas chromatography*

100

101   To help validate the measurements using QMS, measurements were also

102   performed using gas chromatography (GC).

103   This method is often used for quantitative analysis even of very complex gas

104   mixtures. However, its main drawback is the time it takes to obtain a measurement, as

105   this depends on the retention time in the column. If real-time analysis is required (e.g. to

106   follow a transient), then this method is unsuitable. The gas chromatograph used was a

107   Chrompack CP9001, fitted with one pre-column and one molecular sieve column

108   (connected in series), and a thermal conductivity detector. The chromatograph was

109   calibrated using calibration gas mixtures with argon as the carrier gas.

110   To check the repeatability of measurements using GC, a bag-sample of gas was

111   taken during a steam gasification of char experiment, which was run at 800 ℃ over a

112 period of 45 minutes. To this bag a quantity of air was added from a gas cylinder, so

113 that O_2 was also present. The gas was then injected into the column 10 times, and the

114 average gas composition (vol.%) was: H_2 = 28.68 (± 0.56); CO_2 = 7.60 (± 0.50); O_2 =

115 7.51 (± 0.35); N_2 = 48.01 (± 0.73); CO = 7.79 (± 0.82); CH_4 = 0.56 (± 0.09).

116

117 ***2.2. Quadrupole mass spectrometry (QMS)***

118

119 Mass spectrometry identifies the species by using the difference in mass-to-

120 charge ratio (m/z) of ionized atoms or molecules. It is very useful to quantify atoms or

121 molecules, and to determine chemical and structural information about molecules. Each

122 molecule has its own distinctive fragmentation patterns that help to identify its structure.

123 Further information can be found in the literature [11]. In this study, a standard Hiden

124 HPR-20 Quadrupole Mass Spectrometer was used, which made use of Hiden's MASsoft

125 software. This enables data to be reviewed, and it had export facilities that were

126 compatible with the Windows™ operating systems.

127

128 *2.2.1. Setting the operating parameters*

129 Before a methodology can be developed, the operating parameters for QMS

130 need to be set. The resolution and sensitivity of QMS depends on these conditions. After

131 calibration, any changes in these parameters will result in adverse effects on

132 repeatability [10].

133 **Detector selection:** Either a Faraday cup, or an Electron multiplier (SEM

134 detector) may be selected depending on the concentrations of the species in the gas. To

135 detect a trace level of gas, an SEM detector with a detectable pressure range from $1\times10^{-}$

136   [7] to 1×10^{-13} torr (1.3332×10^{-10} to 1.3332×10^{-16} bar) could be selected, whereas, the

137   Faraday detector would be more suitable for a gas with a detectable pressure range from

138   1×10^{-5} to 1×10^{-10} torr (1.3332×10^{-8} to 1.3332×10^{-13} bar) [12].

139   In preliminary experiments, it was found that the selection of a suitable detector

140   (or a combination of both SEM and Faraday) for a particular gas mixture affects not

141   only the sensitivities, but also the measuring time. If the SEM detector is selected, it is

142   necessary to calibrate the voltage applied so that it gives an equivalent signal to that of

143   the Faraday detector. This voltage value changes slightly depending on the mass number

144   and helps to increase the sensitivity when measuring trace levels of gases.

145   **Electron emission:** This maximizes the sensitivity for a particular gas. The

146   value of this parameter is selected for a particular gas mixture by using a calibration

147   facility in MASsoft, in which the highest concentration of gas in the mixture should

148   give approximately 1×10^{-5} torr (1.3332×10^{-8} bar) [12]. Above this value, the signal

149   becomes non-linear, leading to inaccurate results.

150   **Electron energy:** This is normally set at 70 eV [10], and this will singly and

151   doubly ionize most species. However, to minimize second ionization (producing a

152   signal at ½ mass) electron energy can be adjusted to optimize the signal without double

153   ionization.

154   **Measuring time:** For on-line analysis, measuring time is important and depends

155   on a number of operating parameters such as: the detector used, acquisition range, dwell

156   and settle times. It was found that by reducing both the dwell and settle times, and also

157   narrowing the acquisition range, then this helped to increase the number of

158   measurements per minute. However, these values need to be optimized to avoid an

159   undue reduction in accuracy.

160   **Operating Pressure:** During experiments, it was noticed that any change in the

161   base pressure (the vacuum operating pressure), had a strong negative effect on the

162   accuracy of the measurement. This is consistent with findings in Turner *et al*. [10].

163   Thus, during an experiment, this operating pressure must be carefully monitored and

164   adjusted (by using the sample by-pass control valve).

165   **General operating procedure:** This is an important factor, and was also found

166   to affect the accuracy of the measurements (also discussed in Turner *et al*. [10]). In this

167   paper, both the Faraday and the SEM detectors were used to analyze gas mixtures

168   containing: N_2, CO, H_2, CO_2, CH_4, and trace gases of O_2, H_2S and COS. The values of:

169   SEM detector's voltage, electron emission, and electron energy, were all optimized and

170   set at: 910 V, 250 uA and 70 eV, respectively. The analysis frequency was up to 10

171   samples per minute, which was considered adequate for the planned set of experiments.

172
173   The mass spectrometer was started-up and left running for at least two days to

174   obtain ultimate base pressure and stability prior to measurement. Then, the filaments

175   were also switched on and left running for 24 hours (to warm-up) prior to measurement.

176   A final base pressure of 1.6×10^{-6} torr was achieved.

177

178   *2.2.2. Method development*

179   **Challenges:** Turner *et al*. [10] reported that mathematical methods are important

180   to provide both qualitative and quantitative information from mass spectra. Basically,

181   these methods are based on the assumption that the measured spectrum is linear for each

182   pure component [13, 14]. However, if the sample was a complex mixture, then

183   considerable errors were noted [8, 14]. In attempts to solve this problem, some other

184   methods have been developed [9, 14], in which normalization methods are frequently

185   employed.

186   When using QMS to measure a mixture consisting of different species, it is often

187   difficult to separate some of the species in the mixture due to spectral interference and

188   the extensive fragmentation of the ions produced [14], particularly for organic species,

189   which because of their characteristic have complex fragmentation patterns. In theory,

190   this problem may be solved by the selection of non-interfering peaks. However, in

191   practice, this is not always easy to do.

192   The gas stream to be analyzed may consist of H_2, CO, N_2, O_2, CO_2, CH_4, H_2O,

193   C_2 & C_3 hydrocarbons, argon, longer chain hydrocarbons such as tars, and other

194   contaminants such as sulphur and nitrogen compounds. In this study, a method was

195   developed to measure the concentrations of the main gases (H_2, CO, N_2, CO_2, CH_4) and

196   the trace gases (O_2, H_2S and COS) in a dried gas stream. In this case, three gases

197   consisting of N_2, CO and CO_2 exhibit similar fragmentation patterns in the mass spectra.

198   This can be problematic to even the experienced mass spectrometrists. Karlegärd *et al*.

199   [8] also reported that the quantification of N_2 and CO in gas mixtures (biomass

200   gasification) was a problem for QMS analysis. According to Cook *et al*. [9], "in normal

201   operation, a Quadrupole Mass Spectrometer does not have sufficient resolution to

202   distinguish 'isobars' (ions of different elemental composition but the same nominal

203   mass; e.g., CO at 27.99491 Da and N_2 at 28.006 Da both have nominal mass '28')."

204   It can be said that, for building an on-line analysis method using QMS, it is

205   beneficial to deal with as few mass fragments as possible. This helps to reduce the

206   complexity of the method, leading to an increase in the measuring time of

207   measurements. However, for a complex gas mixture, the use of more fragments could

208   improve the accuracy of measurements. For example, Karlegärd *et al*. [8] failed in

209   analyzing the gas produced from gasification of biofuel when they selected mass

210 fragments of m/z(12), m/z(14), m/z(28) and m/z(44) to separate N_2, CO and CO_2. In that

211 study, the authors used an external method that attempted to determine absolute analyte

212 concentrations from absolute signal intensities. This method, according to Cook *et al*.

213 [9] and Hoffmann and Stroobant [14], is considered not to give good measurement

214 repeatability due to the difficulty of controlling operating parameters, such as electron

215 emission from the hot filament, in a precise manner.

216   Therefore, in the present study, with the aim of improving the speed and

217 accuracy of the analysis method, fewer mass fragments would be used. Normalizing to

218 the total ion current (estimated by summing the peaks) was selected to build the method.

219 This method (called internal standard) is based on a comparison of the intensities of the

220 signal, corresponding to the product that has to be quantified, with the signal of a

221 reference compound. It provides the smallest sum of the squares of the difference

222 between the calculated and experimentally measured mixture spectra – this is known as

223 least-squares analysis [9].

224   **Building the method:** In order to quantify the individual components in the gas

225 mixtures (from the experiments), the method consisted of:

226   ▪ The identification of all molecular ions / significant peaks.

227   ▪ The identification of peaks due to known components.

228   ▪ The assignment of remaining peaks noting the general appearance of the

229   spectrum, checking for peak clusters from isotope patterns and low-mass

230   neutral fragment loss.

231   ▪ The comparison of results with reference spectra on the database [13].

232   Then, a number of spectra were selected to create the mathematical method for

233 quantification. Table 1 shows the mass fragments used in the analysis.

234   In general, the ion-molecule fragment of a species is often chosen, as it is the

235   most intensive signal (the base peak) compared to the other spectra. However, for CH_4,

236   because there is an overlap with oxygen at a value of m/z(16), the spectra of CH_4 at

237   m/z(15) was selected.

238   For H_2, CH_4, and CO_2, the values obtained did not need to be corrected. The

239   partial pressures of H_2, CH_4 and CO_2 were derived from peaks corresponding to values

240   at m/z(2), m/z(15) and m/z(44), respectively. Therefore:

$$
\begin{cases}
P_{H_2} = P_{m/z(2)} \\
P_{CH_4} = P_{m/z(15)} \\
P_{CO_2} = P_{m/z(44)}
\end{cases}
\tag{1}
$$

241

242   where: P_i and $P_{m/z(j)}$ are the corrected partial pressure of component i, and the raw partial

243   pressure recorded by the QMS at peak m/z(j), respectively.

244   For N_2 and CO, because there are overlaps with some of the species:

245   ▪   the partial pressure of N_2 was derived from the m/z(14) N_2 spectra, which

246   was corrected for CH_4, and also CO overlaps (possibly from a second

247   ionization peak at ½ mass), while

248   ▪   that of CO was derived from the m/z(28) peak, corrected for N_2 and CO_2

249   overlaps.

250   The following two equations were applied to separate N_2 and CO, and these

251   featured in the iterative mathematical method used.

252   The partial pressure of N_2, after being corrected for CH_4 and CO overlaps:

$$
P_{N_2} = P_{m/z(14)} - P_{CH_4} \frac{C_{CH_4(14)}}{C_{CH_4(15)}} - P_{CO} \times C_{CO(14)}
\tag{2}
$$

253

254   The partial pressure of CO, after being corrected for N_2 and CO_2 overlaps:

255
$$P_{CO} = P_{m/z(28)} - P_{N_2} \times \frac{1}{C_{N_2(14)}} - P_{CO_2} \times C_{CO_2(28)} \qquad (3)$$

256 where: $C_{i(j)}$ is the ratio of partial pressure of component i, at peak m/z(j) to that of

257 component i, at the main peak (the highest peak of component i), and can be collected

258 from the software's library. However, these ratios change, depending on the operating

259 parameters. Thus, in this study, they were calculated from a calibration at operating

260 conditions.

261 For the species, H_2S and COS, very careful checks were performed to avoid

262 spectral interference with other species (e.g. main gases, tars, and other contaminants).

263 Thus, the non-interfering peak of m/z(60) was chosen for COS, whereas H_2S partial

264 pressure was derived from the m/z(34) peak, corrected for O_2 overlap. Similarly, partial

265 pressure of O_2 was derived from the m/z(32) peak, corrected for H_2S overlap.

266 The partial pressure of COS:

267
$$P_{COS} = P_{m/z(60)} \qquad (4)$$

268 The partial pressure of H_2S, after being corrected for O_2 overlap:

269
$$P_{H_2S} = P_{m/z(34)} - P_{O_2} \times C_{O_2(34)} \qquad (5)$$

270 The partial pressure of O_2, after being corrected for H_2S overlap:

271
$$P_{O_2} = P_{m/z(32)} - P_{H_2S} \times C_{H_2S(32)} \qquad (6)$$

272 Finally, the concentrations of the species were calculated from:

273
$$x_i = \frac{(P_i / RS_i)}{\sum_i (P_i / RS_i)} \qquad (7)$$

274 where: x_i and RS_i are the calculated concentration and relative sensitivity (RS value) of

275 component i, respectively.

276

277   *2.2.3. Calibration*

278   To quantify the gases in a mixture, it is necessary to calibrate for RS values. RS

279   is a factor which takes into account the sensitivity of different species dependent on the

280   efficiency of the quadrupole. It is best to determine these for the specific quadrupole

281   mass spectrometer used, at its particular set of operating conditions. The calibration

282   requires a known gas mixture, and the highest concentration of gas is assigned a

283   sensitivity of 1 (in this study, N_2 was selected and became the reference gas).

284    $$RS_i = \frac{P_i}{P_{N_2}} \times \frac{x_{N_2}}{x_i}$$ (8)

285   where: x_{N_2} and x_i are the known concentrations of reference gas N_2 and component i,

286   respectively.

287   The gas mixture used to test the gas chromatograph (see Section 2.1), was then

288   used to calibrate the mass spectrometer, for the main components in the gas. For the

289   trace gases, the RS values of H_2S and COS with N_2 as the reference gas were calculated

290   by calibration with 2000 ppmv H_2S in N_2, and 200 ppmv COS in N_2.

291

292   **2.3. Experimental**

293

294   *2.3.1. Laboratory-scale gasifier*

295   Gasification experiments were performed in a small laboratory-scale quartz-tube

296   gasifier, in which in earlier work [15], it was shown that it can produce a gas stream

297   similar in composition to a pilot-scale gasifier. An outline schematic of the gas sampling

298   scheme is shown in Figure 1.

299   The gas flowed from the bottom of the gasifier, then through a cooler, and any

300   condensate was trapped in the first plastic vessel. The gas then passed through a cooling

301   coil, where more of the liquid was condensed. The gas was then passed through a glass

302   wool filter, and then discharged into the vent from the fume cupboard. Samples of gas

303   were drawn from the exhaust line, and passed through another glass wool filter and a

304   filter coalescer before going to a gas chromatograph and the mass spectrometer for

305   analysis. This system of filters helped to remove the majority of tars and particulates in

306   the gas stream (so as not to damage the analytical equipment). Further details on this

307   experimental set-up are available in earlier work [15].

308

309   *2.3.2. Measurements on a pilot-scale plant*

310   Gas analysis measurements were also taken on a commercial pilot-scale plant

311   operated by Refgas Ltd at a test site in Sandycroft (near Chester, UK). A 'waste-wood'

312   was used as a fuel. The term 'waste-wood' is used to describe a material that has been

313   mainly produced from recycled wood, but may also contain a small amount of other

314   contaminants (e.g. plastic, paper).

315   In its present configuration, this pilot-plant had a nominal capacity of 150 to 250

316   kg/h, depending on the material fed into the gasifier and the choice of operating

317   conditions. The potential electrical output from the gas produced from this plant could

318   vary from 150 to 250 kW$_e$.

319   A simplified schematic of the process flow diagram is shown in Figure 2.

320   The waste-wood chips were fed from a hopper into the gasifier. The down-draft gasifier

321   operates under a negative pressure, and the gases are drawn from the gasifier by the

322   centrifugal gas blower. Because of the negative pressure in the gasifier, air is drawn into

323 the gasifier, and this supports the combustion and partial oxidation reactions that take

324 place inside this unit. Some of this air is preheated in the outer jacket around the two

325 cyclones. Another quantity of air is fed at ambient temperature directly into the gasifier

326 along the central shaft.

327   The gas leaves the reactor at the bottom of the unit, at a temperature of about

328 550 °C. Char is discharged from the base of the gasifier, and char fines/ash are also

329 trapped in the two cyclones. The dirty gas from the cyclones is quenched with water,

330 and then passes through a HESS unit (which is a high efficiency water scrubber). The

331 gas then passes through a heat exchanger (chiller), where additional residual water/tars

332 are condensed. The blower draws the gas from the gasifier, and then blows it (under

333 positive pressure) through the filters, into the storage tank, and then to the gas engine,

334 and/or to the gas flare. The gas engine has the capacity to produce electrical energy.

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

336   The gas sample to the mass spectrometer was drawn from the line, at the point

337 where the gas was sent to flare (see Figure 2). At this point, the gas was at positive

338 pressure. The gas sample then flowed through a glass wool filter and a filter coalescer,

339 (same procedure as shown in Figure 1), before going to the mass spectrometer for

340 analysis.

341

342 **3. Results and discussion**

343

344 *3.1. Experiments in laboratory-scale gasifier*

345

346　　　　　A series of experiments was performed to generate gases that had different

347　compositions, but at the same time reflected compositions which could be encountered

348　in real applications.

349　*3.1.1. Proximate analysis of fuels*

350　　　　　Table 2 shows the proximate analysis of fuels used for the gasification

351　experiments that were done in the laboratory. Experiments were performed with

352　charcoal, wood, straw and refuse derived fuel (RDF) in the form of pellets.

353

354　*3.1.2. Reliability check of the developed QMS method*

355　　　　　A gas stream was generated by the use of a steam in nitrogen mixture to gasify

356　charcoal. The molar ratio $H_2O:N_2$ was 2:1, and N_2 and H_2O flows were 0.1 litre/min and

357　0.196 g/min, respectively, passing through a 9.5 mm i.d. tube reactor, packed with

358　charcoal (4 mm in diameter). The gas composition was measured on-line using QMS

359　over a period of 45 min, while the temperature of the furnace was gradually increased

360　from 600 to 900 ℃, see Figure 3. At 5½ min intervals, gas samples were taken and

361　analyzed using GC equipped with a thermal conductivity detector (TCD). The data from

362　QMS is presented as a continuous curve (because measurements are frequent), and the

363　data using GC is in the form of discrete data points. From these results it is clear that:

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

365　　　-　as the gas composition was measured over a wide range of concentrations

366　　　　　(which arose as a result of the experiment), the match between QMS and GC

367　　　　　remained very good. For example:

368　　　　　▪　For N_2 in the range of 21 to 100 vol.% (it was within $\pm$ 2.1 % of the

369　　　　　　value).

370   ▪   For H_2 in the range of 0 to 44 vol.% (it was within ± 2.7 % of the value).

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

372   value).

373   ▪   For CO_2 in the range of 2 to 14 vol.% (it was within ± 2.1 % of the value).

374   ▪   For CH_4 in the range of 0.45 to 1 vol.% (it was within ±12.7 % of the

375   value).

376   Big differences only occurred at low concentrations of CO, CO_2, and CH_4.

377   To check on the accuracy of the method for H_2S, COS, and O_2 detection, some

378 experiments were done using 2000 ppmv H_2S in N_2, 200 ppmv COS in N_2, and air,

379 respectively. These were tested in 'as supplied form', and they were also diluted with

380 nitrogen (using rotameters). The results show that there was a good match between the

381 measured values and those calculated from gas flows using rotameters (e.g. H_2S in the

382 range of 0 to 2000 ppmv (it was within ± 1.1 %); COS in the range of 0 to 200 ppmv (it

383 was within ± 2.0 %); and O_2 in the range of 0 to 21 vol.% (it was within ± 9.5 %)).

384   In general, these results were most satisfying, as the methodology was shown to

385 work and produce good results.

386

387 *3.1.3. The composition of the producer gas from gasification of wood pellets*

388   Having established that the QMS method worked well for a relatively clean gas,

389 a more complex gas mixture was used. This was produced by the gasification of wood

390 pellets (using partial oxidation). These experiments were performed in a small scale, 21

391 mm i.d. quartz tube gasifier filled with wood pellets (5 mm diameter, and 13 mm long),

392 to a depth of about 400 mm. The air flow was kept constant at 3 litre/min, and

393   temperatures in the hot zone were in the region of 912 to 1046 °C. Further information

394   on that experimental facility is available in Kolaczkowski *et al*. [15].

395   An example of measurements on dry gas is shown in Figure 4. In this example,

396   the average trace gas concentrations were: O_2 = 1510 ppmv; H_2S = 99 ppmv, and COS

397   = 10 ppmv.

398   To check the repeatability of measurements with QMS, a bag-sample of gas was

399   taken during this wood gasification experiment. The gas was then connected to the

400   sampling line to the mass spectrometer. The repeatability was checked over a 10-minute

401   period, during which it was found that the average composition of the species was: N_2 =

402   58.34 (± 0.28) vol.%; CO = 15.62 (± 0.16) vol.%; H_2 = 9.1 (± 0.16) vol.%, CO_2 = 14.31

403   (± 0.09) vol.%, CH_4 = 1.48 (± 0.01) vol.%, O_2 = 9987 (± 80) ppmv, H_2S = 83 (± 5)

404   ppmv, COS = 6.55 (± 0.11) ppmv.

405

406   *3.1.4. The composition of the producer gas from gasification of straw and RDF pellets*

407   The same experimental procedures were repeated, this time using various

408   compositions of the producer gas from gasification of straw and RDF pellets. The

409   average values of concentration of components are presented in Table 3.

410   As can be seen in Table 3, there are obvious differences in the composition of

411   the gas streams generated by gasification of different biomass sources. The straw pellets

412   produce a slightly higher H_2S gas concentration, and the COS concentration is very

413   similar. According to Little [16], the typical sulphur content in straw pellets was about

414   0.1 wt.%, which was higher than those of wood pellets made from heather (0.07 wt.%),

415   gorse (0.08 wt.%), and rhododendron (0.02 wt.%).

416   The concentration of H_2S and COS produced from RDF pellets is about three

417   times higher than values from the wood and straw pellets. This is not surprising, as the

418   RDF was expected to have higher sulphur content. Depending on the source of RDF, its

419   sulphur content will vary. As an example, based on information from one supplier [17],

420   sulphur levels generally vary from 0.12 to 0.17 wt.%, yet can even be as low as 0.09

421   wt.%, or peak as high as 0.3 wt.%.

422   There is also consistency in the molar ratio of the concentration of H_2S to COS

423   (around 10:1) for gasification of wood, straw and RDF pellets, in which the temperature

424   in the hot zone was observed as high as 1084 °C. This information will also be very

425   useful when gas clean-up strategies need to be developed for commercial plants.

426   The results also show that there is a certain amount of O_2 in the gas stream, and

427   this can vary. This clearly depends on the design of the gasifier and operating

428   parameters. For example, the concentration of O_2 in the gas from the RDF pellets was

429   higher, because the pellets were large relative to the i.d. of the tube (higher void fraction

430   and wall channelling). The presence of O_2 in the producer gas streams is also reported in

431   the literature [18].

432   The concentration of the main components in the gas is also compared with

433   earlier experiments [15], using GC (with a TCD) for gas analysis. Although there are

434   slight differences, the comparison in general is very good. Slight differences probably

435   arise from slight variations in operating conditions/composition of pellets used.

436   Thus, it can be concluded that the developed QMS methodology had been

437   upgraded successfully to measure up to 8 species, including the main gases (N_2, H_2,

438   CO_2, CO, CH_4) and other trace gases (O_2, H_2S and COS). It was also shown that an

439   acceptable level of repeatability can be achieved. Also, provided that gas pre-cleaning

440 was effective, the mass spectrometer was stable for months without needing to be re-

441 calibrated.

442

443 ***3.2. Measurements on a pilot-scale plant***

444

445 *3.2.1. The actual waste-wood processed*

446   Samples were taken of the waste-wood that was processed, and this is illustrated

447 in Figure 5. This clearly shows that the sample consists of wood from a variety of

448 different sources (e.g. bark, used wood, painted wood), and that it also contains small

449 quantities of cardboard, brown paper, and even plastics.

450   Samples of the waste-wood and waste-wood-derived char, were analyzed, and

451 their key properties (proximate analysis on a wt.% wet basis), are: moisture = 9.97;

452 volatiles = 70.57; fixed carbon = 19.13; ash = 0.33).

453

454 *3.2.2. The composition of the gas produced from the pilot-plant*

455   **Initiation of reactions in the gasifier:** At the start of each run, reactions in the

456 gasifier are initiated by starting the blower, which draws air through the gasifier. An

457 ignited lance (through which propane flows) is then inserted into the throat of the

458 gasifier, which sustains a flame to initiate reactions in the gasifier. When temperatures

459 start to rise in the throat of the gasifier, and gas temperatures from the gasifier also rise,

460 the supply of propane is turned-off, and the lance is withdrawn.

461   By selecting the following key parameters: (a) temperatures at the top and

462 bottom of the throat (in the gasifier, but measured near the wall of the throat); (b)

463 producer gas flow; (c) producer gas composition (N_2, CO, CO_2, H_2, CH_4 and O_2); and

464 (d) the sulphur species, H_2S and COS, in the gas, the results of one test run are

465 summarized in Figure 6. In general, during this run, temperatures fluctuated at the top

466 and the bottom of the throat, and gas flow varied depending on the choice of operating

467 conditions.

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

469 ▪ As the blower speed was increased, the flow of air into the gasifier increased,

470   and temperatures in the gasifier increased. The flow of gas from the gasifier

471   also increased, as more gas was drawn by the centrifugal blower.

472 ▪ As the unit was started-up, the composition of the gas changed (see Figure 6

473   (b)), providing a very clear indication of the point at which H_2 and CO

474   started to be produced, and O_2 was consumed.

475 ▪ In general, as temperatures in the gasifier increase (above and below the

476   throat), the concentration of CO decreases (from 23 to 16 vol.%), whereas

477   that of H_2 increases (from 10 to 15 vol.%).

478 ▪ At various fixed operating speeds of the blower, the gas composition

479   fluctuates (for example, see Figure 6 (b)), and this most probably arises from

480   the nature of the gasification process (and composition of waste-wood) that

481   is taking place in the throat of the gasifier. Although some gas back-mixing

482   will occur in the pipework and process units before the gas sampling point,

483   the fact that these fluctuations still remain indicates the presence of far

484   bigger variations in gas composition at the base of the actual gasifier.

485   However, considering the nature of the waste-wood feedstock, and the

486   variations in size of the feedstock (Figure 5), this is not surprising. For

487   example, for a fixed operating speed of the blower at 40 %, it is interesting

488	to see that these variations are approximately: $CO = 16.0 (\pm 1.8)$ vol.%, $H_2 =$
489	$11.9 (\pm 2.9)$ vol.%, $CO_2 = 15.8 (\pm 1.4)$ vol.%, $N_2 = 54.1 (\pm 3.3)$ vol.%, $CH_4 =$
490	$1.9 (\pm 0.7)$ vol.%, $O_2 = 0.3 (\pm 0.2)$ vol.%.
491	▪ In Figure 6(c), the changes in H_2S and COS levels are shown. The
492	concentration of H_2S varies from about 200 to 700 ppmv. This is not
493	surprising as this will vary depending on the composition of the waste-wood
494	that is being gasified at a particular moment.
495	▪ The COS concentrations were in the region of 6 to 17 ppmv, which are ~30
496	times smaller than the concentrations of H_2S. This is different from the
497	findings in the laboratory, where the molar ratio of H_2S:COS was around
498	10:1 for all three types of biomass (wood, straw and RDF pellets). This
499	difference might arise from the possibility of COS hydrolysis reactions
500	taking place in the water quench and HESS units with the presence of ash
501	particles as a catalyst - if it occurred, this would lead to the conversion of
502	COS into H_2S.
503	In a recent patent, McDaniel [19] reported a method and apparatus for
504	removing COS from a producer gas stream *via* wet scrubbing in the presence
505	of ash particles. The ash particles contained alumina oxide, which could
506	exhibit catalytic properties for the reaction.

$$H_2O + COS \underset{catalyst}{\leftrightarrow} CO_2 + H_2S \qquad (9)$$

507	
508	McDaniel [19] found that if the producer gas stream from the gasifier went
509	directly into a wet scrubber (without passing through any other particulate
510	removal devices), then up to a 30 % drop in the COS occurred across the

511   scrubber. This depended on the design of the scrubber and its operating

512   conditions, and flooding conditions were preferred.

513

514   **4. Conclusions**

515

516   Using QMS, a quantitative method of on-line gas analysis was developed to

517   measure gas composition when a range of fuels was gasified. The method is informative

518   and the data provides an indication of gas composition, especially on the trace

519   components H_2S and COS for which there is relatively little data. From measurements

520   on a commercial scale down-draft pilot-scale gasifier (with waste wood as fuel),

521   valuable data was obtained during the start-up phase. In addition it was found that the

522   H_2S:COS ratios were higher than obtained in laboratory experiments, and this has

523   important implications for the choice of gas clean-up equipment to remove sulphur

524   compounds.

525

531

532

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580

Figure Captions

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

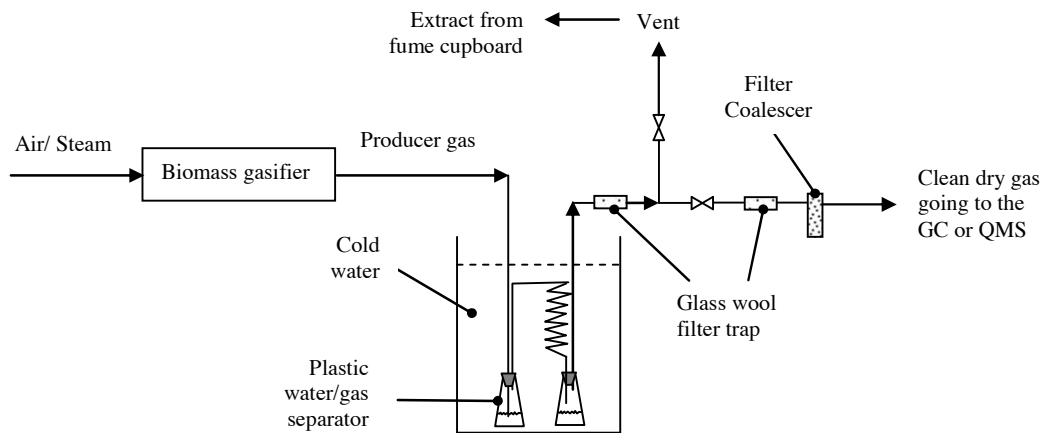**Figurer 2**. Simplified process flow diagram of the commercial pilot-scale plant.

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 H_2S and COS in dry gas.
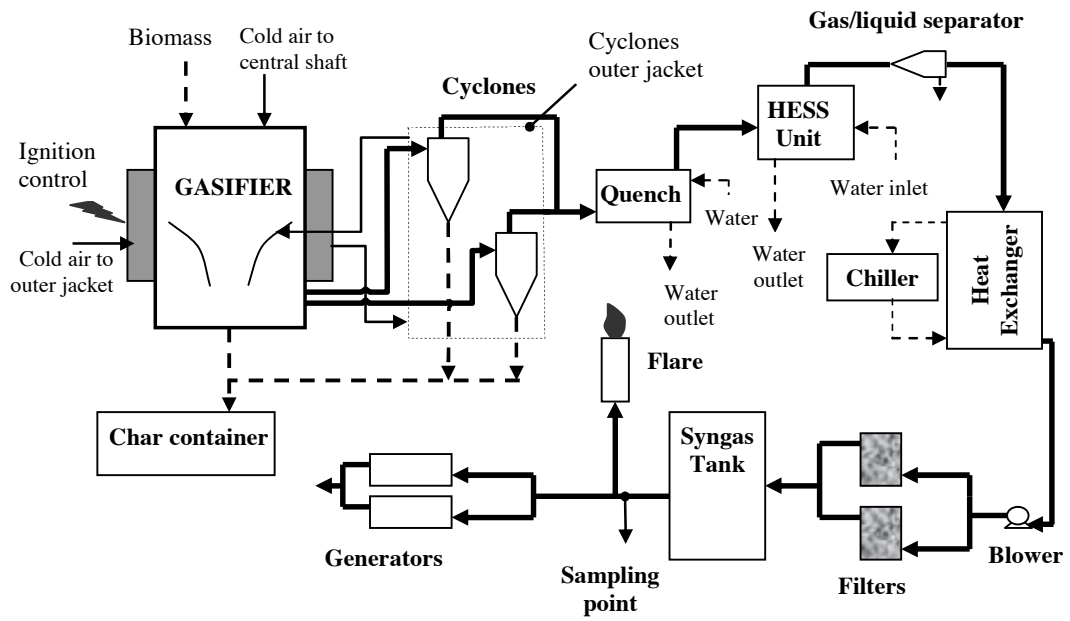
Extract from fume cupboard

Vent

Filter Coalescer

Air/ Steam

Biomass gasifier

Producer gas

Clean dry gas going to the GC or QMS

Cold water

Glass wool filter trap

Plastic water/gas separator

593

594 **Figure 1**

595

Labels in figure: Biomass · Cold air to central shaft · Cyclones · Cyclones outer jacket · Gas/liquid separator · Ignition control · GASIFIER · HESS Unit · Cold air to outer jacket · Quench · Water · Water inlet · Water outlet · Chiller · Heat Exchanger · Water outlet · Char container · Flare · Syngas Tank · Filters · Blower · Generators · Sampling point
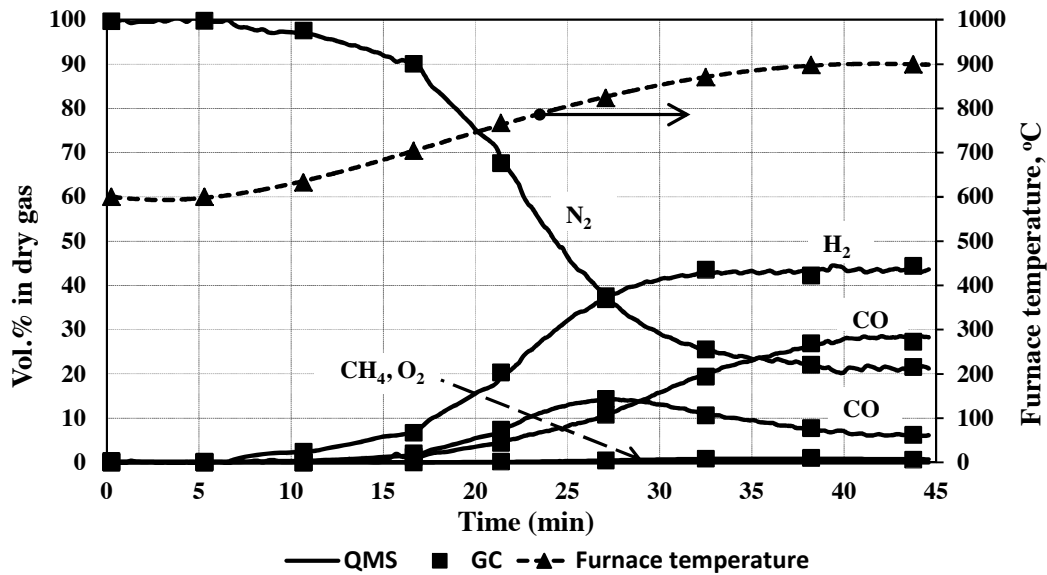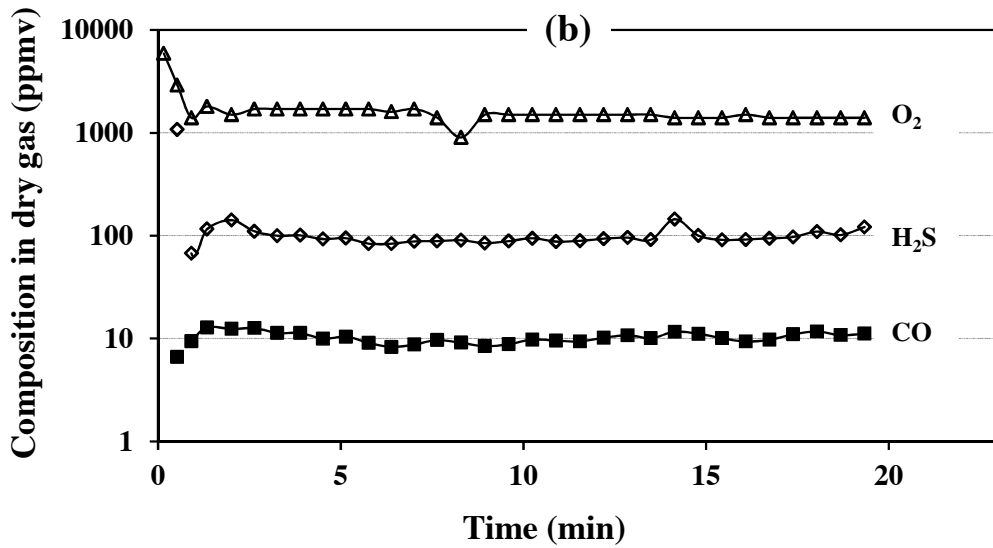
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Figurer 2
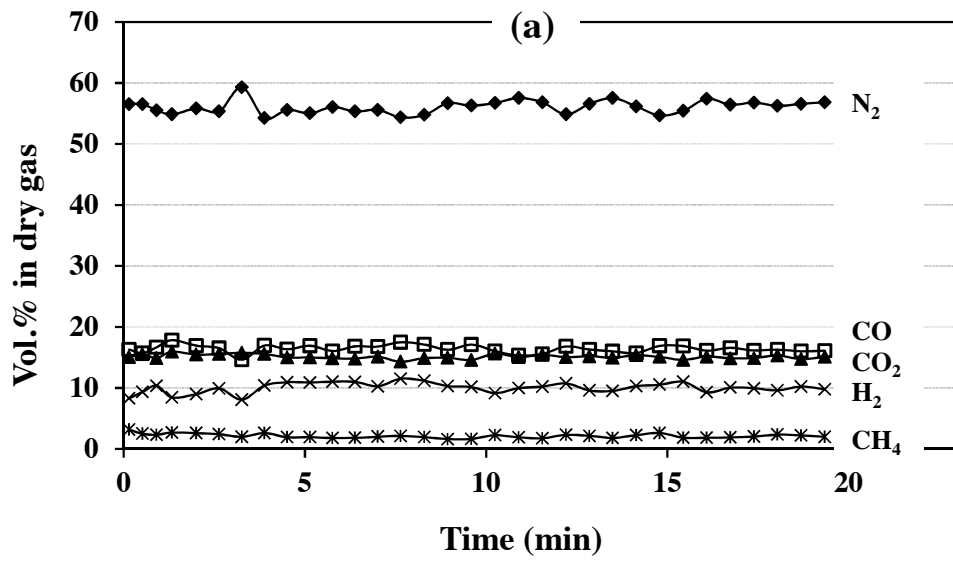
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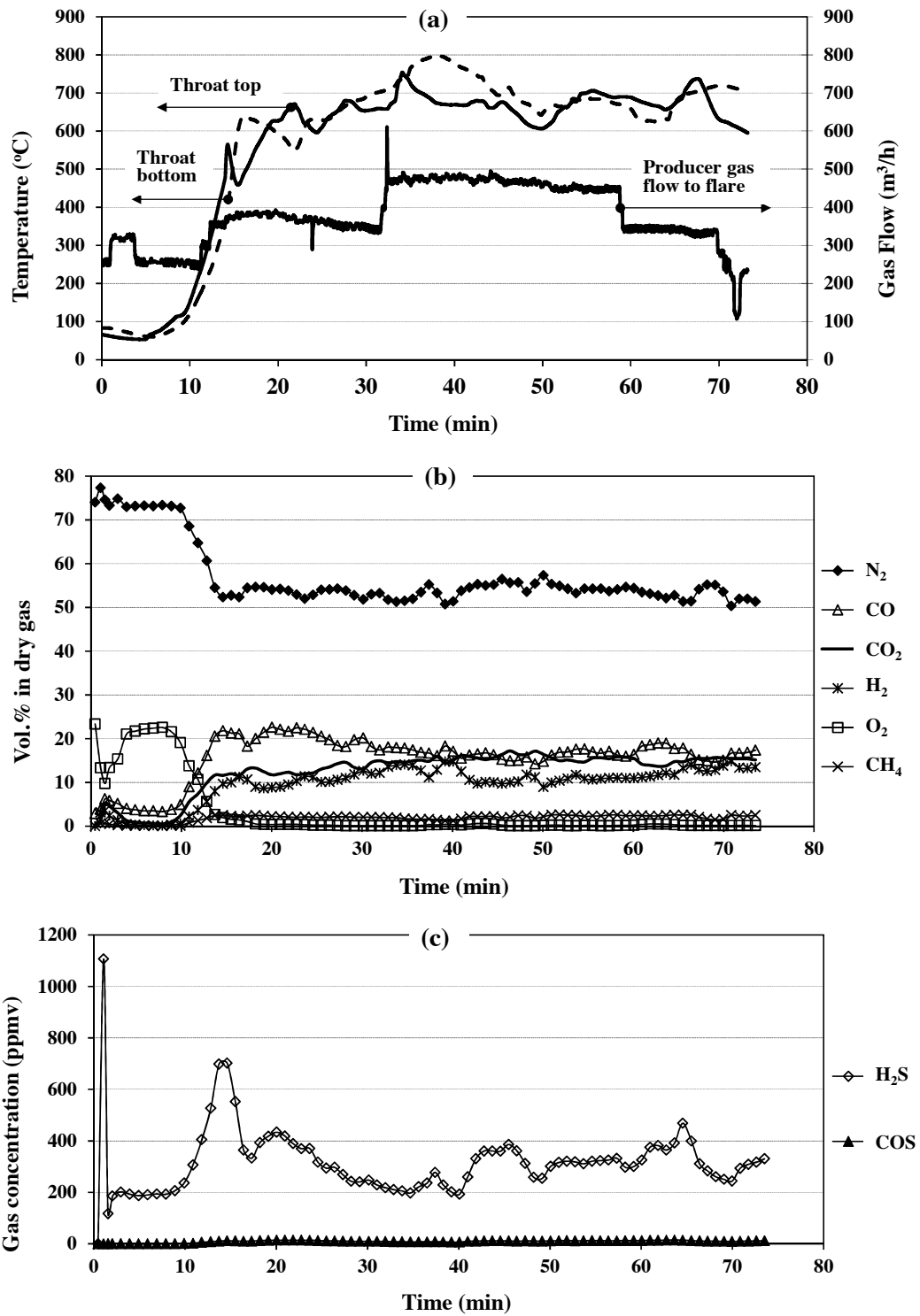
601   **Figure 3**

602

603

Figure 4

605

606

607 **Figure 5**

608

609
610   **Figure 6**
611

612   **Table 1.** Analysis matrix for the gas produced from biomass gasification.

Component	Mass							
	2	14	15	28	32	34	44	60
H_2	x							
CH_4		x	x					
CO_2				x			x	
N_2		x		x				
CO		x		x				
O_2					x	x		
H_2S					x	x		
COS								x

613

614

615 **Table 2**. Properties of the fuels used with proximate analysis.

Properties	Wood Charcoal [1]	Wood pellets [2]	Straw pellets [3]	RDF pellets [4]
Dimensions:				
Diameter, mm	4	5	6	14
Length, mm	4	5 - 17	5 - 17	30 - 80
Moisture (wt.% in wet basic)	4.7	7.4	10.9	7.2
Volatiles (wt.% in wet basic)	11.3	72.6	65.9	39.7
Fixed carbon (wt.% in wet basic)	82.8	18.8	21.7	29.2
Ash (wt.% in wet basic)	1.2	1.3	1.4	23.9

616 [1] Obtained from an actual pilot-plant that has used wood pellets as fuel.

617 [2] Supplied by Treenergy Ltd, Monmouth.

618 [3] Supplied by Agripellets Ltd, Evesham.

619 [4] Supplied by Refgas Ltd, Sandycroft.

620

621 **Table 3**. Comparison of gas compositions produced from different biomass sources.

Component	Previous study (Kolaczkowski *et al.*, 2011b), GC used for analysis		Current study, QMS used for analysis		
	Wood pellets	Straw pellets	Wood pellets	Straw pellets	RDF pellets
CO, vol.%	15.8	14.7	16.44	13.91	10.39
H_2, vol.%	9.5	12.6	10.11	12.83	4.97
CH_4, vol.%	2.0	2.0	2.08	2.11	1.11
CO_2, vol.%	14.5	14.2	15.12	17.17	14.57
N_2, vol.%	58.2	56.5	56.06	53.77	67.90
O_2, ppmv	-	-	1510	1736	10063
H_2S, ppmv	-	-	99	123	286
COS, ppmv	-	-	10	11	28

622

623

624