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Abstract

A new method was developed for collecting, identifying and quantifying contaminants in hot process gas streams using time-weighted average (TWA) passive sampling with retracted solid-phase microextraction (SPME) and gas chromatography. The previous lab scale proof-of-concept with benzene was expanded to include the remaining major tar compounds of interest in syngas: toluene, styrene, indene, and naphthalene. The new method was tested on high T (≥ 100 °C) process gas from a pilot-scale fluidized bed gasifier feeding switchgrass and compared side-by-side with conventional impingers-based method. Fourteen additional compounds were identified, representing 40–60% improvement over the conventional method's detection capacity. Differences between the two methods were 1–20% and as much as 40–100% depending on the sampling location. Compared to the inconsistent conventional method, the SPME-TWA offered a simplified, solvent-free approach capable of drastically reducing sampling and sample preparation time and improving analytical reliability. The improved sensitivity of the new method enabled identification and quantification of VOCs beyond the capability of the conventional approaches, reaching concentrations in the ppb range (low mg/m³). RSDs associated with the TWA-SPME were <10%, with most lab-based trials yielding <2%. Calibrations were performed down to the lowest expected values of tar concentrations in ppb ranges (low mg/N m³, with successful measurement of tar concentrations at times >4000 ppm (up to 10 g/N m³). The new method can be a valid alternative to the conventional method for light tar quantification under certain conditions. The opportunity also exists to exploit TWA-SPME for process gas streams analysis e.g., pyrolysis vapors and combustion exhaust.

Keywords

Analytical method, Syngas, Tar, Biomass, Thermal conversion, Solid phase microextraction

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1 Analysis of trace contaminants in hot gas
2 streams using time-weighted average solid-phase
3 microextraction: pilot-scale validation

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16 hot process gas streams using time-weighted average (TWA) passive sampling with retracted
17 solid-phase microextraction (SPME) and gas chromatography. The previous lab scale proof-of-
18 concept with benzene was expanded to include the remaining major tar compounds of interest in
19 syngas: toluene, styrene, indene, and naphthalene. The new method was tested on high T (≥ 100

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21 by-side with conventional impingers-based method. Fourteen additional compounds were
22 identified, representing 40 to 60% improvement over the conventional method's detection
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27 sensitivity of the new method enabled identification and quantification of VOCs beyond the
28 capability of the conventional approaches, reaching concentrations in the ppb range (low mg/m³).
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32 (up to 10 g/Nm³). The new method can be a valid alternative to the conventional method for
33 light tar quantification under certain conditions. The opportunity also exists to exploit TWA-
34 SPME for process gas streams analysis e.g., pyrolysis vapors and combustion exhaust.

35 **1. Introduction**

36 Thermochemical processing is the application of heat and catalysts to break apart solid
37 carbonaceous materials to produce heat, power, fuels, and chemicals [1]. Many thermochemical
38 processes create a vapor stream as either a direct or intermittent product. These vapor phases
39 must be analyzed to determine product purity and process efficiency. However, many
40 conventional methods of analysis require substantial time and material investment. Developing

41 an alternative means of analysis using fewer steps and less material (i.e. solvents), while
42 maintaining or improving levels of detection and quantification are highly desirable.

43 **1.1 Solid phase microextraction**

44 Solid-phase microextraction (SPME) has been developed to address these issues by combining
45 sampling and sample preparation into a single step [2]. Volatile analytes are collected on a thin
46 sorbent coating the tip of a fused-silica or metal alloy fiber. This fiber can be retracted into
47 protective syringe-like needle housing. The SPME-based samples can then be transferred and
48 introduced into a GC or LC coupled with a FID, MS or other detector [3-5].

49 Unlike conventional SPME in which the fiber is exposed to the sampling environment, time-
50 weighted average (TWA) sampling keeps the fiber coating retracted a known distance (δ) within
51 the needle opening [6]. Analytes diffuse from the needle opening into the retracted fiber and are
52 not subject to variable extraction rates and boundary layer conditions that can be associated with
53 sampling onto exposed SPME fiber. Fick's first law of diffusion is used to describe this
54 extraction and estimate the TWA concentration of analytes using their molecular diffusion
55 coefficient (D_g), the retraction depth (δ), sampling time (t), and the cross-sectional area (A) of the
56 SPME needle. This protects the fiber coating (e.g., from particulates in fast moving gas) while
57 enabling sampling in a variety of conditions by simply varying the (δ) and (t) at first order
58 sampling rates. Properly designed TWA-SPME sampling maintains zero-sink sorption, and
59 minimizes the effects of competitive adsorption onto the SPME coating. Similar to work by
60 Koziel et al. (1999, 2001), a special SPME holder was modified to enable δ of 5 mm, 10 mm, 15
61 mm, and 20 mm (Figure S-1) [7-8].

62 The objective of this work is to test at the pilot scale the proof-of-concept work described in
63 a previous article [9]. Specifically, this paper expands the quantification of a single analyte

64 (benzene) in a high-temperature (115°C) standard gas stream (N₂) to include a matrix of
65 benzene, toluene, styrene, indene, and naphthalene (BTSIN). These analytes represent the
66 primary components of syngas tar existing downstream of a syngas cleaning device [9]. The
67 secondary objective is to demonstrate the newly developed quantification method for BTSIN on
68 a pilot-scale gasification and syngas cleaning process development unit (PDU) feeding 20 kg/h
69 (i.e. ~0.5 metric ton per day) of switchgrass. The new method was compared with
70 conventionally approved quantification methods for syngas tar [10].

71 **1.2 Syngas tar analysis**

72 Syngas exiting a gasification process is contaminated by feedstock impurities as well as an
73 array of larger MW aromatic hydrocarbons developed from the process known as ‘tars’. These
74 tars are typically found in concentrations ranging from 10-100 g/m³ (3-30 ppm_w at standard
75 conditions) or higher depending on the method of gasification [11]. They are a particularly
76 menacing problem given their tendency to condense as temperatures fall below ~400°C,
77 potentially clogging pipes and fouling downstream equipment. Tar reduction also usually
78 becomes more intense and expensive as the removal efficiency is increased, making it beneficial
79 to only reduce tar to levels necessary for downstream applications [11-12].

80 Conventional analysis of syngas tar is performed offline using wet chemical methods [13-
81 15]. They typically involve passage of a slipstream (i.e. a small sample stream diverted
82 isokinetically from the main process stream) into a series of impingers containing solid or liquid-
83 phase sorbents, where the condensable components in the syngas are collected and the non-
84 condensable gases (NCGs) are passed to a gas measurement device such as a micro-gas
85 chromatograph (microGC). The gas stream is ultimately passed through a flow meter to

86 determine the volume of gas analyzed (See Figure 1). The final stage is a multi-step sample
87 preparation process to analyze the collected components via GC-MS or GC-FID for the volatile
88 analytes, and gravimetric analysis for the non-GC detectable components. The concentration is
89 derived by the overall mass of analytes collected divided by the standardized volume of gas
90 analyzed. These methods suffer from long and complicated solvent extraction steps, often
91 requiring days for analysis and suffering from a plethora of potential errors, such as inherently
92 difficult isokinetic sampling trains (see 'Materials'), glassware contamination, insufficient
93 measurement accuracy and precision, and complicated sample matrices and solvent separations.
94 Long sampling times inherent to conventional methods may also confound tar analyses due to
95 difficulty of attaining consistent steady state conditions in the reactor and exhaust gas. It may
96 also be impossible to analyze reactions and gases in a shorter time scale inherent to non-steady
97 state kinetics and research-grade nature of pilot-scale operations. In addition, experimental
98 errors typically result in relative standard deviations ranging from 20 to 50%, but can extend
99 beyond 100% for many kinds of analytes [10, 13].

100 Previous attempts to mitigate the analytical challenges with tars in gas streams have
101 included adoption of a pressure cooker (PC) vessel for collection of non-GC detectable
102 components [16] (primarily heavier tars). This dry-condenser process was compared to the
103 conventional analysis and showed accuracy within 10% of the heavy tar fraction from the
104 conventional approach. However, the light tar fraction, i.e. compounds with vaporization
105 temperatures less than or near 105°C set point of the PC (such as benzene and toluene), could
106 make up a substantial fraction of the syngas tar. Benzene, T, and other light tars may typically
107 represent 10 to 30%, and as much as 50% or more of the overall tar fraction [12, 15, 17-20].
108 These compounds are still a significant threat to end-use applications that require high purity

109 syngas, like catalysis for synthetic fuels [21]. They are also difficult to completely eliminate via
110 typical cleaning methods (e.g. oil washing) without creating waste water issues from the low
111 condensation point [22-23]. Thus, identifying the optimal concentration of these light tar
112 fractions in the syngas is essential to operating a gasification-based synthetic fuels plant at peak
113 operational and financial efficiency.

114 **1.3 Suitability of retracted SPME for fast moving process gas**

115 An accurate, rapid, and dependable light tar quantification method is also needed for
116 research-grade pilot scale reactors and processes where operational steady-state conditions are
117 relatively rare and where the reaction kinetics might be of particular interest. The syngas
118 temperatures found downstream of cleaning equipment and the dry condenser typically fall
119 between 100 to 150°C and provide an ideal side-by-side testing environment for the TWA-
120 SPME method. Woolcock et al (2013) showed that the benefits of the TWA-SPME found in
121 typical ambient air temperature would still apply to contaminant measurement in hot process gas
122 streams in lab conditions [9]. The results indicated potential for the method to effectively
123 determine contaminant concentrations at elevated temperatures. The benefits might potentially
124 include lower detection limits than conventional methods, shorter sample preparation and
125 analysis time, and more accurate measurements.

126 The retracted TWA-SPME approach also offers several advantages compared to
127 conventional extractions using an exposed SPME fiber, which have only been attempted for
128 laboratory scale proof-of-concept tar measurement [24]. These advantages include: controlling
129 sample extraction conditions to enable a much broader range of analyte concentrations, broader
130 range of sampling times that could be adjusted to expected ranges of concentrations, and
131 eliminating the need to consider changing boundary layer conditions, fouling and mechanical

132 stress on the exposed fiber in a rapidly moving process gas stream [25]. Sorptive capacity of
133 retracted SPME is still limited. First order extraction conditions need to be maintained so that a
134 SPME fiber coating is not saturated [9]. This means, in extreme conditions, using shorter
135 sampling time in conditions characterized by high concentrations or using longer sampling times
136 in conditions characterized by low concentrations.

137 This work aimed to test the TWA-SPME method in a pilot-scale gasifier for quantification
138 of BTSI and to compare results with the impinger based dry-condenser gas sampling technique.
139 The TWA-SPME approach can close the gap on analytical methods capable of avoiding
140 problematic condenser trains associated with conventional method and providing rapid feedback
141 on process conditions. Numerous additional analytically challenging process gas environments
142 can benefit from successful application of this technique, e.g. combustion exhaust and pyrolysis
143 vapor streams, and may also enable monitoring of reaction kinetics in much shorter timescales.

144 **1.4 Theory of TWA-SPME sampling**

145 TWA-SPME with retracted fiber operates on the premise derived from Fick's first law that
146 the amount of analyte extracted is proportional to the integral of the concentration over a
147 sampling time (t):

148 Equation 1:
149
$$n = D_g \frac{A}{\delta} \int C_g(t) dt$$

150 where:

151 $A = \text{opening area of SPME needle } [L^2, \text{ cm}^2]$

152 $t = \text{sampling time } [t, \text{ s}]$

153 $D_g = \text{molecular diffusion coefficient for the sample in the gas stream } [L^2/t, \text{ cm}^2/\text{s}]$

154 $C_g = \text{instantaneous concentration in the gas stream } [M/L^3, \text{ g/cm}^3 \rightarrow \text{g/m}^3]$

155 $n = \text{mass extracted on SPME (determined by analytical equipment)} [M, \text{g}]$

156 $\delta = \text{boundary layer (length of diff. path, retraction of SPME fiber inside the needle)} [L, \text{cm}]$

157 In practice, this can be reduced to the following relationship as long as a few essential sampling
158 requirements are met, which are detailed thoroughly in [2, 9].

159 Equation 2:
160
$$\bar{C}_g(t) = \frac{n(t)\delta}{D_g At}$$

161 The work aimed to expand the original lab scale proof of concept (developed for one model
162 compound only) to the mixture of all main tars expected in the actual syngas process stream
163 located downstream of the dry-condenser and the start of the gas cleaning system (Figure 1) [9].

164 **2. Materials and methods**

165 **2.1 Chemicals**

166 Benzene, T (Sigma-Aldrich CHROMASOLV®Plus, for HPLC $\geq 99.9\%$), S (Sigma-Aldrich
167 ReagentPlus® $\geq 99\%$), I and N (Sigma-Aldrich $\geq 99\%$) were used to generate a model tar stream
168 within an ultra-high-purity N₂ gas stream (99.995%). Impingers were filled with either DI water
169 (18.2 MΩ-cm) or 2-Propanol (Sigma-Aldrich CHROMASOLV®Plus, for HPLC $\geq 99.9\%$). 2-
170 Propanol and dry ice were used in in the impinger ice bath during later experiments to ensure
171 analyte capture by reducing temperature. Permanent gases calibrated and analyzed in the Agilent
172 microGC included CO₂ (6 - 45%), CO (1 - 45%), H₂ (2 - 22.5%), CH₄ (2 - 6%), N₂ (0 - 66.5%),
173 ethane (0.25 - 1%), ethylene (0.75 - 5%), acetylene (0.15 - 1%), and O₂ (0.2 - 1%). All work
174 with chemicals was performed following lab safety protocols, using vented fume hoods and
175 approved personal protection gear.

176 177 **2.2. Materials.**

178 A manual SPME device was equipped with a Carboxen/Polydimethylsilosane (85 μm
179 Car/PDMS - Supelco) fiber. This fiber was chosen based on performance criteria for testing
180 syngas streams (see [9]). The high sorptive capacity of Carboxen was an additional benefit for
181 TWA sampling of high analyte concentrations potentially found in process gas [26].

182 This work was performed in two phases requiring different experimental setups. Figure 1 in
183 [9] shows the laboratory setup used for experimental validation of D_g values for target light tars.
184 This original setup was modified with extensive heat tracing upstream of the oven to preheat the
185 gas flowing through the glass bulb to 80°C. Initial testing showed this was necessary to maintain
186 a homogenous concentration of the synthetic BTSI tar mixture in the gas stream. The
187 conventional tar sampling system was significantly more complex. Glassware used on the pilot-
188 scale testing included two sets of impinger trains (seven total impingers) for sampling multiple
189 locations in the syngas process lines simultaneously.

190 Syngas exits the gasifier and enters the cleaning system shown in Figure 2 (detailed in [27]).
191 The hot syngas is maintained at 400°C or higher using high performance cable heaters (Tempco)
192 on the process piping. Cyclones remove most of the particulate matter, and the remaining char is
193 quantified using the thimble filter located in the isokinetic sampling line (A). This heat traced
194 sampling line enters a PC downstream of the thimble filter, where syngas passes through a 3 m
195 polymer tube (Santoprene or Trelleborg) submerged in water heated to 105°C.

196 This environment rapidly transfers heat from the syngas to condense the heavier molecular
197 weight tars from the vapor stream. Syngas exiting the PC enters another heat traced ~9.5 mm
198 (3/8") sampling line equipped with a stainless steel tee, which serves as an SPME sampling port

199 by placing an 11 mm septum into the top nozzle of the tee. Four impingers filled ~1/3 full with
200 200 mL of 2-propanol follow this ~ 0.5 m sampling line.

201

202 **3. Results & Discussion**

203 Validating the TWA-SPME concept for analysis of syngas tar at elevated T required two
204 separate experimental segments: (1) verifying D_g for the primary analytes of interest at lab-scale,
205 and (2) comparing the retracted SPME gas sampling technique to conventional tar measurement
206 techniques on a pilot-scale gasifier and gas cleaning system.

207 **3.1 Phase I: Lab-scale experiments to estimate D_g for target analytes at elevated T**

208 D_g is the only parameter on the right side of Equation 2 that is not provided by analytical
209 equipment or known a priori. Proof-of-concept work performed in [9] on a standard benzene/N₂
210 hot gas stream indicated the possibility of a secondary boundary layer existing at the face of the
211 SPME fiber's Car/PDMS extraction phase [6-7]. This boundary layer has the potential to
212 significantly affect D_g under certain conditions. A series of tests was performed as described in
213 [9] using a mixture of BTSIN compounds (the main tars remaining in cleaned syngas) to
214 determine this phenomenon's impact on a sample matrix that contains multiple analytes. An
215 equal weight mixture of these five compounds was created and used in the injection syringe of
216 the sampling system depicted in Figure 1 of [9]. Hot gas mixture stream was maintained at
217 temperatures simulating ranges of process equipment parameters and gas sampling ports of the
218 pilot-scale reactor (i.e., between 105 to 130 °C). Despite several attempts to address repeated
219 difficulties with N (described in Supplementary Information and [27]), this tar vapor mixture was
220 reduced to BTSI to substantially improve precision of the small laboratory system.

221 BTSI adsorption onto the fiber was highly linear with small sample variations as a result of
222 retraction depth (Figures 3, S-2, and S-3), despite the secondary boundary layer effect that was
223 shown in the first paper [9] and described in depth in the Supplementary Information and [27].
224 RSDs for B were all < 5% with an average of 3.0%, and remaining RSD averages were 2%,
225 3.5%, and 5% for T, S, and I, respectively). These results warranted continuing trials of the
226 retracted SPME method in real-world pilot-scale testing and comparison of measured tar
227 concentrations with conventional tar analysis technique.

228 **3.2 Phase II: Method comparison between retracted TWA-SPME and conventional** 229 **impingers**

230 Field testing of the TWA-SPME approach was performed on a fluidized bed gasification
231 and gas cleaning pilot-plant located at Iowa State University's BioCentury Research Farm
232 (BCRF) [28]. Due to the scale of the system and the expense of pilot operation, the comparison
233 between the conventional analytical approach and the TWA-SPME approach was performed
234 jointly with other experimental research, which made it difficult to reach acceptable sampling
235 conditions during more than a few tests over a 6 month period (see SI for more information)
236 [29].

237 Syngas samples were taken at two different locations during each test (Figures 1 and 2).
238 The TWA-SPME sampling location for B was located immediately downstream of the tar
239 scrubber and ~1.5 m upstream from the impinger sampling point at a process temperature of
240 between 110-125°C depending on the test. Typical sampling time was 5 min with retraction
241 depth of 5 mm. See SI for further details on sampling design. An inherent challenge to side-by-
242 side comparisons of sampling methods is the difference in sampling time scales: the
243 conventional methods require much longer sampling time and long sampling preparation.

244 Raw results from the TWA-SPME analysis required multiple adjustments to account for
245 temperature, pressure, and sampling variables according to Eq. 1 and 2. Initial D_g values were
246 based on lab experiments (discussed in *Phase I* results) conducted at 115°C and 101 kPa using a
247 gas stream composed only of N₂ and the analytes of interest. However, the samples taken from
248 the PDU were at different conditions which varied slightly with each testing environment.
249 Accounting for these conditions was done using a combination of approaches. The T and p were
250 easily accounted for by utilizing the three theoretical equations previously discussed (Wilke-Lee,
251 FSG, and Huang et. al) [9, 30-32]. The baseline analyte adsorption was also accounted for by
252 alternating samples in the PDU with SPME assemblies that were missing a Car/PDMS coating.
253 The corresponding mass of analytes that adsorbed onto the outer and inner surface of SPME
254 needle was then subtracted from the amount collected on the SPME fiber coating.

255 The effects of gas mixture composition on D_g required a more thorough investigation (Table
256 1). Most D_g are calculated only in a bimolecular mixture, and very few theoretical equations are
257 available to accurately adjust for multiple gas phase species [33]. Adjustments were made using
258 the technique described in [33], in which the FSG equation is calculated for each bimolecular
259 species and adjusted for the total depending on C_g of each major species. The microGC used at
260 the end of the impinger trains during all PDU research was used to estimate the average gas
261 composition during each test. This composition was normalized to the six major gas species (N₂,
262 CO₂, CO, H₂, CH₄, and H₂O) which accounted for 95% or more of the hot stream gas phase.
263 Unfortunately H₂O has at times been shown to affect the Car/PDMS adsorption process as well,
264 by taking up active sites in the Carboxen [34-36]. However, its effect is varied and may
265 sometimes be insignificant due to molecular analyte size and hydrophobicity [37-38]. Due to
266 this uncertainty, mathematical adjustments were not made for the effect of H₂O on the SPME

267 adsorption process, and this is cited as a potential source of error to be considered for further
268 analysis in future experiments.

269 Initial results from the impinger analyses also required substantial revision. The 2-propanol
270 impingers were chilled to -70°C , which caused significant amounts of NCG to dissolve and
271 collect into the impingers (e.g., Figure S-6). This dissolved gas was subsequently not accounted
272 for in the wet-test meter results. Immediately after sampling, the impinger samples were
273 weighed and then allowed to reach ambient conditions to vent the dissolved gases. This was
274 done to prevent violent release of the samples once bottled and readied for transport. Once the
275 dissolved NCGs were released, the samples were weighed again and the difference was
276 accounted for in the wet-test meter as CO_2 . The complicated matrix of 2-propanol, H_2O from the
277 steam/ O_2 gasification process, and similarly low boiling point analytes of interest also created
278 significant problems in GC-FID analysis. A separate analysis was performed by an independent
279 lab (Minnesota Valley Testing Laboratory – MVTL) to verify the in-house GC-FID results, and
280 showed potential matrix effects were possible with the varied concentration of H_2O in the
281 impinger samples. Despite matching readings between in-house and third party analyses, all
282 subsequent tests were also sent to MVTL to consistently verify analyte concentrations prior to
283 final comparison of the conventional and TWA-SPME analytical methods.

284 Final results from the three successful comparison trials (summarized in Table 2) indicate a
285 general level of success in terms of a comparable light syngas tars C_g . Differences between runs
286 are expected given the non-steady state and varying operating conditions. The tar values in
287 Table 3 correspond as expected with the equivalence ratios [39]: lower equivalence ratio yields
288 more heavy tars [12, 40]. The overall trend in light tar is difficult to discern from the two
289 different methods of measurement, but may indicate according to data from location A (prior to

290 the cleanup stage in the tar scrubber) a tendency of heavier tars to crack at higher T and yield
291 larger quantities of lighter tars (Runs 1 and 3 compared to 2). This phenomenon directly
292 corresponds to conventional knowledge of tar formation and methods of destruction: multi-ring
293 tars may crack above 850°C and single ring tars remain intact until temperatures exceed 1000°C
294 [21, 41]. More fundamental kinetic studies in the laboratory may further confirm this
295 phenomenon.

296 The tar samples taken with the TWA-SPME method at sampling point A were always
297 less than that of the impinger approach, **but still aligned closely with literature values**. Typical
298 literature values for benzene for instance may range from a few g/m^3 to up to 45% by weight of
299 the total tar volume quantified [12, 15, 18-20].

300 Measured C_g from the conventional and TWA-SPME analyses were substantially more
301 similar at sampling location B, with relative differences typically $< 10\%$. This is beneficial when
302 considering deployment in commercial gasification systems since trace tars are of greatest
303 concern downstream of the cleaning processes. The inability of the impingers to detect the S
304 while it was detected in the TWA-SPME-based analysis also shows the significance of the new
305 method's ability to quantify otherwise undetected compounds.

306 A variety of potential issues could be responsible for differences occurring between
307 samples taken at different locations. The different methods of removal for heavy tar may play a
308 primary role. The PC method utilizes indirect contact heat exchange limited by convection to
309 reduce the syngas temperature. Tar is collected via condensation and deposition on the surface
310 of the tubing and small canister of glass wool inside the PC. The tar scrubber utilizes a much
311 more efficient direct-contact heat exchange process with cooler heat transfer oil. In addition to
312 rapid condensation, it also applies a counter-flowing oil spray to achieve a very efficient removal

313 of aerosol vapors. Compounds such as *N* should condense in the PC and be included in the
314 heavy tar fraction of Table 2 as its dew point is > the 105°C set point. However, as seen by the
315 coloration in Figure S-6 and noted in Table S-3, compounds such as *N* are less efficiently
316 removed with the PC and may also deposit in the impinger train, yielding much higher tar
317 concentrations when compared against the post cleanup location. Lower tar C_g at location B
318 compared to location A may also be due to the much lower T attained at times in the syngas
319 cleaning unit. Due to the short sampling times allowed by the gasifier, there was insufficient
320 time to reach a steady operating state in the oil scrubber. Typical operating conditions were
321 ~115°C, but periods of operation occurred < 80°C. This causes greater tar condensation and
322 potentially absorption into H₂O condensed from the high concentration of steam in the syngas.
323 Some discrepancy between the two sampling methods at location A could also be explained by
324 the inconsistent vacuum pump and thimble filter p disturbances located on the sampling line.
325 These devices made it difficult to accurately predict the p at the SPME sampling point for proper
326 adjustment of the D_g values during analysis.

327 The high inherent variability in the conventional method may also be a source of
328 discrepancy between the two techniques. According to Neeft et al. (1999) and Bahng et al.
329 (2009), the overall variability in the conventional impinger approach is typically 20-40% for
330 many analytes [12, 14]. In addition, the high quantity of H₂O vapor in the syngas from the
331 steam/O₂ gasification process may cause analytes to preferentially separate in the impinger
332 containers and vials while awaiting analysis. GC-FID trials were conducted to test this
333 hypothesis using a calibration standard of the analytes of interest that was spiked with 20%
334 water. Results reflected the hydrophobicity of the analytes with a minimal but noteworthy 2%,

335 5%, 10%, 14% and 17% increase in response for B, T, S, I, and N respectively. The sampling at
336 location A also requires isokinetic sampling to maintain proper collection of heavy tars. Data
337 analysis later indicated that isokinetic rates were missed by up to 30% on occasion during the 6
338 months of trials, and was attributed to random error with no discernible association to the wet-
339 test and rotameter discrepancies. This would also affect the collection of heavy tars giving a false
340 indication of the light/heavy tar ratio.

341 TWA-SPME sampling configurations during gasification were also altered from the lab-
342 scale analysis due to higher than expected tar C_g . Despite the higher concentrations, the
343 adjustments in sampling depth and time of extraction were able to keep analyte quantity on the
344 fiber for all tests within an order of magnitude of the calibrations performed in the lab. This
345 should be noted however as a potential source of error, resulting in a possible under-estimate of
346 tar via the TWA-SPME technique at location A. However, because there was zero carry over in
347 the fiber after analysis and the samples stayed below the 5-10% saturation levels required by the
348 zero-sink hypothesis (the high capacity of Carboxen is orders of magnitude higher yet), it is
349 unlikely that the under-estimate was off by more than a few percent [42]. Evidence for this is
350 seen by the linear response in the higher C_g lab experiments of previous work [9].

351 Total light tar concentrations in Table 3 were estimated from the relative abundance of
352 quantified compounds in the chromatograms. The light tars were calculated as BTSI and then a
353 correction was applied to account for the missing mass percentage in the chromatograms that
354 was not due to those 4 calibrated compounds. A second calculation was performed by
355 discounting all compounds smaller than B (termed: without light ends, or WoLE). This
356 adjustment was made to reflect the inability to detect some analytes in the impingers due to the

357 co-elution in the GC-FID with the solvent. It also more accurately reflects the true definition of
358 'tar', which is typically considered as benzene compounds and larger [11].

359 The discrepancies between samples become exacerbated when comparing total tars using
360 only 4 calibrated analytes, but the table is useful for comparing typical light tar values to those
361 reported in aforementioned literature. As many as 14 additional compounds were identified and
362 quantified with the retracted SPME method (Figure S-8, Table S-4). A majority of the
363 compounds identified are single ring aromatics, as shown in Table S-4. For each test, three
364 extractions and three baselines were taken successively for TWA-SPME in the PDU trials, which
365 allowed for an average, a standard deviation and RSD calculation. Unfortunately the impinger-
366 based analysis was not amenable to taking several different samples from each location given the
367 longer time required per sample. RSD information for the impingers is limited to the 2% or less
368 RSD values attained during direct injection of liquid samples into the GC-FID for analysis.

369 Large RSD values for the SPME samples in the pilot scale trials may reflect the drastic
370 changes that can occur in the sampling train at a shorter time-scale. Samples for the
371 conventional method were collected over a 50 min period on average, whereas TWA-SPME
372 samples were collected over several different 5 min sampling periods. Inconsistent pump
373 performance, changes in sampling line pressure drop, or changes in gas composition are captured
374 by the TWA-SPME method but are averaged out in the conventional analysis. Unlike
375 commercial-scale operations, the gasification pilot plant is only operated when research tests are
376 conducted. The large thermal mass of the gasifier and cleaning equipment make it difficult to
377 attain true steady state conditions in all aspects prior to sampling. Commercial operations will
378 still suffer from inconsistencies in sampling lines, but the TWA-SPME method can extract
379 samples directly from the process stream eliminating this unwanted variation while providing the

380 possibility of capturing the dynamic nature of the system if desired. Finally, the TWA-SPME-
381 based measured C_g was available within hours, whereas the conventional analysis required 1-3
382 days for estimating C_g , further increasing the potential for data corruption. Summary of possible
383 sources of errors in both methods is presented in Table S-5.

384

385 **4. Conclusions**

386 The TWA-SPME concept for analysis of syngas tar at elevated T is a valuable technique
387 compared to the conventional solvent-based impinger approach. The presence of a secondary
388 boundary layer at the SPME surface (unrelated to δ) as shown in original proof-of-concept
389 testing was confirmed in multicomponent testing, but was found again to have minimal effect on
390 the usefulness of the method.⁹ Comparison of the new and conventional method was performed
391 using a pilot-scale gasification and gas cleaning system. The complicated nature of the
392 conventional method made it difficult to collect reliable samples during every test. However, the
393 few sample collections that were successful showed the new method was capable of staying
394 within 20% of the conventional method for light tars downstream of a syngas cleaning unit.
395 Some of the difficulties that were experienced during conventional sampling included: deviation
396 of isokinetic sampling rates from their intended set points; T and p fluctuations in the PC and
397 sample lines making steady-state sampling and C_g measurements difficult; and complicated
398 sample matrices requiring repeated wet chemical analyses for verification of analyte
399 concentrations. The TWA-SPME samples also required multiple corrections for temperature,
400 pressure, and gas-phase composition, but still provided useful data for comparison. In addition,
401 the new method was capable of showing the dynamic nature of the syngas, and was able to
402 identify and quantify more analytes than that of the conventional solvent-based approach.

403 Future TWA-SPME comparisons to other conventional approaches that do not suffer from
404 the same difficulties as the impingers would be highly useful to confirm and more accurately test
405 this method. Solid phase extraction (SPE) and multibed solid phase adsorbent (SPA) are a
406 potential candidate given its resemblance to SPME, despite the need for solvent-based lab work
407 [43-45]. Expanding the laboratory testing environment to include multiple other temperatures
408 may help develop an improved model for compounding effects of different T , p , and analytes
409 (C/H numbers or MW correlation).

410 A major disadvantage of the method is the 300°C or lower T limit on the SPME fibers,
411 which currently restricts sampling to only GC-detectable tars. An internally-cooled SPME
412 device that would enable sample extraction from higher T environments may overcome this
413 limitation. Future work may also consider testing the effects of thermophoresis on this device
414 and its potential for sampling all high T contaminants directly from process gas streams such as
415 pyrolysis or combustion processes. This technique would potentially avoid the time consuming
416 and complicated conventional sampling trains.

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420 **References**

- 421 [1] R. C. Brown, *Thermochemical Processing of Biomass - Conversion into Fuels, Chemicals*
422 *and Power*. Wiley & Sons: ed.; 2011.
423 [2] J. Pawliszyn, *Handbook of solid phase microextraction*. Chemical Industry Press: Beijing,
424 ed.; 2009; p 410 p.
425 [3] G. Vas; Vékey, K., *J Mass Spec* 39 (2004) 3.
426 [4] G. Ouyang; Pawliszyn, J., *Anal Chim Acta* 627 (2008) 2.

427 [5] G. Ouyang; Pawliszyn, J., *Trends Anal Chem* 25 (2006) 7.

428 [6] P. A. Martos; Pawliszyn, J., *Anal Chem* 71 (1999) 8.

429 [7] J. Koziel; Jia, M.; Khaled, A.; Noah, J.; Pawliszyn, J., *Anal Chim Acta* 400 (1999) 1-3.

430 [8] J. A. Koziel; Pawliszyn, J., *J Air Waste Manag Assoc* 51 (2001) 2.

431 [9] P. J. Woolcock; Koziel, J. A.; Cai, L.; Johnston, P. A.; Brown, R. C., *J Chrom A* 1281 (2013).

432 [10] K. Maniatis; Beenackers, A. A. C. M., *Biomass Bioenerg* 18 (2000) 1.

433 [11] T. A. Milne; Evans, R. J.; Abatzoglou, N. *Biomass Gasifier "Tars": Their Nature Formation*

434 *and Conversion*; National Renewable Energy Laboratory: Golden, CO, 1998.

435 [12] J. P. A. Neeft; Knoef, H. A. M.; Onaji, P.; Nederland, S. E. C.; Group, B. B. T., *Behaviour*

436 *of Tar in Biomass Gasification Systems: Tar Related Problems and Their Solutions*. Novem: ed.;

437 1999.

438 [13] W. L. v. d. Kamp; Wild, P. J. d.; Knoef, H. A. M.; Neeft, J. P. A.; Kiel, J. H. A. *Tar*

439 *measurement in biomass gasification, standardisation and supporting R&D*; Netherlands, 2006;

440 p 168.

441 [14] M.-K. Bahng; Mukarakate, C.; Robichaud, D. J.; Nimlos, M. R., *Anal Chim Acta* 651 (2009)

442 2.

443 [15] P. Stahlberg; Lappi, M.; Kurkela, E.; Simell, P.; Oesch, P.; Nieminen, M. *Sampling of*

444 *contaminants from product gases of biomass gasifiers*; VTT Energy: Technical research center

445 of Finland, 1998; p 49.

446 [16] M. Xu; Brown, R. C.; Norton, G.; Smeenk, J., *Energy Fuels* 19 (2005) 6.

447 [17] A. V. Bridgwater, *Progress in thermochemical biomass conversion*. Oxford: Blackwell

448 Science: ed.; 2001.

449 [18] E. Kurkela; Stahlberg, P., *Fuel Proc Technol* 31 (1992) 1.

450 [19] E. Kurkela; Stahlberg, P.; Laatikainen, J., *VTT Publications* 871 (1993) 161.

451 [20] K. Stahl; Neergaard, M.; Nieminen, J., Varnamo Demonstration Programme - Final Report.

452 In *1st World Conference on biomass for Energy and Industry*, James & James (Science

453 Publishers) Ltd: Sevilla, Spain, 2000; pp 730-736.

454 [21] P. J. Woolcock; Brown, R. C., *Biomass & Bioener* 52 (2013).

455 [22] R. W. R. Zwart; Drift, A. V. d.; Bos, A.; Visser, H. J. M.; Cieplik, M. K.; Könemann, H. W.

456 J., *Environ Prog Sustainable Energy* 28 (2009) 3.

457 [23] P. C. A. Bergman, Sander V.B. van Paasen, Harold Boerrigter, The novel "OLGA"

458 technology for complete tar removal from biomass producer gas. In *Pyrolysis and Gasification of*

459 *Biomass and Waste, Expert Meeting*, Strasbourg, France, 2002.

460 [24] M. Ahmadi; Svensson, E.; Engvall, K., 27 (2013).

461 [25] M. Hlina; Hrabovsky, M.; Kavka, T.; Konrad, M. In *Tar measurement in synthetic gas*

462 *produced by plasma gasification by solid phase microextraction (SPME)*, ISPC Conference.

463 [26] Y. Chen; Pawliszyn, J., *Anal Chem* 75 (2003) 9.

464 [27] P. Woolcock. Development and application of a rapid sampling technique for identification

465 and quantification of compounds in high temperature process gas streams produced from

466 biomass gasification and pyrolysis" (2013). Graduate Theses and Dissertations. Paper 13241.

467 <http://lib.dr.iastate.edu/etd/13241>.

468 [28] Gasification and Syngas Cleaning Process Development Unit.

469 <http://www.biocenturyresearchfarm.iastate.edu/capabilities/thermochemical/gasification.html>

470 (accessed Feb 20, 2015).

471 [29] K. Broer; Woolcock, P.; Johnston, P.; Brown, R., *Energ Sci & Eng* (2013 (submitted)).

- 472 [30] W. J. Lyman; Reehl, W. F.; Rosenblatt, D. H., *Handbook of chemical property estimation*
473 *methods: environmental behavior of organic compounds*. American Chemical Society:
474 Washington, D.C., ed.; 1990.
- 475 [31] G. Karaiskakis; Gavril, D., *J Chromatogr A* 1037 (2004) 1-2.
- 476 [32] R. C. Reid; Prausnitz, J. M.; Poling, B. E., *The properties of gases and liquids*. ed.; 1977.
- 477 [33] A. Leahy-Dios; Firoozabadi, A., *AIChE J.* 53 (2007) 11.
- 478 [34] V. Larroque; Desauziers, V.; Mocho, P., *Anal Bioanal Chem* 386 (2006) 5.
- 479 [35] V. Larroque; Desauziers, V.; Mocho, P., *J Environ Monitoring* 8 (2006) 1.
- 480 [36] J. Koziel; Jia, M.; Pawliszyn, J., *Anal Chem* 72 (2000) 21.
- 481 [37] C.-Y. Chen; Hsieh, C.; Lin, J.-M., *J. Chrom A* 1137 (2006) 2.
- 482 [38] S.-W. Tsai; Wu, K.-K., *J Chrom A* 991 (2003) 1.
- 483 [39] R. C. Brown, *Biorenewable resources: engineering new products from agriculture*. Iowa
484 State Press: Ames, Iowa, 1st ed.; 2003; p xii, 286 p.
- 485 [40] J. J. Hernández; Ballesteros, R.; Aranda, G., 50 (2013) 0.
- 486 [41] J. Kiel; Paasen, S. V. B. v.; Neeft, J.; Devi, L.; Ptasinski, K. J.; Janssen, F. J. J. G.; Meijer,
487 R.; Berends, R. H.; Temmink, H. M. G.; Brem, G.; Padban, N.; Bramer, E. A. *Primary measures*
488 *to reduce tar formation in fluidised-bed biomass gasifiers*; Energy Research Center of the
489 Netherlands (ECN): 2004; p 108.
- 490 [42] Y. Chen. New calibration methods for solid phase microextraction for on-site analysis.
491 University of Waterloo, Ontario, Canada, 2004.
- 492 [43] S. Osipovs, *Anal Bioanal Chem* 391 (2008) 4.
- 493 [44] D. Bull. Performance improvements to a fast internally circulating fluidized bed (FICFB)
494 biomass gasifier for combined heat and power plants. University of Canterbury, Canterbury,
495 New Zealand, 2008.
- 496 [45] A. Dufour; Girods, P.; Masson, E.; Normand, S.; Rogaume, Y.; Zoulalian, A., 1164 (2007)
497 1-2.

498 **Figure Captions**

499 **Figure 1:** Schematic of the conventional tar sampling and collection system (all process piping
500 and sampling lines are heat traced to reduce probability of tar condensation): (1) syngas process
501 piping; (2) isokinetic sampling probe and particulate thimble filter; (3) pressure cooker (PC)
502 heavy tar sampling system (refer to [16]); (4) TWA-SPME sampling port; (5) 4 impingers each
503 with 200 mL 2-propanol immersed in a dry ice 2-propanol bath; (6) vacuum pump; (7)
504 rotameter; (8) micro gas-chromatograph (mGC); (9) wet-test meter; (10) SPME sampling port
505 sample; (11) 3 impingers each with 200 mL 2-propanol immersed in a dry ice 2-propanol bath;
506 (12) rotameter; (13) mGC; (14) wet-test meter.

507

508 **Figure 2:** Schematic of the pilot-scale gasifier and gas cleaning system at ISU's BioCentury
509 Research Farm (gas samples taken immediately prior to and downstream of the tar/char scrubber,
510 with *A* taken at ~135°C and *B* at ~110°C)

511 **Figure 3:** Mass of the target analytes adsorbed on SPME fiber vs. changes in sampling time and
512 SPME fiber retraction depth (see Figures S-2 and S-3 for benzene and toluene extractions
513 individually)