Comparison of a Solvent-Free Tar Quantification Method to the International Energy Agency's Tar Measurement Protocol

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This paper presents a new method for measuring tar concentration in biomass-derived producer gas streams. This solvent-free method is much simpler than the evaporative method of the International Energy Agency (IEA) tar protocol. In tests on producer gas from a fluidized bed biomass gasifier this so-called dry condenser method yielded tar measurements with precision better than 5% and accuracy averaging to within 10% of the IEA tar protocol. Comparisons of water vapor concentrations in producer gas as determined by the two methodologies showed poor agreement, which appears to be due to the low precision of both techniques for this measurement, possibly the result of dissolved hydrocarbons in the recovered aqueous phases.

Introduction

Producer gas generated by biomass gasification inevitably contains condensable hydrocarbons known as tar.[1] If not removed, tar can cause operational problems in equipment located downstream of the gasifier. Accurate measurement of this contaminant is important in monitoring gasifier performance.[2]

A large variety of sampling and analysis methods have been developed to determine the concentration of tar in biomass-derived producer gas,[3−6] which makes the comparison of data among researchers and manufacturers difficult. Most tar measurements are based on cold trapping in impinger trains with various organic solvents followed by laboratory analysis.[1] In an effort to improve accuracy and repeatability of tar measurements, the Working Group of the Biomass Gasification Task of the International Energy Agency (IEA) Bioenergy Agreement[7] developed a protocol for sampling and analysis of particulates and tar from biomass gasifiers, which is commonly referred to as the IEA tar protocol. This protocol, originally designed to use dichloromethane (DCM) as a tar solvent, has recently been revised to recommend the use of less volatile and toxic 2-propanol.[8] However, the work reported here employs the original protocol because of the ease in separating water from the DCM/tar solution and its continuing usefulness to researchers.

Regardless of the solvent used, the IEA tar protocol has several prominent shortcomings. Handling of organic solvents requires special skills and extra attention to prevent toxic exposure and environmental contamination. In the case of DCM, operators must wear gloves, masks, or properly fitted organic vapor respirators, and unprotected personnel must be kept away from the sampling and analysis areas. In addition, the IEA tar protocol requires considerable time for equipment setup, sampling, analysis, and cleanup. As a result, it is difficult to obtain more than one data point every few hours, and in many cases it is inconvenient to obtain more than one data point per day. Finally, the procedure requires extreme operator skill, which results in significant variation in results among less skilled operators.

We have developed a solvent-free tar quantification method as an alternative to the IEA tar protocol that is suitable for routine field applications and yields results comparable to the evaporative method of the IEA tar protocol. This dry condenser method, as it is called, condenses organic compounds at 105 °C (referred to as "heavy tar") in a disposable tube and a fiberglass mat. By operating above the boiling point of water, the heavy tar is not contaminated with moisture. A simple gravimetric analysis of the tube and fiberglass mat allows the mass of heavy tar to be determined. No solvents are employed for collection or analysis, and the tube and fiberglass mat can be disposed of upon completion of the analysis. This methodology was hypothesized to yield results comparable to the evaporative method of the IEA tar protocol, which recovers "heavy tar" from DCM−tar solutions by evaporation at 105 °C. This

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(1) Milne, T. A.; Abatzoglou, N.; Evans, R. J. *Biomass Gasifier 'Tars': Their Nature, Formation, and Conversion*; NREL/TP-570-25357, 1998.

(2) Lopamudra, D.; Ptasinski, K. J.; Janssen, F. J. *Biomass Bioenergy* **2003,** *24,* 125−140.

(3) Hasler, Ph.; Nussbaumer, Th. *Guideline for Sampling and Analysis of Tars and Particulates from Biomass Gasifiers*; Swiss Federal Office of Energy: Berne, 1998.

(4) Moersch, O.; Spliethoff, H.; Hein, K R. G. A New System for Tar Sampling and Analysis. In *Biomass Gasification and Pyrolysis*; CPL Press: Newbury, U.K., 1997.

(5) Moersch, O.; Spliethoff, H.; Hein, K. R. G. *Biomass Bioenergy* **2000,** *18,* 79−86.

(6) Hasler, Ph.; Nussbaumer, Th. *Biomass Bioenergy* **2000,** *18,* 61−66.

(7) Simell, P.; Stahlberg, P.; Kurkela, E.; Albrecht, J.; Deutsch, S.; Sjostrom, K. *Biomass Bioenergy* **2000,** *18,* 19−38.

(8) Neeft, J. P. A.; Knoef, H. A. M.; Zielke, U.; Sjostrom, K. *Guideline for Sampling and Analysis of Tar and Particles in Biomass Producer Gases*, Version 3.1; Energy Project EEN5-1999-00507.
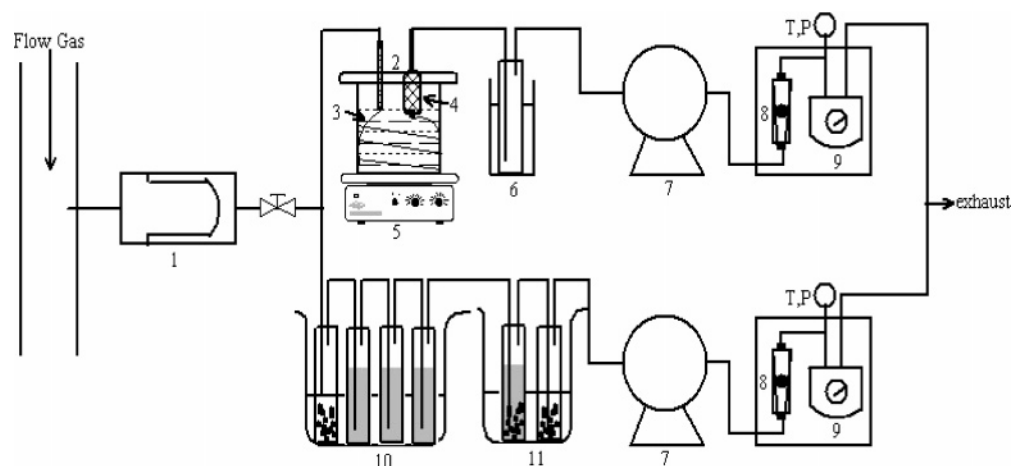
Figure 1. Schematic of the tar sampling and collection system (the upper flow path is the dry condenser system, while the lower flow path is the system employed by the IEA tar protocol): (1) particulate thimble filter; (2) pressure cooker; (3) Santoprene tubing; (4) glass-wool-packed canister; (5) hot plate; (6) chilled bottle; (7) vacuum pump; (8) rotameter; (9) dry gas volume meter; (10) water/ice bath; (11) acetone/dry ice bath.

paper describes the dry condenser method of tar sampling and analysis and compares it to the IEA tar protocol.

Experimental Method and Apparatus

The evaporative method of the IEA tar protocol yields a heavy tar fraction consisting of compounds with boiling points greater than about 105 °C. Toluene, with a boiling point of 110 °C, is a constituent of heavy tar in this context, while benzene, with a boiling point of only 80 °C, is not.

The gas sampling systems used for the IEA tar protocol and the dry condenser method are illustrated in Figure 1. Gas drawn from the slipstream passed through a particulate thimble filter heated to 450 °C, after which the gas flow was split into separate streams, one for each of the two tar measurement systems. Sampling times depend on the concentration of tar in producer gas, which varies with gasifier type, feedstock, and operating conditions. Sampling time increases as tar concentration decreases to ensure that the mass of tar collected is large compared to the uncertainty in the measurements to be performed. The IEA protocol, which claims a detection limit of 0.001 g/m³, suggests that tar be collected from a volume of producer gas exceeding 0.1 N m³. Since our sampling system drew 2 L/min, we chose sampling durations of 60 min.

In the case of the IEA tar protocol, the gas sample flowed through a series of six impinger bottles placed in cooling baths. The first four bottles were immersed in a water/ice bath, while the last two bottles were immersed in an acetone/dry ice bath. The first and sixth bottles were filled with glass beads, while the second, third, and fourth bottles were filled with DCM. The fifth bottle contained both glass beads and dichloromethane. The gas mixture leaving the impinger train passed through a vacuum pump before exiting through a dry gas volume meter, which was corrected to standard temperature and pressure for calculating tar concentrations in the producer gas. The pressure and temperature just ahead of the gas meter were recorded periodically throughout the experiment.

The composition of the gas exiting the sampling train (H_2, CO, N_2, O_2, CO_2, CH_4, and C_2H_4) was periodically measured with a Varian model CP-4900 Micro Gas Chromatograph to determine when the gasifier reached steady-state operation, the point at which tar sampling commenced. This instrument also allowed us to check for air leaks into the impinger system, which existed under slight vacuum. Upon completion of a test the total gas flow through the impinger train was recorded. Dichloromethane was rinsed through the glass connectors

between impingers to remove any tar condensed in them. This rinse liquid was combined with the impinger catch and refrigerated until tar analysis was performed.

Evaporative analysis began by filtering solids from the DCM/tar/water mixture and decanting the water. Fifty milliliters of filtered DCM/tar mixture was pipeted into a ceramic dish, which was then left in a fume hood overnight. The next day the sample was heated in an oven to 105 °C for 1 h, after which the remaining residue was weighed. The weight of this residue divided by the total volume of sampled gas gave the heavy tar concentration in the producer gas. Similarly, the weight of the decanted water divided by the total volume of sampled gas yielded an estimate of the water vapor concentration in the producer gas.

The dry condenser methodology is designed to capture a heavy tar fraction comparable to that measured by the IEA tar protocol. The upper flow path in Figure 1 represents the gas sampling system for the dry condenser method. It consists of the heated thimble particulate filter described previously, a dry condenser constructed from a household pressure cooker, a chilled bottle to condense water and possibly some light hydrocarbons, a vacuum pump, and a dry gas meter. The dry condenser consists of a 6-m coil of Santoprene tubing and a fiberglass-filled stainless steel canister installed inside the pressure cooker. Santoprene was chosen as tubing material because of its low cost and durability at elevated temperatures. The removable lid of the pressure cooker is pierced by compression fittings to admit gas flow to and from the pressure cooker. Gas entering the pressure cooker flowed serially through the Santoprene tubing and the stainless steel canister before exiting the pressure cooker. Before sealing the pressure cooker it was filled with sufficient distilled or deionized water to submerge the Santoprene tubing and most of the canister. The pressure cooker was placed on an electric hot plate adjusted to sufficient power to boil water within the pressure cooker. The pressure cock on the cooker was adjusted to boil water at 105 °C, which prevented water vapor in the sampled producer gas from condensing inside the Santoprene tubing and on the fiberglass. Gas exiting the pressure cooker flowed through an impinger bottle submerged in an ice bath for the purpose of removing water (and possibly some light hydrocarbons) from the gas before it flowed through the vacuum pump. A dry gas meter was used to measure total gas flow through the dry condenser. The pressure and temperature just ahead of the gas meter was recorded periodically throughout the testing run.

When the gas sample flowed through the dry condenser at 105 °C, most of the heavy tar compounds directly condensed

onto the inner surface of Santoprene tubing. Tarry aerosols that passed through the tubing were captured by the fiberglass in the stainless steel canister, which was also maintained at 105 °C. Thus, determination of tar is accomplished by measuring the weight change of the Santoprene tubing and the fiberglass-packed canister before and after a test. This gravimetric measurement was slightly complicated by the possibility of devolatilization of plasticizers from the tubing when operated at 105 °C, which would result in underestimation of tar concentrations. Santoprene was chosen because of its resistance to devolatilization. Nevertheless, the following pretest preparation of the Santoprene tubing was performed to account for weight changes due to devolatilization.

Compression fittings were attached to both ends of a 6-m-length of fresh Santoprene tubing. The tubing was coiled in a beaker and placed in an oven at 105 °C for 12 h, which was found to be long enough to dispel all volatile components from the tubing. The devolatilized tube was stored in a desiccator to acclimatize to room temperature for 1 or 2 h. Although the fiberglass does not require devolatilization, it was also stored in the desiccator to remove moisture.

When gas sampling was completed, the Santoprene tubing and fiberglass-filled canister were immediately removed from the pressure cooker and the outer surfaces wiped dry. The ends of the Santoprene tubing were sealed, and the tubing was placed in an oven at 105 °C for 1 h, after which its weight change was determined while the canister was immediately weighed. Tar concentration in the producer gas was calculated by dividing the total weight gain in the tubing and canister by the total dry gas volume that passed through the dry condenser. Similarly, the weight of liquid collected in the cooled impinger bottle downstream of the pressure cooker divided by the dry gas volume gives an estimate of the water vapor concentration in the raw producer gas.

Tests were conducted on the atmospheric fluidized bed gasifier at Iowa State University. The system is rated at approximately 7k W and designed to have a fuel feed rate of 2−5 kg/h. The fluidized reactor, made of Inconel 625, has a diameter of 10 cm and a height of 240 cm. The gasifier is equipped with a fluidization gas preheater as well as four pairs of heaters that encase the fluid bed reactor. Fluidized air is evenly distributed into the reactor through a distributor plate at the bottom of bed. Particulate-laden fuel gas exits the reactor through the freeboard and passes through a cyclone that removes much of the particulate matter larger than 10 μm in size. Typically the bed will reach a steady-state temperature based on the equivalence ratio (air-to-fuel ratio) but is also dependent on reactor heat loss and fuel moisture.

The current experiments employed discard seed corn as fuel, which is a waste stream of interest to one segment of the agricultural processing industry. A variable-speed auger metered fuel into a rotary airlock where it fell into a constant-speed injection auger. The high-speed auger injected the fuel into the bottom of the fluidized bed. A small amount of air introduced immediately below the airlock prevented backflow of fuel gas into the fuel hopper.

Experiments were performed to provide direct comparisons between the dry condenser method and the evaporative method of the IEA tar protocol. Table 1 details the operating conditions for the fluidized bed gasifier and the sampling system. The equivalence ratio was maintained at 0.3 for all experiments, while three different gasification temperatures were investigated.

Results and Discussion

To ensure a valid comparison between the two methodologies the two tar collection systems were run in parallel with data collected for about 1 h from the same producer gas stream. At this point the IEA tar protocol

Table 1. Test Conditions for Tar Sampling

gasification temp. (°C)	650, 705, 788
equivalence ratio	0.3
feedstock	seed corn
sampling flow rate (L/min)	2
sampling duration (min)	~60

system was shut down because of the difficulty in substituting another impinger train for the first one. However, the simplicity of the dry condenser allowed a second pressure cooker loaded with fresh tubing and fiberglass to be substituted for the first, allowing a second test of this system under comparable gasifier operating conditions. Thus, the first hour of testing allowed the relative accuracy of the two methods to be compared, while the second hour of testing allowed evaluation of the precision of the dry condenser method of tar evaluation by comparing results from the first and second hours where operating conditions are assumed to remain constant for the duration of the gasification trial.

The tar analysis for the IEA tar protocol was performed immediately after sampling since other tests in our laboratory revealed that aging of tar/moisture/DCM samples affects the results of the tar analysis.[9] For each DCM−tar sample the results were reported as the average of five parallel evaporation determinations to minimize analysis errors, as described in the IEA tar protocol.[7] Also, blank determinations with pure DCM were made in parallel to minimize systematic errors. Precision of measurements was estimated as the 95% confidence interval about the mean of a collection of measurements.

Table 2 summarizes data used to estimate the precision of the dry condenser. Notice that this table includes duplicate measurements from the same gasification trials as well as measurements obtained from different gasification trials but performed at the same temperature and equivalence ratio. Tar concentrations as determined by the dry condenser ranged between 7.5 and 15.6 g/N m³ and decreased with increasing gasification temperature. Whether comparing across gasification trials or within gasification trials, the precision of measurements by the dry condenser are very good. Regardless of gasification temperature, duplicated measurements within a gasification trial agreed to within 5%. Variation between gasification trials at the same temperature also agreed to within 5% except for the comparison of the two trials performed at 705 °C, which showed a variation of 18%. This instance of reduced precision is probably an indication of our inability to closely control gasifier operating conditions rather than a reflection on the precision of the dry condenser methodology.

Table 2 also includes data on water vapor concentrations in the producer gas as determined from the amount of liquid caught in the cold trap downstream of the pressure cooker (calculated on the basis of dry sample gas volume). Water vapor concentrations as determined by the dry condenser method ranged between 120 and 367 g/N m³ and, like tar concentrations, decreased with increasing gasification temperature. Precision of these measurements ranged between 6%

(9) Ming, X.; Brown, R. C.; Norton, G. The Effect of Sample Aging on the Accuracy of the IEA Tar Protocol. *Energy Fuels,* in press.

Table 2. Data Collected To Evaluate the Precision of the Dry Condenser Method for Measuring Tar and Water Concentrations

gasification trial	gasification temp. (°C)	dry condenser (first hour)		dry condenser (second hour)	
		tar loading (g/N m^3)	water loading (g/N m^3)	tar loading (g/N m^3)	water loading (g/N m^3)
1	650	15.6	329.3	15.1	366.9
2	650	14.3	291.8	14.9	321.7
3	705	8.3	265.2	7.8	217.8
4	705	9.8	286.8	9.6	261.8
5	788	7.6	120.2	7.4	128.4
6	788	8.0	137.3	8.0	153.9

Table 3. Comparison of Tar and Water Concentrations as Determined by the Dry condenser method and compared to the IEA tar protocol

gasification trial	gasification temp. (°C)	dry condenser (averaged over two, 1-h trials)		IEA tar protocol	
		tar loading (g/N m^3)	water loading (g/N m^3)	tar loading (g/N m^3)	water loading (g/N m^3)
1	650	15.4	348.1	16.5	245.6
2	650	14.6	306.8	14.8	190.6
3	705	8.1	241.5	8.9	181.1
4	705	9.7	274.3	10.3	169.1
5	788	7.5	124.3	8.0	126.2
6	788	8.0	145.6	8.4	117.6

Table 4. Average and 95% Confidence Interval for Tar and Water Concentrations as Determined by the Dry Condenser Method and the IEA Tar Protocol

gasification temp. (°C)	tar loading (g/N m^3)		water loading (g/N m^3)	
	dry condenser[a]	IEA tar protocol[b]	dry condenser[a]	IEA tar protocol[b]
650	14.9 ± 0.5	15.6 ± 1.2	327.4 ± 30.8	218.1 ± 38.9
705	8.8 ± 0.9	9.6 ± 0.9	257.9 ± 28.9	175.1 ± 8.5
788	7.7 ± 0.3	8.2 ± 0.3	134.9 ± 14.4	121.9 ± 6.1

[a] Calculated from the four data points at the specified temperature given in Table 2. [b] Calculated from the two data points at the specified temperature given in Table 3.

and 20%, averaging about 12%, and appeared to get larger with decreasing temperature. The reasons for this relative lack of precision are subsequently discussed.

The precision of tar and water measurements obtained with the IEA tar protocol required comparison of data for different gasification trials performed at similar operating conditions since it was not possible to obtain more than one tar sample during a given gasification trial. Table 3 summarizes data for both the dry condenser methodology and the IEA tar protocol, which allows an evaluation of the accuracy of the dry condenser methodology as well as the precision of the IEA tar protocol. Examination of Table 3 shows that the variation between tar measurements at a given gasification temperature as determined by the IEA tar protocol ranges between 5% and 14%. Thus, the precision of the dry condenser in measuring tar concentrations appears to be as good if not better than the IEA tar protocol. Furthermore, Table 3 indicates that the variation between water vapor measurements for a given gasification temperature as determined by the IEA tar protocol ranges between 6% and 25%. Thus, the precision of the dry condenser methodology in measuring water vapor is comparable to the precision of the IEA tar protocol for this purpose.

Determination of the accuracy of the dry condenser method can only be made by way of comparison with the IEA tar protocol, which is commonly accepted as a standard for tar determinations. Table 4 is a compilation of average values and uncertainty bands for tar and water concentrations as a function of gasification temperature for both methodologies. Each average and uncertainty band reported for the dry condenser was based on four data points obtained from Table 2, while those for the IEA tar protocol were each based on two data points obtained from Table 3. Uncertainty bands were taken to be equal to the 95% confidence intervals for the averaged data. As illustrated in Figure 2, tar concentrations as determined by the two methodologies agree to within the precision of the data. Thus, the dry condenser method appears to be an excellent alternative to the evaporative version of the IEA tar protocol for measuring tar concentrations in producer gas streams.

As shown in Figure 3, the agreement between the two methodologies in measuring water vapor content of the producer gas is poor. At the lowest gasification temperature (650 °C) the discrepancy is the largest, with the dry condenser method reporting water vapor concentrations that are 50% larger than those obtained by the IEA tar protocol. At the highest temperature (788 °C) the dry condenser method yields a water concentration only 10% higher than the IEA tar protocol. However, inclusion of error bars with these data reveals that the precision of both the dry condenser method and the IEA tar protocol decreases with decreasing temperature to
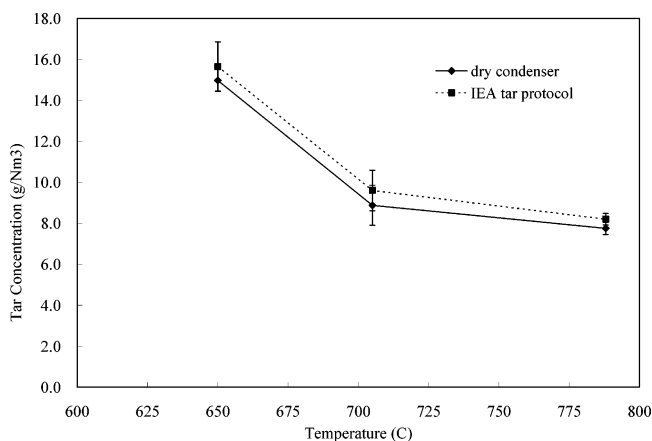
Figure 2. Comparison of tar concentration as determined by the dry condenser method and the IEA tar protocol.
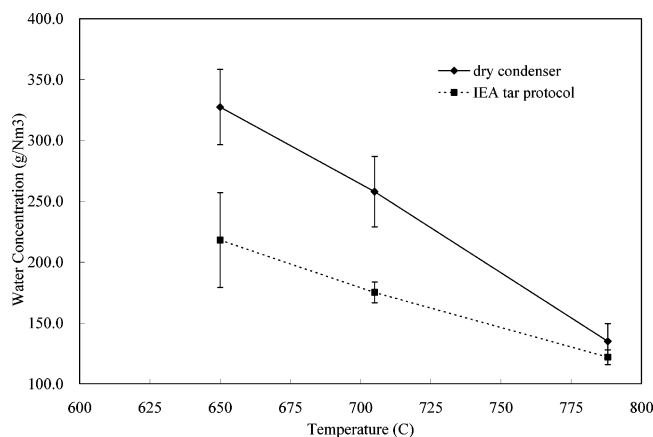
Figure 3. Comparison of water concentrations as determined by the dry condenser method and the IEA tar protocol.

the extent that much of the discrepancy between the two methods can be attributed to the uncertainty in the data.

The reason for the poor precision of the two methodologies in measuring water concentration (in contrast to their high precision in measuring tar concentration) is not completely understood but is probably related to the assumption that the water recovered by both methodologies is a pure phase. In fact, it is well known that the water decanted from the tar/DCM mixture in the IEA tar protocol contains water-soluble organic compounds.[7] Very likely, the water collected in the cold trap after the pressure cooker in the dry condenser methodology also contains low-boiling-point organic compounds. Thus, both methods are expected to over-estimate water vapor concentrations, although smaller errors are expected for the IEA tar protocol since the DCM is likely to preferentially dissolve most of the light hydrocarbons. Furthermore, test-to-test variations in the amount of dissolved organic compounds in the aqueous phase very likely account for the relative lack of precision in the determination of water concentration. Evidence in support of this hypothesis is the improved precision in measurement of water concentrations as gasification temperature increases: increasing gasification temperature decreases both the absolute quantity of hydrocarbons in producer gas as well as the relative

fraction of light hydrocarbons.[1] Further tests are required to support this hypothesis.

Conclusions

The dry condenser method for tar analysis proposed in this paper provided both precise and accurate measurements of tar concentration in producer gas during trials with a fluidized bed gasifier. Precision was within 5%, which is as good as or better than the precision of the IEA tar protocol. Accuracy was within 5% of the IEA tar protocol, which is now widely accepted as a standard method for tar determination. Considering its simplicity, the dry condenser method is an attractive alternative to the evaporative version of the IEA tar protocol for the determination of heavy tar in producer gas. The lower detection limit was not explicitly determined for the dry condenser method, although measurements to 0.01 g/m^3 should be possible. Since this is a gravimetric method, longer sampling times or higher gas sampling rates can ensure accurate tar analysis down to concentrations much lower than those evaluated in this study.

Neither the dry condenser methodology nor the IEA tar protocol yielded high precision in measurements of water vapor concentration in producer gas, with some measurements varying by as much as 25%. Comparisons between the dry condenser methodology and the IEA tar protocol diverged by as much as 50%, with much of the discrepancy attributable to the poor precision of the two methodologies. Both precision and accuracy appeared to improve with increasing gasification temperature, which suggests that light hydrocarbons dissolved in the aqueous phase were at least partly responsible for the poor results when attempting to measure water concentration.