

Clarifications on Chapter 7.3 Methane Emissions during the Pyrolysis Process

Global Biochar C-Sink Standard (2024)

Initial Situation

Chapter 7.3. of Global Biochar C-Sink Standard (2024) defines that: “[...] at least two CH₄-emission tests per pyrolysis unit with the same feedstock representing the typical operation of the unit are required, or the pyrolysis unit must have a type certification according to EBC or WBC.”

It further states that: “For CH₄ emission tests, a detailed measurement strategy with precise details of the measurement technology, measurement intervals, and measurement accuracy must be submitted in advance to Carbon Standards for review. Once the procedures are accepted, the methane emissions factor of the pyrolysis unit is calculated as the mean of the two measurements plus one standard deviation as the margin of security.”

Many producers find it challenging to find a suitable agency for measurements. For this reason, we developed the following rules on using proxy emission values that are easier to determine. Especially the rule update point 4, using CO as a proxy, should facilitate the task for many producers.

Carbon Standards International recommends that producers measure CH₄ emissions directly. Given the inherent uncertainties of proxies, safety margins are significantly higher when CH₄ emissions are calculated from proxies rather than measured directly.

Clarifications

1. Methane measurement strategy must be submitted in advance to Carbon Standards for review.
2. Two independent measurements of at least 1 hour have to be conducted. It may be necessary to adapt this specification for batch systems.
3. Next to methane, the following parameters have to be measured:
 - a. feedstock input flow (DM)
 - b. biochar output flow (DM)
 - c. exhaust gas volume flow
 - d. CO concentration
4. Measurements should be conducted at regular operation.

Rule Update

1. If CH₄ emission values are available, these are used for the certification. The CH₄ emission factor shall be calculated as mean + standard deviation + expanded uncertainty.
2. If no CH₄ but the C_xH_y value is available from flue gas measurements, the CH₄ value is set equal to the C_xH_y value. C_xH_y includes CH₄ emissions but also

- numerous other compounds, which are usually less abundant than CH₄ in the burnt exhaust gas. The CH₄ emission factor shall be calculated as mean + standard deviation + expanded uncertainty of the C_xH_y measurement.
3. If no CH₄ or C_xH_y but the TOC value is available from the flue gas measurements, the CH₄ value is set equal to the TOC value. TOC emission factors include CH₄ emissions but also numerous other organic compounds, which are usually less abundant than CH₄ and other C_xH_y molecules in the burnt exhaust gas. The TOC emission factor is usually expressed in g C (gram carbon) and has to be multiplied with 16/12 to account for the difference in molar weights between C and CH₄ and thus to translate it into g CH₄. The CH₄ emission factor shall be calculated as mean + standard deviation + expanded uncertainty of the TOC measurement.
 4. In the absence of CH₄, VOC, C_xH_y, and TOC measurements of the flue gas, it can be conservatively assumed that the CH₄ value is not higher than 50% of the CO value. Therefore, the CH₄ value to be offset is set to 50 % of the CO emission factor (g kg⁻¹ biochar). The CO emission factor shall be calculated as mean + standard deviation + expanded uncertainty. For this approach, however, O₂, CO₂, and CO flue gas concentrations must be provided.
 5. If the expanded uncertainty is not provided, a 20% security margin must be applied to the sum of mean and standard deviation.

Reasoning

1. The relative abundance of CH₄ to CO in unburnt pyrolysis gas has been documented in the literature and is relatively constant. The CH₄:CO ratio (g g⁻¹) is, on average, 1:5 (0.2 g g⁻¹), with a maximum value of 1:2.5 (0.41 g g⁻¹) found in the literature (Table 1).
2. During combustion, the ratio of CH₄ to CO is expected to shift towards CO, if the pyro-gas is combusted with temperatures above 1000 °C. The assumption that the CH₄ to CO ratio of the non-oxidized pyrogas is maintained throughout combustion is considered the highly unlikely worst case. The assumption that the CH₄ to CO is always below 0.5 g CH₄ g⁻¹ CO is thus conservative.

Background Information

The composition of unburnt pyrolysis gases can deliver valuable insights into potential (worst case) methane emissions caused during pyrolysis if pyrolysis gas is not combusted properly. The physicochemical properties of the feedstocks and the pyrolysis reactions set boundaries to the potential methane emissions produced during pyrolysis. A literature review including various biomass feedstocks reveals the following carbonaceous gas concentrations and ratios between CO and CH₄ for unburnt pyrolysis gases (Table 1). A certain trend can be observed for CH₄ to CO ratios. There are usually (mean ± standard deviation) 0.35 ± 0.15 CH₄ molecules per CO molecule. This molar ratio represents a ratio of 0.2 g CH₄ per g CO (± 0.09 g g⁻¹) in the unburnt pyrolysis gas.

Table 1: Overview of unburnt pyrolysis gas composition ratios for CO and CH₄.

Study	Temp. °C	Feedstock	Mol. Ratio CH ₄ :CO	Emission factor Ratio CH ₄ :CO [g g ⁻¹]
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Amini et al. 2019	400-800	dead biomass, leaves, twigs, grasses	0.34	0.20
Park et al. 2014	500	rice straw	0.27	0.15
Park et al. 2014	600	rice straw	0.40	0.23
Park et al. 2014	700	rice straw	0.42	0.24
Fu et al. 2011	600	Maize stalk, rice straw, cotton straw and rice husk	0.29	0.17
Fu et al. 2011	700	Maize stalk, rice straw, cotton straw and rice husk	0.27	0.15
Fägernas et al. 2012	450	birch hardwood	0.20	0.11
Waheed et al. 2013	750	Wood, rice husk, forest residue	0.26	0.15
Dutta 2023			0.15	0.09
Encinar et al. 2000	500	Cynara cardunculus	0.24	0.14
Encinar et al. 2000	600	Cynara cardunculus	0.30	0.17
Encinar et al. 2000	700	Cynara cardunculus	0.29	0.16
Manya et al. 2018	600	Vine pruning, corn stover, olive mill waste	0.58	0.33
Dunnigan et al. 2018	500-800	grape pruning	0.71	0.41
Dunnigan et al. 2018	500-800	rice husk	0.18	0.10
Flatabo et al. 2023	500-800	waste timber	0.52	0.30
Flatabo et al. 2023	500-800	commercial wood pellets	0.51	0.29
Moltó et al. 2020	600-950	starch PVA films	0.45	0.26
Moreno and Font, 2015	500	Solid wood and wood waste	0.18	0.10
MEAN			0.35	0.20
SD			0.15	0.09

While an increase of the CH₄ to CO ratio in the flue gas after combustion of the pyrolysis gas is theoretically possible, it is only plausible under highly fuel-rich, low-temperature conditions with limited oxygen. In most real-world combustion scenarios, CO would oxidize faster than CH₄, meaning the ratio would either stay the same or shift in favor of more CO, not CH₄. In order to ensure it, the following conditions have to be met:

1. Sufficient oxygen is provided in the combustion chamber to ensure oxidative conditions. This can be deduced from O₂ or CO₂ levels in the flue gas stream. O₂ levels should be above 5 %, the air excess ratio above 1.2.
2. Temperatures during combustion must be higher than 1000 °C to ensure the activation energy required for CH₄ oxidation is available.

Accounting for a) a high CH₄ to CO ratio (0.5 g CH₄ g⁻¹ CO) in the pyro-gas and b) ensuring that high temperatures and sufficient oxygen are available during combustion we can conservatively assume that the CH₄ value is not higher than 50% of the CO value in the flue gas composition of pyrolysis plants.

References

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