On 14C-based methods for measuring the biogenic carbon fraction in fuels and flue gases
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Chapter 4

Radiocarbon-based determination of biogenic and fossil carbon partitioning in the production of synthetic natural gas

Abstract
The applicability of the radiocarbon ($^{14}$C) method for the quantification of the biogenic carbon fractions at different stages of the Synthetic Natural Gas (SNG) production process is demonstrated in this study. The $^{14}$C-based biogenic carbon fractions were determined in process flue gas and raw SNG and were 38% and 89% respectively, for a mixture of wood and fossil lignite with 75 ± 3% biogenic carbon as input material. The differences in biogenic carbon fractions between the input material, flue gas and raw SNG are caused by bio-fossil carbon partitioning during the SNG production process. This study demonstrates that the main bio-fossil carbon partitioning took place during the gasification of the input material. This is due to the large differences in volatility and char content of the wood and lignite materials. For the determination, verification or certification of the biogenic carbon fraction in process flue gas and (raw) SNG in the SNG production process, separate investigations of the gases are inevitable. The $^{14}$C method is a useful and reliable independent method for these purposes.

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$^b$Energy research Centre of the Netherlands (ECN), Petten, The Netherlands
4.1 Introduction

Several policy measures, on international and national levels, aim to reduce fossil carbon emissions. One of the applied measures is the financial stimulation of the production and use of biomass-based fuels, such as wood, bio-diesel, bio-ethanol and biomethane, as alternatives for fossil fuels. As a consequence, the production of bio-based fuels has increased on a global scale over the last 10 years (webpage IEA). One of the consequences of these developments involving financial interests is the need for methods to independently determine, verify or certify the biogenic carbon fraction in fuels and CO₂ containing process streams. The \(^{14}\text{C}\) method, in which the carbon isotope \(^{14}\text{C}\) (radiocarbon) is used as a tracer for the fraction of biogenic carbon, has proven itself as the most independent, accurate and suitable determination method for many different fuel types and flue gases (Dijs et al., 2006; Mohn et al., 2008; Staber et al., 2008; Palstra and Meijer, 2010; Palstra and Meijer, 2014). Several international standards (ASTM, CEN and ISO) are already available to facilitate industrial companies in using the \(^{14}\text{C}\) method for the biogenic carbon fraction determination of different kind of materials (such as CEN/TR 15440 for waste; ISO 13833 for flue gas CO₂ and CEN 16640 for bio-based materials in general).

In this study the \(^{14}\text{C}\) method is used to determine the biogenic carbon fraction in Synthetic Natural gas (SNG). SNG is produced since the 1960s from fossil materials such as coal and lignite (Kopyscinski et al., 2010). Recently, it has become popular in China, as shown by Ding et al. (2010). However, due to the increased interest in producing and using bio-based fuels, the SNG production from biomass materials is now also investigated. As biomass-based materials differ in chemical and physical properties from the conventionally used fossil materials, new SNG production processes suitable for biomass-based materials are developed and tested. There are currently several (mainly European) demonstration projects for bio-based SNG (Kopyscinski et al., 2010), but there are no large-scale production plants yet.

Beside pure fossil and pure biomass-based materials, mixed biogenic and fossil materials and mixed waste streams can also be used for SNG production (website “Swindon”; Van der Meijden et al. 2011). These mixed input materials offer the possibility to obtain SNG that is partly bio-based, while the costs of the used materials are lower compared to the use of pure biomass. To optimise these co-gasification processes, the \(^{14}\text{C}\) method can be very helpful to investigate the (probably different) partitioning of bio-based and fossil-based carbon along the SNG process. Other applications of the \(^{14}\text{C}\) method in the production of (partly) bio-based SNG are the determination of the biogenic carbon content in the final SNG product and/or in the flue gas CO₂ emissions of the production plant. For producers and large purchasers of SNG it can be of (financial)
interest to determine the fraction of biogenic methane in the obtained SNG product if this product is to be sold on the energy market. Due to the global demand for reductions of fossil CO₂ emissions and increasing demand for biofuels (website IEA), partly bio-based SNG can be favoured above fossil SNG by customers. A quantified biogenic carbon fraction could then enhance the selling of the product. Standards ASTM 6866 and CEN/TS 16440 can be used for the biogenic carbon fraction determination of gas samples. For SNG producers with large CO₂ emissions at the production site that need to be reported to national emission authorities, it can be of interest to determine the fraction of biogenic CO₂ emissions with the ¹⁴C method (ISO 13833), if these emissions have been made financially more attractive than fossil CO₂ emissions (examples of these kinds of regulations within the European Union: 2007/589/EC, 2009/29/EC, 2011/540/EC).

The first aim of this study is to demonstrate the applicability of the ¹⁴C method for quantifying the biogenic carbon fractions in two different gas streams of the SNG production process (raw SNG and process flue gas), when a mixture of biomass and material of fossil origin is used as input material. The second aim is to investigate differences in biogenic carbon fractions between the input material, the process flue gas and raw SNG. If fossil and biogenic input materials differ in chemical composition and properties (such as carbon content, volatility and combustion temperature), the biogenic and fossil carbon fractions do not end up proportionally in the carbon-containing output streams of the SNG process (e.g. flue gas, ash, tar, raw SNG). This is defined here as bio-fossil carbon partitioning. Bio-fossil carbon partitioning is demonstrated in this paper for the investigated SNG production process.

The research was part of project A2 ‘Agate-1’ of the green gas project EDGaR (Energy Delta Gas Research) and was performed in cooperation with ECN.
4.2 Methods

4.2.1 SNG sample information

The samples investigated in this study were obtained from an SNG production system at the Energy research Centre of the Netherlands (ECN), in Petten. For the present study, tests were performed with two different fuels: beech wood and a mixture of beech wood and lignite. Figure 4.1 shows a scheme of this SNG production system. Essentially, the system is the one shown in Figure 5 in van der Meijden et al. (2010), but without recycling of ash and tar to the gasifier and without the final upgrading of raw SNG to remove H₂O and CO₂. It consists of the MILENA allothermal gasifier, dust removal, OLGA tar removal, a compression step, organic sulphur conversion (HDS) and sulphur removal, a pre-reformer (REF) for conversion of aromatic compounds, and reactors filled with nickel methanation catalysts.

![Figure 4.1. Simplified SNG production scheme as applied for the experiments by ECN. For a more elaborate scheme see van der Meijden et al. (2010).](image)

The MILENA gasifier consists of two sections, indicated by C and R in Figure 4.1. In section R, solid fuel is quickly heated by contact with hot bed material, which is fluidized by a small amount of steam. The fuel is converted into producer gas and a solid carbon-rich residue, further called char. Bed material and char are transported to the combustion section C. There, combustion of char with air produces flue gas with CO₂ and the heat needed in section R. The producer gas consists mainly of the volatile fraction of the fuel and some gas produced by reaction of char with steam. Table 4.1 lists the MILENA producer gas composition for the present experiments. Beside these listed components, the producer gas also contains dust, which is a mixture of fly ash with fines from the bed material and char. In the experiments, dust was removed using a hot-gas filter.
Table 4.1. Approximate MILENA producer gas composition (in vol% dry) from beech wood and from a mixture of 71% beech wood and 29% lignite. The gas moisture content was about 32%.

<table>
<thead>
<tr>
<th></th>
<th>Wood (% v/v, dry)</th>
<th>Wood + Lignite (% v/v, dry)</th>
</tr>
</thead>
<tbody>
<tr>
<td>CO</td>
<td>29</td>
<td>23</td>
</tr>
<tr>
<td>H₂</td>
<td>27</td>
<td>31</td>
</tr>
<tr>
<td>CO₂</td>
<td>22</td>
<td>26</td>
</tr>
<tr>
<td>CH₄</td>
<td>12.5</td>
<td>10.5</td>
</tr>
<tr>
<td>C₂H₄</td>
<td>3.5</td>
<td>2.5</td>
</tr>
<tr>
<td>C₆H₆</td>
<td>0.8</td>
<td>0.8</td>
</tr>
<tr>
<td>Sum other hydrocarbons</td>
<td>0.7</td>
<td>0.5</td>
</tr>
<tr>
<td>N₂</td>
<td>4</td>
<td>5</td>
</tr>
</tbody>
</table>

*Mainly from shield gas on the fuel system and carrier gas of the steam supply.*

The producer gas contains significant amounts of heavy aromatic hydrocarbons, further called tar. The OLGA tar removal system removes all but the most volatile tar compounds. Remaining aromatic hydrocarbons, mainly benzene, toluene and xylene (BTX) are converted in the prereformer (REF) with steam into CH₄, CO₂, CO and H₂. Tar removed by OLGA contains about 93 wt% carbon. The total amount of carbon in dust and tar is estimated to be 5 ± 2 % of the total carbon input. Downstream the prereformer, two methanation reactors with nickel catalysts promote the reactions of higher hydrocarbons and CO with H₂ into CH₄ and H₂O. Shortage or excess of H₂ are taken care of by the watergasshift reaction CO + H₂O ⇌ CO₂ + H₂. After water removal downstream the methanation reactors, “raw SNG” is obtained. With both fuels, the conditions applied yielded raw SNG which, after water removal, contained about 48% CO₂ and 40% CH₄, some H₂ and N₂, and traces (<0.02%) of CO and C₂H₆.

Dried flue gas and raw SNG were sampled simultaneously on two different days, using 1-L gasbags (Tedlar with polypropylene fitting). The sampling flow was 0.5 L/minute. Each day, flue gas and raw SNG gas were sampled twice. The difference in time between the first and the second sampling was on both days only 5 minutes. On the first sampling day beech wood particles were used as input material to obtain 100% bio-flue gas CO₂ and 100% bio-raw SNG. The second sampling day, beech wood particles (from the same batch as the first day) mixed in about 2:1 mass ratio with fossil lignite were fed into the system.
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4.2.2 Applied $^{14}$C method

Equation 4.1 (similar to 1.3) was used to calculate the biogenic carbon fractions of the different samples from the SNG production process. In this calculation the size of dilution of the biomass $^{14}$C signal due to mixing with $^{14}$C-free fossil carbon is employed as a measure for the biogenic carbon fraction:

$$f_{bioC} = \frac{^{14}C_{sample}}{^{14}C_{bio}} \quad \text{(Expressed as %)} \quad (4.1)$$

In this study, $^{14}C_{sample}$ is the measured $^{14}$C value of a sample material, $^{14}C_{sample\ measured}$ (calculated according to eq. 1.4). $^{14}C_{bio}$ is the $^{14}$C value of the biogenic carbon fraction in the sample and is approximated based on the average $^{14}C_{sample\ measured}$ values of the gas samples obtained from 100% wood particles (both raw SNG and flue gas CO$_2$). In chapters 1 and 3 a detailed overview is given of the principle of the $^{14}$C method and its calculations, corrections and method uncertainties. The reported $^{14}$C values in this chapter are $^{14}a_N$ values.

To obtain the $^{14}C_{sample\ measured}$ values, samples were pre-treated to pure CO$_2$, graphitized and their $^{14}$C/$^{12}$C and $^{13}$C/$^{12}$C carbon ratios were measured with a $^{14}$C-dedicated Accelerator Mass Spectrometer (AMS) at the Centre for Isotope Research, University of Groningen (Van der Plicht et al., 2010). To obtain pure CO$_2$ the flue gas samples, raw SNG samples and a few solid lignite samples were pre-treated in slightly different ways.

The CO$_2$ fraction in the flue gas samples (10% v/v the first day and 15% v/v the second day) was the main carbon component in the flue gas and this fraction was separated cryogenically (liquid N$_2$, -196°C) from the other gas components.

The raw SNG samples contained approximately 48% v/v CO$_2$ and 40% v/v CH$_4$ on both days. These were the main carbon components in the raw SNG. The fractions of CO and C$_2$H$_6$ were very small (< 0.02% v/v) and have not been taken into account in the results of this study. To investigate bio-fossil carbon differences between the CO$_2$ and CH$_4$ fractions in the raw SNG samples, the two fractions were separated and the carbon isotopes were analysed for both. For this investigation the CO$_2$ fraction of the raw SNG was first cryogenically separated from the CH$_4$ fraction (using a special cryogenic trap filled with melting iso-pentane at -160°C). The remaining carbon fraction in the gas (mainly CH$_4$) was combusted to CO$_2$ and then cryogenically trapped (with liquid N$_2$, -196°C). A combustion system was used in which any formed CO was oxidized to CO$_2$ as well. In addition to the CO2-CH4 separation treatment, three of the four sampled raw SNG samples were also pre-treated to CO$_2$ without separation of the CO$_2$ and CH$_4$ fractions. In the combustion system, the CO$_2$ fraction of the raw SNG sample was then immediately cryogenically
trapped (liquid N₂, -196°C). After the combustion of the CH₄ fraction, the produced CO₂ was trapped and mixed with this raw SNG CO₂ fraction in the same glass device.

All obtained CO₂ samples from the flue gas and raw SNG samples were additionally purified by removal of NOₓ and sulphurous components. In appendix A.4 additional information is given about the used “SCS” (“Separation and Combustion System”) system at CLO and the applied methods.

A few solid subsamples of the used lignite batch were analysed for ¹⁴C as well, to check whether it was legitimate to define the lignite material as ‘0% biogenic’ and ¹⁴C-free’. A few grams of lignite were ground to particle sizes < 1 mm and three subsamples of ≈ 6 mg lignite were weighed in small tin capsules. The subsamples were combusted to CO₂ with a combined Elementar Isotope Cube-Isoprime100 system.

Each AMS-batch with unknown samples contained a set of reference materials to calibrate (using Oxalic acid-II; SRM-4990c) and verify the measured carbon isotope amounts. It also contained a set of background reference materials to correct for carbon contamination during the pre-treatment and measurement. The measured AMS results were then calculated to produce ¹⁴Csample values according to the description given in chapter 4. The measured ¹⁴C results were corrected for isotope fractionation, based on the δ¹³C values measured with the AMS. As the δ¹³C values of the biogenic and fossil carbon were very similar, no correction had to be applied in the isotope fractionation correction to exclude the contribution of the fossil carbon in this correction (chapter 3).

### 4.2.3 Determination of bio-fossil carbon partitioning of solid input materials

To investigate bio-fossil carbon partitioning in the applied SNG process, the biogenic carbon fractions as determined with the ¹⁴C method for flue gas and raw SNG were compared with each other and were also compared to the biogenic carbon fraction of the mixed bio-fossil input materials that were fed into the SNG production system. The biogenic carbon fraction of the total mixed input was determined based on the known carbon composition and dry mass flow (kg/h) of the separate wood and lignite batches that were fed into the SNG system.

The biogenic carbon fraction of the mixed wood and lignite as used for the production of SNG was calculated according to the following equation.

\[ fC_{bio} = (C_{content \ wood} \cdot flow_{dry \ wood})/(C_{content \ wood} \cdot flow_{dry \ wood} + C_{content \ lignite} \cdot flow_{dry \ lignite}) \] (4.2)
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The $C_{\text{content wood}}$ and $C_{\text{content lignite}}$ values show the carbon contents that were measured in the dried wood and lignite materials respectively. The $flow_{dry}$ values for wood and lignite were calculated as follows:

$$flow_{dry} = flow_{not\_dry} \times (1 - f_{\text{moisture mass}})$$  \hspace{1cm} (4.3)

The flows are in kg/h. $flow_{not\_dry}$ is the mass flow of the particular investigated not-dried material and $f_{\text{moisture mass}}$ is the fraction of moisture in this material. The uncertainty range as calculated for the obtained $fC_{bio}$ value, is the combined uncertainty of the (estimated) relative errors in the different variables used to calculate $fC_{bio}$ (Eq. 4.2 and 4.3).
4.3 Results and discussion

4.3.1 Biogenic carbon fraction of mixed solid input materials

To investigate the differences in biogenic carbon fraction between the input material and the flue gas and raw SNG, the biogenic carbon fraction of the input material was calculated first, according to the procedure described in section 4.2.3.

Table 4.2 gives an overview of the data that were used to calculate this biogenic carbon fraction of the mixed input material. The non-dried material flow, moisture content, and ash and carbon content in dried material were determined by ECN. The lignite used in this case has a relatively low carbon content (lignite usually has around 60% (m/m)). This is because the batch with lignite material also contained not-identified grey-white particles rich in carbonate. The biogenic carbon fraction of the mixed input materials was 75 ± 3%.

Table 4.2. Data used to calculate the biogenic carbon fraction according to equation 4.2, for a mixture of wood and lignite. The given uncertainty ranges are largely based on practical experience.

<table>
<thead>
<tr>
<th></th>
<th>Wood</th>
<th>Lignite</th>
</tr>
</thead>
<tbody>
<tr>
<td>Not-dried material flow (kg/h)</td>
<td>3.70 ± 0.10</td>
<td>1.50 ± 0.05</td>
</tr>
<tr>
<td>Moisture content (% , m/m/)</td>
<td>9.5 ± 1.0</td>
<td>11.1 ± 1.0</td>
</tr>
<tr>
<td>Dried material flow (kg/h)</td>
<td>3.35 ± 0.10</td>
<td>1.33 ± 0.05</td>
</tr>
<tr>
<td>Ash content in dried material (% , m/m)</td>
<td>1.10 ± 0.10</td>
<td>33 ± 2</td>
</tr>
<tr>
<td>Carbon content in dried material (% , m/m)</td>
<td>48.8 ± 0.5</td>
<td>41 ± 2</td>
</tr>
<tr>
<td>Carbon flow (kg/hour)</td>
<td>1.63 ± 0.05</td>
<td>0.55± 0.03</td>
</tr>
</tbody>
</table>

Biogenic carbon fraction input material 75 ± 3 %

4.3.2 Biogenic carbon fraction of flue gas CO₂ and raw SNG

Table 4.3 lists the \(^{14}\text{C}_{\text{sample measured}}\) results for the investigated gas samples obtained from the SNG process with the input of only wood particles. The \(^{14}\text{C}_{\text{sample measured}}\) results are very similar between the different investigated carbon components and between the duplicates. The average \(^{14}\text{C}_{\text{sample measured}}\) value matches with all individual measurements within 1-sigma sample measurement uncertainty. The similarity between the duplicates shows that the average \(^{14}\text{C}\) composition of the used wood particles was constant during the sampling period of the two duplicates. The average measured \(^{14}\text{C}\) result of 116.55 ± 0.13 % is used in this study as reference \(^{14}\text{C}\) value for 100% biogenic carbon, \(^{14}\text{C}_{\text{bio}}\).
Table 4.3. $\delta^{13}\text{C}_{\text{sample}}$ and $^{14}\text{C}_{\text{sample\_measured}}$ values, both measured with AMS, of gas samples obtained from the SNG process with only wood particles as input material. The standard deviation in this average value is shown as well. Samples 1 and 2(a/b) were taken simultaneously, as were samples 3 and 4(a/b).

<table>
<thead>
<tr>
<th>Sample</th>
<th>$\delta^{13}\text{C}_{\text{sample}}$ (%)</th>
<th>$^{14}\text{C}_{\text{sample_measured}}$ (%)</th>
<th>± (1σ)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1_Flu gas CO₂</td>
<td>-25.4</td>
<td>116.5</td>
<td>0.4</td>
</tr>
<tr>
<td>2_SNG total gas</td>
<td>-24.8</td>
<td>116.4</td>
<td>0.3</td>
</tr>
<tr>
<td>2a_SNG CO₂ fraction</td>
<td>-13.3</td>
<td>116.7</td>
<td>0.4</td>
</tr>
<tr>
<td>2b_SNG CH₄ fraction</td>
<td>-37.7</td>
<td>116.6</td>
<td>0.4</td>
</tr>
<tr>
<td>3_Flu gas CO₂</td>
<td>-29.3</td>
<td>116.4</td>
<td>0.4</td>
</tr>
<tr>
<td>4a_SNG CO₂ fraction</td>
<td>-13.0</td>
<td>116.6</td>
<td>0.3</td>
</tr>
<tr>
<td>4b_SNG CH₄ fraction</td>
<td>-38.7</td>
<td>116.7</td>
<td>0.4</td>
</tr>
</tbody>
</table>

Reference value 100% bioC: $^{14}\text{C}_{\text{bio}}$ 116.55 ± 0.13

The $\delta^{13}\text{C}_{\text{sample}}$ values in Table 4.3 illustrate the process of isotope fractionation during the SNG process: the CH₄ fraction contains relatively less $^{13}\text{C}$ than the CO₂ fraction. Such (relatively) large fractionation was also observed in biogas samples of several digestion processes (Palstra and Meijer, 2014). This isotope fractionation occurs for $^{14}\text{C}$ as well, but is corrected for, based on the measured $\delta^{13}\text{C}_{\text{sample}}$ values. The close match of all $^{14}\text{C}_{\text{sample\_measured}}$ values in Table 4.3, which all have the same carbon composition, show the validity of the applied isotope fractionation correction. Without the correction for isotope fractionation, the $^{14}\text{C}_{\text{sample}}$ values of samples 1 and 2(a/b) would have been: 116, 116, 120 and 114% respectively, while these differences are not related to differences in biogenic carbon fraction. For a correct application of the $^{14}\text{C}$ method to determine the biogenic carbon fraction for gases, it is therefore essential, especially for gases but also for other materials (Norton and Devlin, 2006; Palstra and Meijer, 2014) that this isotope fractionation correction is always applied (and thus that the $\delta^{13}\text{C}$ value is always determined). Due to this correction, differences in calculated $^{14}\text{C}_{\text{sample\_measured}}$ values can be related to differences in bio-fossil carbon composition only.

To verify whether the lignite batch contained no biogenic carbon (and was therefore 0% biogenic), the $^{14}\text{C}$ values were measured for three subsamples. The average $^{14}\text{C}_{\text{sample\_measured}}$ value of the three investigated lignite subsamples was 0.01 ± 0.04 %, which is background level (this is: no measurable $^{14}\text{C}$ in the sample itself). The lignite was indeed $^{14}\text{C}$ free and contained no carbon from recent biomass materials.
Table 4.4 lists the $^{14}\text{C}_{\text{sampleMeasured}}$ and $f_{\text{Cbio}}$ results for the investigated gas samples obtained from the input of a mixture of wood and lignite with $75 \pm 3\%$ biogenic carbon. Obviously, all gas samples from the wood/lignite mixture have lower $^{14}\text{C}_{\text{sample}}$ values than those obtained with the input of 100% wood. The $^{14}\text{C}_{\text{sample}}$ values of the process flue gases are much lower than those from the raw SNG samples. Compared to the $f_{\text{Cbio}}$ value of the input fuel mixture, the values of the process flue gases are lower and those of the SNG samples are higher. This shows large bio-fossil carbon partitioning in the SNG production process of carbon from different sources (materials).

Table 4.4. $\delta^{13}\text{C}_{\text{sample}}$ and $^{14}\text{C}_{\text{sampleMeasured}}$ values, measured with AMS, and calculated biogenic carbon fractions ($f_{\text{Cbio}}$) of gas samples obtained from the SNG process with a mixture of wood and lignite with $f_{\text{Cbio}} = 75 \pm 3\%$ as input material. Samples 5 and 6(a/b) were taken simultaneously, as were samples 7 and 8(a/b).

<table>
<thead>
<tr>
<th>Sample</th>
<th>$\delta^{13}\text{C}_{\text{sample}}$ (%)</th>
<th>$^{14}\text{C}_{\text{sampleMeasured}}$ (%)</th>
<th>$f_{\text{Cbio}}$ (%)</th>
<th>$\pm$ (1σ)</th>
</tr>
</thead>
<tbody>
<tr>
<td>5_Flue gas CO₂</td>
<td>-25.0</td>
<td>44.5</td>
<td>38.2</td>
<td>0.2</td>
</tr>
<tr>
<td>6_SNG total gas</td>
<td>-26.7</td>
<td>102.5</td>
<td>88.0</td>
<td>0.3</td>
</tr>
<tr>
<td>6a_SNG CO₂ fraction</td>
<td>-13.2</td>
<td>103.0</td>
<td>88.4</td>
<td>0.3</td>
</tr>
<tr>
<td>6b_SNG CH₄ fraction</td>
<td>-40.3</td>
<td>103.5</td>
<td>88.8</td>
<td>0.3</td>
</tr>
<tr>
<td>7_Flue gas CO₂</td>
<td>-24.8</td>
<td>44.1</td>
<td>37.8</td>
<td>0.2</td>
</tr>
<tr>
<td>8_SNG total gas</td>
<td>-27.3</td>
<td>103.0</td>
<td>88.3</td>
<td>0.3</td>
</tr>
<tr>
<td>8a_SNG CO₂ fraction</td>
<td>-14.9</td>
<td>103.5</td>
<td>88.8</td>
<td>0.3</td>
</tr>
<tr>
<td>8b_SNG CH₄ fraction</td>
<td>-36.9</td>
<td>103.9</td>
<td>89.2</td>
<td>0.3</td>
</tr>
</tbody>
</table>

The duplicate sets of the different wood/lignite samples show good agreement, with differences between the $^{14}\text{C}_{\text{sampleMeasured}}$ values for the different fractions that agree within the (purely analytical) 1σ uncertainty in these values. The differences in $^{14}\text{C}_{\text{sampleMeasured}}$ values between the SNG and the separated CO₂ and CH₄ fractions are slightly larger than those observed for the SNG samples from wood (table 4.3). This could be due to the $^{14}\text{C}$ contribution of the small CₓHᵧ fraction to the measured $^{14}\text{C}$ values, if this fraction is more fossil than the other carbon fractions and was not part of the measured separated fractions (not known in this case).

To compare the obtained $f_{\text{Cbio}}$ results of the flue gas CO₂ and raw SNG with the carbon composition of the input materials, contributions to the SNG process of other (“foreign”) carbon sources than the input material should be investigated and, if relevant (that is: with large carbon fraction and/or large difference in $^{14}\text{C}$ value with the sample material), be corrected for. As is explained in chapter 2, the contribution of atmospheric air CO₂ can
become (slightly) visible in the calculated $f_{C_{bio}}$ result if the biogenic carbon fraction in the sample carbon is below 10% (combined with a certain carbon fraction size). The atmospheric air that is used in the SNG process (in the combustion part ‘C’ in Figure 4.1) is the main foreign carbon source that was identified in the investigated SNG process. It contains only 0.04% v/v CO₂. The contribution of this CO₂ to the total CO₂ fraction in the flue gas (15% CO₂) is at most 1:300. As producer gas contains about 20% CO₂ and at most a few % vol. N₂ from air, the relative contribution of CO₂ from air is even smaller than in the flue gas. Hence, the effect of atmospheric CO₂ on the calculated $^{14}C_{sample measured}$ values and $f_{C_{bio}}$ fractions shown in Tables 4.3 and 4.4 (all $>10\% f_{C_{bio}}$) is indeed completely negligible.

According to the results obtained with the $^{14}$C method, the biogenic carbon fractions in flue gas and raw SNG were 38% and 89%, respectively. The $^{14}$C method thus quantifies differences in carbon composition at different stages of the SNG process.

In addition to the published results appendix B.4 gives the results of IRMS $^{13}$C measurements of the different investigated gases and the results of the new SCS system are discussed in more detail.

4.3.3 Bio-fossil carbon partitioning

The calculated biogenic carbon fractions of the flue gas CO₂ and raw SNG samples from mixed bio-fossil input materials show that the flue gas CO₂ contains more fossil carbon than the raw SNG samples. It shows that different carbon materials react differently in the SNG process. In this case, with mixed biogenic and fossil carbon input materials, this has resulted in bio-fossil carbon partitioning. If unknown input materials are used or if flue gas and/or SNG are investigated for verification and certification purposes, separate investigations (using preferably the $^{14}$C method) of the flue gas and SNG are inevitable.

Figure 4.2 gives an overview of the rate of bio-fossil carbon partitioning during different particular steps in the SNG process that results from this study. Bio-fossil carbon partitioning might also occur in the catalytic shift and methanation reactions. In that case it would be likely that CO₂ and CH₄ in the raw SNG would get different biogenic carbon fractions. The results from samples 6a/b and 8a/b in Table 4.4, however, suggest that this effect is minor or non-existent.
Figure 4.2. Overview of bio-fossil carbon partitioning in the investigated SNG production process. Estimated values are indicated with italic font.

Figure 4.2 gives an estimation of the distribution of biogenic and fossil carbon input flows over the different process steps. This distribution is estimated based on the input carbon flows, the $^{14}$C-based biogenic carbon fractions in the flue gas and raw SNG and estimations of tar and dust carbon flows. The amount of dust and its bio-fossil carbon composition were not determined, but it seems reasonable to assume that the dust was relatively rich in fossil carbon. The biogenic carbon fraction of the tar removed by OLGA was not determined either, but is likely to be similar to that of producer gas.

The main partitioning takes place during the gasification. During this step, the released gases are ‘producer gas’ while the remaining material is ‘char’. The amount of remaining char is, among other process-related parameters, influenced by the volatility of the materials. Because the volatility of the wood particles is much higher than that of the lignite particles, the remaining char materials are likely to contain relatively more fossil carbon than the original input materials, whereas the producer gas will contain relatively more biogenic carbon. The difference in determined $^{14}$C-based biogenic carbon fractions between the flue gas CO$_2$ and raw SNG confirms this.
The average biogenic carbon fraction of the carbon components in the producer gas was not determined in this study; it is estimated in Fig. 4.2. The biogenic carbon fraction in the producer gas is expected to be slightly lower than determined in the raw SNG samples, because the removed dust was assumed to be rich in fossil carbon. Still, the mixed tar and dust fraction has a higher biogenic carbon fraction than the input material. In a large-scale production facility, dust and tar would be recycled to the combustion section of the gasifier. In that case, \( f_{C_{bio}} \) of the process flue gas would therefore increase, to about 45%.

In this study a MILENA allothermal gasifier was used which showed particular bio-fossil carbon partitioning for a certain mixture of wood and lignite. With other gasifier types different partitioning results are expected when the same input mixture is used. In other allothermal gasifier types in which more steam is used during the gasification step or that allow char more reaction time with steam or producer gas (such as the Fast Internally Circulating Fluidized Bed (FICFB) gasifier or the Heatpipe Reformer), more char will be converted into producer gas. For these types of gasifiers the \( f_{C_{bio}} \) result in the producer gas will be lower than with the MILENA gasifier, but will still be higher than the \( f_{C_{bio}} \) value of the mixed wood/lignite input material. In gasifier processes in which not only char, but also part of the producer gas or input mixture is combusted to cover the process heat demand, the \( f_{C_{bio}} \) value in the flue gas will increase, but is likely to remain below \( f_{C_{bio}} \) of the input mixture.

In direct gasifiers, combustion and gasification reactions occur in a single reactor, resulting in producer gas diluted by combustion products. If in this process (with a wood and lignite mixture) char is produced, it is expected that the residue will contain more lignite carbon than wood carbon (similar to the char production in the MILENA gasifier). The \( f_{C_{bio}} \) value of the producer gas will then be slightly higher than \( f_{C_{bio}} \) of the input mixture, but is likely to be lower than the value obtained with the MILENA gasifier. If in this direct gasifier all carbon is converted to gaseous products, the \( f_{C_{bio}} \) values of the raw SNG gas and the input material will be identical. For these latter direct gasifiers separate \(^{14}\text{C} \) analysis of the SNG product would not be necessary for determination purposes if the biogenic carbon fraction of the input material is already very well known. However, if the biogenic carbon composition of the input material is unknown (waste materials) or the SNG needs to be verified, the best way to determine the biogenic carbon fraction of the produced SNG for direct gasifiers is by measuring the SNG gas on its biogenic carbon fraction using the \(^{14}\text{C} \) method.
4.4 Conclusions

The applicability of the $^{14}$C method for the quantification of the biogenic carbon fractions at different stages of the SNG production process is demonstrated in this study. The $^{14}$C-based biogenic carbon fractions of flue gas and raw SNG were 38% and 89% respectively if a mixture of wood and lignite with 75% of biogenic carbon was used as input materials. The applied $^{14}$C method makes differences visible in bio-fossil carbon composition at different stages of the SNG process.

The flue gas and raw SNG have very different biogenic carbon fractions compared to the ‘input’ value of 75 ± 3%. This change in biogenic carbon fraction is caused by bio-fossil carbon partitioning during the SNG production process. The main bio-fossil carbon partitioning in this study took place during the gasification of the input material and was related to the large differences between the used wood particles and lignite in volatility and char content. A considerable preference was found for the biogenic input materials to end up as raw SNG, making this fuel product more biogenic and the process flue gas more fossil than the original input mixture.

For the determination, verification or certification of the biogenic carbon fraction in the SNG production process (not to be confused with its biogenic energy content), analysis of each of the process gas streams is inevitable. The $^{14}$C method is probably the most reliable independent method for these purposes.

Acknowledgements

Herman Bodenstaff and Marco Geusebroek are thanked for their contributions to the production of the investigated SNG gas and the sampling of the gases at ECN. Maarten Vervoort, Henk Jansen, Dicky van Zonneveld, Fsaha Ghebru, Henk Been and Marc Bleeker are thanked for their contributions at the CIO to the development of a new gas combustion system, the pre-treatment of the different samples and the $d^{13}$C and $^{14}$C analyses.

This research was financed by a grant of the Energy Delta Gas Research (EDGaR) program. EDGaR is co-financed by the Northern Netherlands Provinces, the European Union, European Fund for Regional Development, the Ministry of Economic Affairs and the Province of Groningen.
Appendix A.4
Applied method for separation of CO₂ and CH₄ fractions in gases and combustion of CH₄

A.4.1 Introduction
In the period 2011-2013, CIO was involved in one of the sub-projects of the EDGaR (Energy Delta Gas Research) project: (A2) AGATE-1. In this sub-project CIO worked on two research topics. The first topic was the investigation of the application of the ¹⁴C method for mixtures of biogas and natural gas and the investigation of specific uncertainties in this method. The results of that study are described in chapter 4. In that study a laboratory set up was developed and used to first separate the CO₂ and CH₄ fractions and then combust the CH₄ fraction to CO₂. The volumes of gas that were pre-treated in that way were between 250 and 500 ml (STP), to obtain enough CO₂ for bio-fossil mixture experiments. These amounts are, however, not necessary for (single) carbon isotope analyses of gases. For ¹⁴C analysis 4 ml of CO₂ per sample is sufficient. Also, the used separation and combustion set-ups had a relatively large volume (> 2 liter) which makes them not suitable for < 50 ml gas samples, due to higher risks of contamination (due to large wall surfaces) and because the amount of CO₂ in the system parts would be too small to be quantified based on the used pressure sensors in the system. Therefore, a new separation and combustion system (SCS) was developed and built in 2013. This new system was used for the SNG samples investigated in this chapter 5. In this appendix A, the used separation and combustion method is described in more detail. The applied method was tested once on a mixture of CO₂ and CH₄ with known and very different δ¹³C values, before it was used for the SNG samples. This test showed that CO₂ and CH₄ were separated well and the combustion of CH₄ gave CO₂ with the right δ¹³C value.

Several control (check) and maintenance aspects of the developed system are still to be investigated. Such as the calibration of the different glass volumes (to be able to calculate amounts of CH₄ and CO₂ in the system) and investigations of the reproducibility of the combustion to find out the number of combustions that can be performed before the CuO oven needs to be oxidized with pure O₂.

A.4.2 Separation and combustion system (SCS) and applied method
Figure A.4.1 gives an overview of the developed system that was used for the SNG samples investigated in this chapter. The numbers 1- 4 show the separation part, combustion part, pumping system and input/storage part, respectively.
A.4.2 Separation and combustion system (SCS) and applied method

A.4.2.1 Separation of the CO₂ fraction

To investigate the carbon isotope values for the CO₂ and CH₄ fractions of gases separately, the CO₂ fraction was first separated. Approximately 50 ml of gas sample was brought in the ‘sample input volume’ of the vacuum pumped separation part (Figure A.4.1 – right upper part). Then a valve was opened to a glass volume in which gas molecules like H₂O were cryogenically trapped (−78 °C with ethanol/dry ice). Another valve was opened to a glass volume that was surrounded with a glass volume filled with melting isopentane. This iso-pentane was first frozen (−196 °C) using liquid nitrogen and then warmed up again by removal of the liquid nitrogen. The melting temperature of the isopentane was approximately -160 °C. At this temperature the main part of the CO₂ fraction was trapped in the glass volume while the CH₄ fraction was not trapped. A second cryogenic trap (196 °C; liquid N₂) was used to trap remaining CO₂ that was not trapped in the iso-pentane trap. The remaining gas with the CH₄ fraction was then cryogenically trapped in a cooled (−196 °C; liquid N₂) 20-mL flask, which was filled with a few gram of molecular sieve 5A. This particular set up was used because experiments of the separation system used in the study of chapter 3, had shown that this second CO₂ trap, between the iso-pentane CO₂-trap and the cooled molecular sieve CH₄ trap, was crucial to trap the
entire CO₂ fraction. Without the second CO₂ trap part of the CO₂ was also trapped in the flask with the CH₄ fraction. The obtained CO₂ in both cryogenic CO₂ traps was mixed together and cryogenically trapped.

The obtained CO₂ fraction was then divided over two 20-mL flasks. The CO₂ of one of these flasks was measured on δ¹³C with a SIRA-10 IRMS. The other flask was used for ¹⁴C measurement. This latter flask contained Sulfix (WAKO, 8–20 mesh) and was heated for one night at 200 °C. It was used to remove sulphur-containing components from the trapped gas as these components hamper a fast graphitization of the CO₂. Biogases often contain traces of sulphur-containing components.

A.4.2.2 Combustion of the CH₄ fraction

The flask with the CH₄ fraction was then moved from the separation part of the system to the combustion part and connected to this vacuum pumped combustion part of the SCS system (Fig. A.4.1, left – lower input entrance). The CH₄ fraction was released from the molecular sieve material by warming the flask with a blower. The gas from the flask was led into a system consisting a CuO-oven (heated at 850 °C), a cryogenic H₂O trap (-78 °C; ethanol/dry ice) and a volume with a magnetic stirrer that pumps the gas in the system from the volume behind the CuO-oven towards the volume before the CuO-oven with a certain flow rate. In this way, the CH₄ is forced several times through the CuO-oven to obtain maximal combustion efficiency and CO₂ yield. After a certain time period, the formed CO₂ fraction in the gas sample was cryogenically trapped (-196 °C; liquid N₂). The combustion of the CH₄ fraction was ended as soon as the pressure in the system did not drop any further (which indicates that no CO₂ is formed and trapped anymore). The remaining gas was pumped away and the trapped CO₂ fraction was let through a vacuum pumped Ag/Cu-oven (450 °C) to remove any formed sulphur and nitrogen oxides before it was trapped in a second cryogenic CO₂ trap (-196 °C; liquid N₂).

Finally the CO₂ was divided over two separated volumes in the system to obtain two samples for ¹³C and ¹⁴C measurements, respectively. The CO₂ was divided over the volume of the second CO₂ trap and the volume to the 20-mL flask plus volume of the flask. The valve between the CO₂ trap and the other volume was then closed. The CO₂ in the volume after the CO₂ trap was then cryogenically trapped in the flask. This flask was removed from the system and a new one was attached to the system and vacuum pumped. Then the CO₂ volume that was still stored in the CO₂ trap was cryogenically trapped in the second flask. The flask for ¹⁴C measurement contained Sulfix and was heated for one night, to remove any sulphur-components that would not have been trapped with the Cu/Ag oven.
Appendix B.4
δ\(^{13}\)C IRMS measurement results of the investigated flue gas and SNG samples

B.4.1 Introduction
To investigate differences in δ\(^{13}\)C values between the different investigated carbon components in the SNG production process, all obtained CO\(_2\) from the gas samples were not only analysed on \(^{14}\)C values with AMS, but also with an Isotope Ratio Mass Spectrometer on δ\(^{13}\)C values. Also the different carbon materials of the input material for the SNG process were analysed on δ\(^{13}\)C with IRMS. The results of these IRMS measurements are given in this appendix as additional information. The applied separation procedure with the new SCS system is discussed based on the measured IRMS δ\(^{13}\)C results for the gas samples. The analytical precision of a IRMS δ\(^{13}\)C measurement is typically ≤ 0.05‰.

B.4.2 Measurement results

<table>
<thead>
<tr>
<th>Sample</th>
<th>IRMS δ(^{13})C(_{\text{sample}}) (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1_Flue gas CO(_2)</td>
<td>-25.4</td>
</tr>
<tr>
<td>2_SNG total gas</td>
<td>-26.3</td>
</tr>
<tr>
<td>2a_SNG CO(_2) fraction</td>
<td>-12.5</td>
</tr>
<tr>
<td>2b_SNG CH(_4) fraction</td>
<td>-37.4</td>
</tr>
<tr>
<td>3_Flue gas CO(_2)</td>
<td>-26.7</td>
</tr>
<tr>
<td>4a_SNG CO(_2) fraction</td>
<td>-12.4</td>
</tr>
<tr>
<td>4b_SNG CH(_4) fraction</td>
<td>-37.8</td>
</tr>
<tr>
<td>5_Flue gas CO(_2)</td>
<td>-24.0</td>
</tr>
<tr>
<td>6_SNG total gas</td>
<td>-27.2</td>
</tr>
<tr>
<td>6a_SNG CO(_2) fraction</td>
<td>-12.8</td>
</tr>
<tr>
<td>6b_SNG CH(_4) fraction</td>
<td>-39.4</td>
</tr>
<tr>
<td>7_Flue gas CO(_2)</td>
<td>-24.1</td>
</tr>
<tr>
<td>8_SNG total gas</td>
<td>-27.3</td>
</tr>
<tr>
<td>8a_SNG CO(_2) fraction</td>
<td>-12.3</td>
</tr>
<tr>
<td>8b_SNG CH(_4) fraction</td>
<td>-38.6</td>
</tr>
</tbody>
</table>
Table B.4.2 Carbon content (% m/m) and IRMS $\delta^{13}$C values of solid input materials (wood, lignite/carbonate, lignite, carbonate)

<table>
<thead>
<tr>
<th>Sample name</th>
<th>% C</th>
<th>IRMS $\delta^{13}$C (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Wood particles_sub_1</td>
<td>44.7</td>
<td>-26.5</td>
</tr>
<tr>
<td>Wood particles_sub_2</td>
<td>45.4</td>
<td>-26.3</td>
</tr>
<tr>
<td>Wood particles_sub_3</td>
<td>44.6</td>
<td>-26.0</td>
</tr>
<tr>
<td>Lignite/carbonate_sub_1</td>
<td>38.6</td>
<td>-23.4</td>
</tr>
<tr>
<td>Lignite/carbonate_sub_2</td>
<td>42.1</td>
<td>-23.6</td>
</tr>
<tr>
<td>Lignite/carbonate_sub_3</td>
<td>38.6</td>
<td>-23.1</td>
</tr>
<tr>
<td>Lignite</td>
<td>59.5</td>
<td>-26.6</td>
</tr>
<tr>
<td>Carbonate_sub_1</td>
<td>12.2</td>
<td>0.13</td>
</tr>
<tr>
<td>Carbonate_sub_2</td>
<td>12.1</td>
<td>0.23</td>
</tr>
<tr>
<td>Carbonate_sub_3</td>
<td>12.1</td>
<td>0.22</td>
</tr>
</tbody>
</table>

Table B.4.3 Composition (in v/v %) of the sampled flue gas and SNG, measured by ECN on sampling dates 25-10-2013 and 28-10-2013. ‘n.m.’ means ‘not measured’.

<table>
<thead>
<tr>
<th>Fuel gas composition</th>
<th>25-10-2013 (%)</th>
<th>28-10-2013 (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>O$_2$</td>
<td>7.4</td>
<td>1.5</td>
</tr>
<tr>
<td>CO$_2$</td>
<td>10.0</td>
<td>15.2</td>
</tr>
<tr>
<td>CO</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>C$_x$H$_y$</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>N$_2$</td>
<td>n.m.</td>
<td>n.m.</td>
</tr>
<tr>
<td>Ar</td>
<td>n.m.</td>
<td>n.m.</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>SNG gas composition</th>
<th>25-10-2013 (%)</th>
<th>28-10-2013 (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>CO$_2$</td>
<td>47.5</td>
<td>47.5</td>
</tr>
<tr>
<td>CH$_4$</td>
<td>40.0</td>
<td>38.5</td>
</tr>
<tr>
<td>H$_2$</td>
<td>3.0</td>
<td>3.0</td>
</tr>
<tr>
<td>N$_2$</td>
<td>5.5</td>
<td>6.0</td>
</tr>
<tr>
<td>Ar</td>
<td>4.5</td>
<td>5.0</td>
</tr>
</tbody>
</table>
B.4.3 Discussion about the separation of CO₂ and CH₄ with the new SCS system based on the measured IRMS δ¹³C values

Based on the results given in table B.4.1 it becomes clear that isotope fractionation mainly occurs in the methanation step of the SNG production process. The δ¹³C values of the separated SNG-CO₂ fractions are very different from the δ¹³C values of the SNG-CH₄ fractions and for both fractions the values are different from the input material. The δ¹³C values of the flue gas CO₂ are relatively similar to the input materials. Combining the measured δ¹³C values of the SNG-CO₂ and SNG-CH₄ fractions with the composition data gives the overall δ¹³C value of each raw SNG sample and should be the same as the measured δ¹³C value of this sample (following eq. B.4.1). Table B.4.4 gives the δ¹³C value of the SNG gas based measurements of this gas and based on the measurement results of the CO₂ and CH₄ fractions combined with composition data (% v/v of CO₂ and CH₄ in the SNG gas):

\[
\delta^{13}C = \left( \frac{v / v\%_{CO_2}}{v / v\%_{CO_2} + CH_4} \right) \delta^{13}C_{CO_2} + \left( \frac{v / v\%_{CH_4}}{v / v\%_{CO_2} + CH_4} \right) \delta^{13}C_{CH_4} \quad (B.4.1)
\]

<table>
<thead>
<tr>
<th>Sample</th>
<th>IRMS δ¹³Csample (%)</th>
<th>δ¹³Csample (%) based on separate fractions</th>
</tr>
</thead>
<tbody>
<tr>
<td>2_SNG total gas</td>
<td>-26.3</td>
<td>-23.9</td>
</tr>
<tr>
<td>6_SNG total gas</td>
<td>-27.2</td>
<td>-25.0</td>
</tr>
<tr>
<td>8_SNG total gas</td>
<td>-27.3</td>
<td>-24.3</td>
</tr>
</tbody>
</table>

The δ¹³C values as determined based on the separately measured raw SNG CO₂ and CH₄ fractions are systematically higher (less negative values) than the values measured in the raw SNG samples (with no separation step in the pre-treatment to CO₂). Higher values can in this case occur if the separate CO₂ and/or CH₄ fractions were not pure or if the measured CO₂/CH₄ v/v% ratio applied in equation B.4.1 was not correct anymore. In the latter case the composition of the SNG gas would have changed, for instance due to non-proportional leakage of the carbon components out of the gas bag during the time period between measurement (= sampling time) at ECN and pre-treatment at CIO, approximately 6-8 weeks later.

The observed differences between the measured and the fraction-based δ¹³C values are too large to contribute them (entirely) to fractionation processes during the separation and combustion steps. Deviations in the δ¹³C value of the CO₂ fraction due to
the presence of not-separated CH₄ are not likely, as the δ¹³C value of the CH₄ molecules is not measured with IRMS. The measured δ¹³C value of combusted CH₄ fraction could be too high if not all CO₂ was separated from this fraction. Table B.4.5 gives the δ¹³C values of the SNG CH₄-fractions that are needed to obtain the measured IRMS δ¹³C values according to equation B.4.1 and using the measured δ¹³C values of the CO₂ fraction and the measured gas composition data. This table also lists the percentage of CO₂ that would be needed in the CH₄-fraction to obtain the measured δ¹³C values in the separated (and combusted) CH₄ fractions. It this is indeed the explanation for the observed discrepancies, it would mean that the separation process would have been far from complete.

Alternatively, we can assume that all measured δ¹³C values of the total SNG gas and the separate CO₂ and CH₄ fractions were correct, but that the composition of the SNG has changed. Table B.4.6 lists the measured volume fraction ratio (relative to the total CO₂ and CH₄ in the gas) of CO₂ and CH₄ and the calculated percentages needed to explain the discrepancies (based on these δ¹³C values). It is clear that in this case significant changes in composition must have taken place.

Table B.4.5. δ¹³C of the SNG CH₄-fractions as expected based on the gas composition and measured δ¹³C of the raw SNG and the SNG-CO₂ fraction. The table also gives the fractions of raw SNG-CO₂ in the measured raw SNG-CH₄ fractions needed to explain the measured δ¹³C for the SNG-CH₄ fraction.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Approximated δ¹³C (%a) of raw SNG-CH₄ fraction</th>
<th>% of raw SNG-CO₂ in raw SNG-CH₄ fraction</th>
</tr>
</thead>
<tbody>
<tr>
<td>2_SNG total gas</td>
<td>-43.3</td>
<td>10.5</td>
</tr>
<tr>
<td>6_SNG total gas</td>
<td>-44.8</td>
<td>9.5</td>
</tr>
<tr>
<td>8_SNG total gas</td>
<td>-45.9</td>
<td>12.7</td>
</tr>
</tbody>
</table>

Table B.4.6. Measured CO₂/CH₄ ratio in the raw SNG samples after sampling and the CO₂/CH₄ ratio in the raw SNG samples pre-treated at CIO after 6-8 weeks after the sampling based on δ¹³C measurement results.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Measured CO₂/CH₄ ratio (%v/%v)</th>
<th>6-8 weeks after measurement CO₂/CH₄ ratio (%v/%v)</th>
</tr>
</thead>
<tbody>
<tr>
<td>2_SNG total gas</td>
<td>54/46</td>
<td>45/55</td>
</tr>
<tr>
<td>6_SNG total gas</td>
<td>55/45</td>
<td>46/54</td>
</tr>
<tr>
<td>8_SNG total gas</td>
<td>55/45</td>
<td>43/57</td>
</tr>
</tbody>
</table>

Either way both tables B.4.5 and B.4.6 show that the influences are very similar for all three cases (even more for the composition change than for the incomplete separation).
Separation tests of the CO₂/CH₄ separation method with a former system (with a similar set up in which larger volumes of gas were handled) and a separation test with the current used system, did not indicate incomplete separation of the CO₂ and CH₄ fractions. It is therefore assumed that non-proportional leakage of CO₂ and CH₄ from the Tedlar gasbags, with more leakage of CO₂ than of CH₄, could very well be the main reason for the observed differences. The time period between sampling and ClO-pretreatment was relatively large (almost 2 months). Contrary to incomplete separation, leakage is not a problem for the ¹⁴C-based biogenic carbon fraction determination of (raw) SNG (CO₂ + CH₄ fraction) or of its separate CO₂ and CH₄ fractions.

B.4.4 Conclusions

The separation procedure of the applied SCS system method should be tested more intensively, to obtain more insight in the completeness and variability of the separation of CO₂ from CH₄ for different gas samples.
Chapter 5

Application of 14C-based methods for fuels, flue gases and bio-based materials − An overview with discussion & outlook