

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

L.P.L.M Rabou (**ECN**)

Sanne W.L. Palstra (**Centre for Isotope Research (CIO),
Energy and Sustainability Research Institute Groningen (ESRIG), University of Groningen**)

Harro A.J. Meijer (**Centre for Isotope Research (CIO),
Energy and Sustainability Research Institute Groningen (ESRIG), University of Groningen**)

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Sanne W.L. Palstra^a, Luc P.L.M. Rabou^b, Harro A.J. Meijer^a

^a Centre for Isotope Research (CIO), Energy and Sustainability Research Institute Groningen (ESRIG), University of Groningen, Nijenborgh 4, 9747 AG Groningen, The Netherlands, s.w.l.palstra@rug.nl; h.a.j.meijer@rug.nl

^b Energy research Centre of the Netherlands (ECN), P.O. Box 1, 1755 ZG Petten, The Netherlands, rabou@ecn.nl

Corresponding author:

Sanne W.L. Palstra, Nijenborgh 4, 9747 AG Groningen, The Netherlands, s.w.l.palstra@rug.nl, +31 50 363 4123.

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 $75 \pm 3\%$ 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.

Keywords: Radiocarbon; SNG, biomass; fuel; bio-methane; carbon

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 bio-methane, 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 [1]. 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 CO_2 containing process streams. The ^{14}C method, in which the carbon isotope ^{14}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 [2-6].

In this study the ^{14}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 [7]. Recently, it has become popular in China, as shown by Ding et al. [8]. 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 [7], 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 [9]. 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. For producers and large purchasers of this kind of mixed bio-fossil SNG it can be of (financial) interest to know the fraction of biogenic methane in the obtained SNG product. For large producers it can also be of interest to know the biogenic fraction of CO₂ containing streams at the SNG-production site. In addition, quantifying the (probably different) partitioning of fossil and biogenic materials along the SNG process will be helpful for the optimization of the SNG production process itself. These purposes require a reliable determination method that quantifies the biogenic carbon fractions in different gases in the SNG process for specific time periods or SNG batches.

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 (flue gas and raw SNG), 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.

2. Methods

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 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. [10], 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 sulfur conversion (HDS) and sulfur removal, a pre-reformer (REF) for conversion of aromatic compounds, and reactors filled with nickel methanation catalysts.

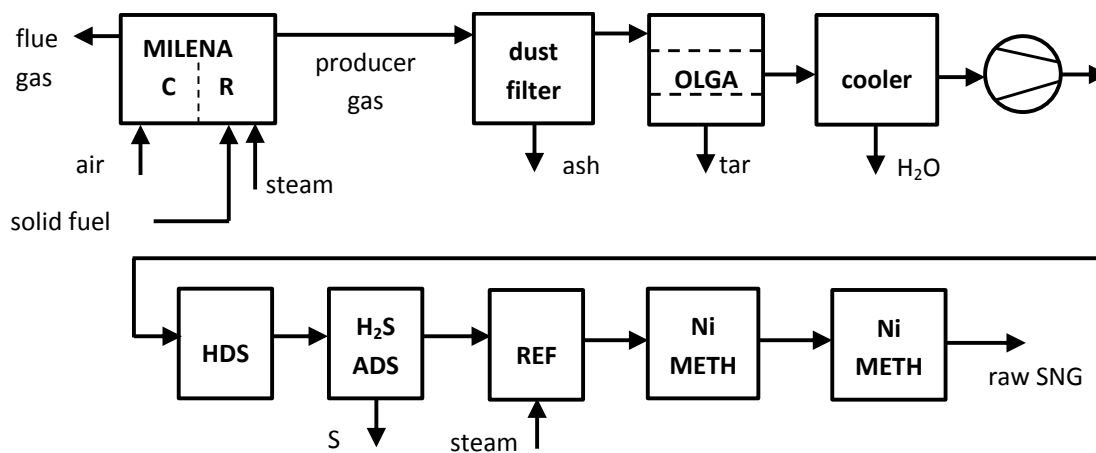


Figure 1. *Simplified SNG production scheme as applied for the experiments by ECN. For a more elaborate scheme see [10].*

The MILENA gasifier consists of two sections, indicated by C and R in Figure 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 1 lists the MILENA producer gas composition for the present experiments.

Table 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%.*

	Wood (% v/v, dry)	Wood + Lignite (% v/v, dry)
CO	29	23
H ₂	27	31
CO ₂	22	26
CH ₄	12.5	10.5
C ₂ H ₄	3.5	2.5
C ₆ H ₆	0.8	0.8
Sum other hydrocarbons	0.7	0.5
N ₂ ^a	4	5

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

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. 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 $\text{CO} + \text{H}_2\text{O} \rightleftharpoons \text{CO}_2 + \text{H}_2$. 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.

The conversion into char and producer gas results in (bio-fossil) carbon partitioning of volatile and solid carbon components. For principally different gasifiers, in which combustion and gasification are not separated, a different (bio-fossil) carbon partitioning in producer gas and flue gas is expected.

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.

2.2 The 14C method

In the ¹⁴C method, ¹⁴C measurement results are used to determine the biogenic carbon fraction in a sample. Carbon consists almost exclusively of the stable isotopes ¹²C (≈99%) and ¹³C (≈1%). The ¹³C/¹²C abundance ratios of different carbon components show some variation due to mass-dependent chemical and physical reactions during the formation of these components: ‘isotope fractionation’. Only ≈10⁻¹⁰ % of the global carbon

atoms are radioactive ^{14}C ($t_{1/2} = 5730$ yr). These atoms are mainly produced in the high stratosphere by nuclear reactions between cosmic ray neutrons and N_2 at a relatively constant rate. ^{14}C from the stratosphere is then oxidized and mixed with the lower atmospheric layers and is taken up by plants as $^{14}\text{CO}_2$ in the photosynthesis process. Biomass-based materials therefore have a ^{14}C concentration that equals that of atmospheric $^{14}\text{CO}_2$. Like the $^{13}\text{C}/^{12}\text{C}$ abundance ratio, the $^{14}\text{C}/^{12}\text{C}$ ratio varies between organic materials due to isotope fractionation. Decay of ^{14}C is another factor that gives differences in $^{14}\text{C}/^{12}\text{C}$ ratio between different carbon components. As soon as an organism dies the uptake of ^{14}C atoms stops and the $^{14}\text{C}/^{12}\text{C}$ ratio decreases in time. Fossil carbon materials, with ages of millions of years, therefore contain no ^{14}C anymore. Due to the detection limit of the ^{14}C measurement techniques, all materials older than ≈ 50.000 years, have carbon with practically spoken 0% ^{14}C .

In the ^{14}C method, the size of dilution of the biomass ^{14}C signal due to mixing with ^{14}C -free fossil carbon is used as a measure for the biogenic carbon fraction, f_{bioc} , in a sample:

$$f_{\text{bioc}} = {}^{14}\text{C}_{\text{sample}} / {}^{14}\text{C}_{\text{bio}} \quad (\text{expressed in \%}) \quad (1)$$

Here, ${}^{14}\text{C}_{\text{sample}}$ is the measured ^{14}C value of a sample material and ${}^{14}\text{C}_{\text{bio}}$ is the ^{14}C value of the biogenic carbon fraction in the sample (reference ^{14}C value for 100% biogenic carbon). Both values are by convention corrected for isotope fractionation based on $^{13}\text{C}/^{12}\text{C}$ measurements ($\delta^{13}\text{C}$ values) and a certain relation in isotope fractionation rates between $^{13}\text{C}/^{12}\text{C}$ and $^{14}\text{C}/^{12}\text{C}$. In Palstra and Meijer [6] a detailed overview is given of the principle of the ^{14}C method, the used symbols (the reported ^{14}C values in this study are $^{14}\text{a}_\text{N}$ values) and units (% for ^{14}C values and ‰ for $\delta^{13}\text{C}$), the calculation of the ^{14}C value from the measured signals, the needed (isotope fractionation) corrections, and the main method uncertainties.

${}^{14}\text{C}_{\text{bio}}$ is in this study the average measured ${}^{14}\text{C}_{\text{sample}}$ value of the gas samples (both process flue gas and raw SNG) obtained from 100% biomass. If a measured ^{14}C value in an unknown sample equals this reference ^{14}C value, then this sample is considered to contain 100% biogenic carbon. The larger the fossil carbon fraction in the sample is, the lower the measured ^{14}C value and calculated biogenic carbon fraction are.

To determine ${}^{14}\text{C}_{\text{sample}}$ values, samples were pre-treated to pure CO_2 , graphitized and their $^{14}\text{C}/^{12}\text{C}$ and $^{13}\text{C}/^{12}\text{C}$ carbon ratios were measured with a ^{14}C -dedicated Accelerator Mass Spectrometer (AMS) at the Centre for Isotope Research, University of Groningen [11]. 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_2H_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 CO_2 - CH_4 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 N_2 , -196°C). After the combustion of the CH_4

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 NO_x and sulfurous components.

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.

All obtained CO₂ samples were graphitized and the ¹⁴C/¹²C and ¹³C/¹²C carbon ratios of the graphite samples were measured with the AMS. 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 and a set of background reference materials to correct for carbon contamination during the pre-treatment and measurement. The AMS measurement results were standardized and normalized to produce ¹⁴C_{sample} values according to the description given by Palstra and Meijer [6]. 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 (see Palstra and Meijer [6] for more information about δ¹³C values and isotope fractionation corrections in gas research).

2.3 Determination of bio-fossil carbon partitioning of solid input materials

To investigate bio-fossil carbon partitioning in the SNG process used, 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.

$$f_{\text{bioC}} = (C_{\text{content wood}} \cdot \text{flow}_{\text{dry_wood}}) / (C_{\text{content wood}} \cdot \text{flow}_{\text{dry_wood}} + C_{\text{content lignite}} \cdot \text{flow}_{\text{dry_lignite}}) \quad (2)$$

Where the C_{content} values of wood and of lignite are the fractions of carbon in the total mass flow (in kg/h) of dried material (flow_{dry}).

3. Results and discussion

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 2.3.

Table 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 2. *Data used to calculate the biogenic carbon fraction according to equation 2, for a mixture of wood and lignite. The given uncertainty ranges are largely based on practical experience.*

	Wood	Lignite
Not-dried material flow (kg/h)	3.70 ± 0.10	1.50 ± 0.05
Moisture content (%)	9.5 ± 1.0	11.1 ± 1.0
Dried material flow (kg/h)	3.35 ± 0.10	1.33 ± 0.05
Ash content in dried material (%)	1.1 ± 0.1	33 ± 2
Carbon content in dried material (%)	48.8 ± 0.5	41 ± 2
Carbon flow (kg/hour)	1.63 ± 0.05	0.55 ± 0.03
Biogenic carbon fraction input material	$75 \pm 3 \%$	

3.2 Biogenic carbon fraction of flue gas CO₂ and raw SNG

Table 3 lists the $^{14}\text{C}_{\text{sample}}$ results for the investigated gas samples obtained from the SNG process with the input of only wood particles. The $^{14}\text{C}_{\text{sample}}$ results are very similar between the different investigated carbon components and between the duplicates. The average ^{14}C value matches with all individual measurements within 1-sigma sample measurement uncertainty. The similarity between the duplicates shows that the average ^{14}C composition of the used wood particles was constant during the sampling period of the two duplicates. The average measured ^{14}C result of $116.55 \pm 0.13 \%$ is used in this study as reference ^{14}C value for 100% biogenic carbon, $^{14}\text{C}_{\text{bio}}$.

Table 3. *$\delta^{13}\text{C}_{\text{sample}}$ and $^{14}\text{C}_{\text{sample}}$ 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).*

Sample	$\delta^{13}\text{C}_{\text{sample}} (\text{‰})$	$^{14}\text{C}_{\text{sample}} (\%)$	$\pm (1\sigma)$
1_Flue gas CO ₂	-25.4	116.5	0.4
2_SNG total gas	-24.8	116.4	0.3
2a_SNG CO ₂ fraction	-13.3	116.7	0.4
2b_SNG CH ₄ fraction	-37.7	116.6	0.4
3_Flue gas CO ₂	-29.3	116.4	0.4
4a_SNG CO ₂ fraction	-13.0	116.6	0.3
4b_SNG CH ₄ fraction	-38.7	116.7	0.4
Reference value 100% bioC: $^{14}\text{C}_{\text{bio}}$	116.55 ± 0.13		

The $\delta^{13}\text{C}$ values in Table 3 illustrate the process of isotope fractionation during the SNG process: the CH₄ fraction contains much less ^{13}C than the CO₂ fraction. Such (relatively) large fractionation was also observed in biogas samples of several digestion processes [6]. This isotope fractionation occurs for ^{14}C as well, but is corrected for, based on the measured $\delta^{13}\text{C}$ values. The close match of all $^{14}\text{C}_{\text{sample}}$ values in Table 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}C method to determine the biogenic carbon fraction for gases, it is therefore essential 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 (beyond measurement uncertainty) in calculated ^{14}C values can be related to differences in bio-fossil carbon composition only.

To verify that the lignite batch contained no biogenic carbon (and was therefore 0% biogenic), the ^{14}C values were measured for three subsamples. The average $^{14}\text{C}_{\text{sample}}$ value of the three investigated lignite subsamples was $0.01 \pm 0.04 \%$, which is background level (this is: no measurable ^{14}C in the sample itself). The lignite was indeed ^{14}C free and contained no carbon from recent biomass materials.

Table 4 gives the $^{14}\text{C}_{\text{sample}}$ and f_{bioc} 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_{bioc} 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. $\delta^{13}\text{C}_{\text{sample}}$ and $^{14}\text{C}_{\text{sample}}$ values, measured with AMS, and calculated biogenic carbon fractions (f_{bioc}) of gas samples obtained from the SNG process with a mixture of wood and lignite with $f_{\text{bioc}} = 75 \pm 3\%$ as input material. Samples 5 and 6(a/b) were taken simultaneously, as were samples 7 and 8(a/b).

Sample	$\delta^{13}\text{C}_{\text{sample}}$ (‰)	$^{14}\text{C}_{\text{sample}}$ (%)	$\pm (1\sigma)$	f_{bioc} (%)	$\pm (1\sigma)$
5_Flue gas CO_2	-25.0	44.5	0.2	38.2	0.2
6_SNG total gas	-26.7	102.5	0.3	88.0	0.3
6a_SNG CO_2 fraction	-13.2	103.0	0.3	88.4	0.3
6b_SNG CH_4 fraction	-40.3	103.5	0.3	88.8	0.3
7_Flue gas CO_2	-24.8	44.1	0.2	37.8	0.2
8_SNG total gas	-27.3	103.0	0.4	88.3	0.3
8a_SNG CO_2 fraction	-14.9	103.5	0.3	88.8	0.3
8b_SNG CH_4 fraction	-36.9	103.9	0.3	89.2	0.3

The duplicate sets of the different wood/lignite samples show good agreement, with differences between the ^{14}C values for the different fractions that agree within the (purely analytical) 1σ uncertainty in the ^{14}C values. 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.

3.3 Bio-fossil carbon partitioning

The calculated biogenic carbon fractions of the flue gas CO_2 and raw SNG samples from mixed bio-fossil input materials show that the flue gas CO_2 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 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 CO_2 and CH_4 in the raw SNG would get different biogenic carbon fractions. The results from samples 6a/b and 8a/b in Table 4, however, suggest that this effect

is minor or non-existent. Figure 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.

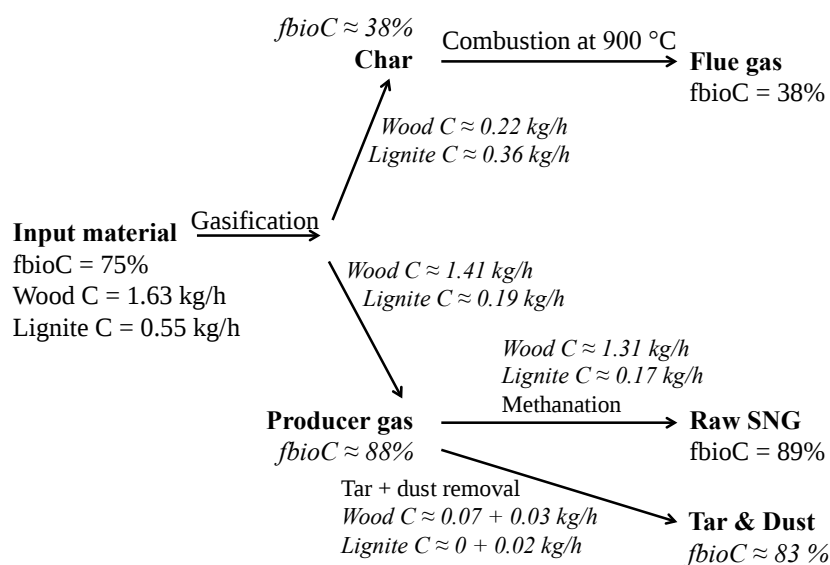


Figure 2. Overview of bio-fossil carbon partitioning in the investigated SNG production process. Estimated values are indicated with italic font.

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 product 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. 2. The biogenic carbon fraction in the producer gas is expected to be slightly lower than determined in the raw SNG samples, because the estimated carbon amounts in tar and dust that were removed from the producer gas contained a higher fossil carbon fraction than the raw SNG. In a large-scale production facility, dust and tar would be recycled to the combustion section of the gasifier. In that case, f_{bioC} of the process flue gas would increase to about 45%.

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% biogenic carbon was used as input material. The applied ^{14}C method makes differences in bio-fossil carbon composition at different stages of the SNG process visible.

The flue gas and raw SNG have very different biogenic carbon fractions compared to the 'input' value of $75 \pm 3\%$. 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 arguably the most reliable independent method for these purposes.

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ECN

Westerduinweg 3
1755 LE Petten
The Netherlands

P.O. Box 1
1755 LG Petten
The Netherlands

T +31 88 515 4949
F +31 88 515 8338
info@ecn.nl
www.ecn.nl

