Introduction

Increased use of materials based on fossil carbon, especially the combustion of fossil fuels, has resulted in large CO₂ emissions into the atmosphere over the last century. Because CO₂ is a greenhouse gas, absorbing thermal infrared radiation, the increased measured temperatures on Earth can be related to the increased concentrations of CO₂ and also other greenhouse gases in the atmosphere. Global warming can induce climate changes and disruption of ecosystems. It threatens life of Earth as we know it today and may have a great impact on human societies in future years.

International policy measures therefore try to stop a further increase of greenhouse gas emissions. One of these measures, focused on CO₂ reduction, is the financial stimulation of fuels and products from biomass-based materials. Biomass-based carbon is part of the global carbon cycle and its uptake by plants and its release by anthropogenic activities (like combustion) are in balance: a CO₂ neutral solution, with in the ideal situation no net increase of atmospheric CO₂. Fossil and biomass-based (‘biogenic’) carbon materials are treated differently in several regulations and because of financial interests, determination methods are needed for producers and authorities to distinguish and quantify fossil and biogenic carbon fractions in fuels, flue gas CO₂ emissions and several ‘bio-based’ products.

The most specific tracer for biogenic and fossil carbon fractions is the radioactive carbon isotope ¹⁴C. Fossil carbon is millions of years old and contains no ¹⁴C anymore due to radioactive decay (the half-life of ¹⁴C is 5730 yr.). Measuring the ¹⁴C amount of fossil carbon would yield a zero, that is background value. This represents 0% biogenic carbon. ¹⁴C measurement of carbon from biogenic material on the other hand, gives a certain ¹⁴C value. This value represents 100% biogenic carbon. Mixtures of fossil and biogenic carbon show ¹⁴C values proportional to the fraction of biogenic carbon, between the zero-value of 0% biogenic carbon and the ¹⁴C value of 100% biogenic carbon. To calculate the biogenic carbon fraction, the ¹⁴C value of a sample material (¹⁴C_sample) is measured and divided by the ¹⁴C value representing 100% biogenic carbon (¹⁴C_bio): fC_bio = ¹⁴C_sample / ¹⁴C_bio.

¹⁴C-based methods to determine biogenic carbon fractions have been applied since the 1950s for different applications, such as aerosol research and food authentication.
More recently (since approximately 10 years), the $^{14}\text{C}$-based methods are also applied to different fuels and flue gas CO$_2$ to distinguish fossil and biogenic carbon in these materials. Although the principle of the $^{13}\text{C}$-based methods is very straightforward, different factors within the methods can affect the size of the calculated biogenic carbon fraction value and thus can cause anomalies in the final obtained result. This differs between different sample materials and also depends on the size of the biogenic carbon fraction in the sample. For optimal application of the $^{14}\text{C}$-based methods for different materials, those factors affecting the final result and their uncertainties need to be known and, if required for the specific application, taken into account and/or minimized.

The main aim of the research described in this thesis was to gain knowledge about the application of the $^{14}\text{C}$ method for different flue gases and fuels and to identify and quantify the main factors influencing the accuracy of calculated biogenic carbon fractions.

$^{14}\text{C}$-based method for flue gas

In a first study, the application of a $^{14}\text{C}$-based method was investigated for flue gas CO$_2$ samples taken from a power plant and a waste incineration plant in cooperation with the Dutch energy company Essent (RWE). At the power plant, coal mixed with biomass (wood pellets) was combusted. The biogenic carbon fraction of the combusted fuels in the power plant was known and the investigated $^{14}\text{C}$-based biogenic carbon fractions could be verified with these data. This kind of verification of the $^{14}\text{C}$ method for flue gas CO$_2$ samples was not published before. The flue gas CO$_2$ was sampled in cooperation with ECN. An ECN-sampler was used in which the CO$_2$ was trapped in an alkaline solution (NaOH). Another series of flue gas samples were sampled with the same sampler at a Dutch waste incineration plant. Variable waste materials, mainly municipal waste, were combusted at this incineration plant. The biogenic carbon fraction of the waste materials at this specific plant was estimated to be approximately 50%, but had not been verified before due to the lack of suitable determination methods.

The $^{14}\text{C}$-based biogenic carbon fractions as determined at the power plant were 10% at the first day and dropped to 5% on the second day after malfunction of one of two biomass suppliers. This decrease in biogenic carbon fraction was directly visible in the $^{14}\text{C}$ signature of the sampled flue gas CO$_2$. The $^{14}\text{C}$-based results showed excellent comparison with the biogenic carbon fractions as calculated based on biogenic and fossil carbon mass input and output data of the power plant. The biogenic carbon fraction determined in the combusted waste materials varied between 46 and 51%.

The $^{14}\text{C}$-based results of the power plant showed that the method as applied to flue gas CO$_2$ samples, gives biogenic carbon fraction results that reflect the compositions of the combusted fuel/materials with high temporal resolution. Hence, the observed variation in the biogenic carbon fractions of the waste incineration plant samples was most likely due to biogenic carbon variations in the combusted waste materials.
Combined with the observed close agreement of the $^{14}$C-based results with the known biogenic and fossil carbon data of the power plant, this study showed the reliability and the sensitivity of the $^{14}$C method applied to flue gas CO$_2$. It also showed the factors that should be taken into account in the calculations for these particular samples: (possible) CO$_2$ contamination during sampling and contribution of (combustion) air CO$_2$ if the biogenic carbon fraction is <10%.

$^{14}$C-based method for biogas and mixtures of biogas and natural gas

In a second project, part of the Energy Delta Gas Research (EDGaR) subproject A2 “Agate-1”, the application of a $^{14}$C-based method was investigated for raw biogas samples and for carbon mixtures from biogas methane and natural gas methane. The focus of the research was on the variation and uncertainties in the $^{14}$C reference values for 100% biogenic carbon ($^{14}$C$_{bio}$) and on quantification of anomalies in the determined $^{14}$C$_{sample}$ values related to the applied isotope fractionation correction method. For the latter investigations, differences in $\delta^{13}$C values between biogas-CH$_4$ and natural gas samples were of interest. $\delta^{13}$C and $^{14}$C values were determined in eight raw biogases from different digestion plants and in three different natural gas samples. For these carbon isotope measurements the CO$_2$ and CH$_4$ fractions in each raw biogas sample were first separated and the CH$_4$ fraction was combusted to CO$_2$. The natural gas samples were combusted to CO$_2$ and then measured on carbon isotopes as well.

The measured $^{14}$C values of the raw biogases were between 102 and 116 pMC. The variation is related to differences between biomass materials their time of growth, and thus in the average time period they have been taking up atmospheric CO$_2$. $^{14}$C$_{bio}$ is therefore not a constant value for biogases and must thus be approximated. To minimize the uncertainty and systematic errors in approximated $^{14}$C$_{bio}$ values, an approach was proposed in which different types of biogases are divided into groups with different $^{14}$C$_{bio}$ values and uncertainties. This group division was based on average time periods of growth (atmospheric CO$_2$ uptake) of the biomass materials used in the production of the particular group of biogases. With this approach the absolute uncertainty in the determined biogenic carbon fraction is between ±0.5% and ±3.5%, depending of the type of biogas.

The measured $\delta^{13}$C values of the raw biogases were between -6‰ and +31‰ for the CO$_2$ fraction of the gases and between -28‰ and -62‰ for the CH$_4$ fractions. This difference in the values between CO$_2$ and CH$_4$ is due to isotope fractionation; it also affects measured $^{14}$C values and should be corrected for. If, however, a correction for isotope fractionation is applied, it can still introduce systematic errors in the calculated biogenic carbon fraction. This is the case if the fossil $\delta^{13}$C contribution has not been left out in the applied isotope fractionation correction method and the biogenic and fossil $\delta^{13}$C values differ considerably. The absolute error in the biogenic carbon fraction is maximal
±2.5%. This happens if the biogenic carbon fraction is 50% and the difference between the biogenic and fossil δ\(^{13}\)C values in the sample material is 50‰ (which is about the maximum value that can occur).

\(14\)C-based method for biogenic and fossil carbon partitioning of a SNG production process

In a third project, in cooperation with ECN and as part of “EDGaR Agate 1” as well, the application of the \(14\)C method was demonstrated for the investigation of bio-fossil carbon partitioning in the production process of Synthetic Natural Gas (SNG). In the applied SNG production process of ECN, solid input material was first converted in a gasifier to so-called “producer gas” and a solid carbon-rich residue (char). The char was combusted with air, giving flue gas with \(\text{CO}_2\) and heat. After removal of tar, dust, sulphur and water, the producer gas was converted into approximately 48% v/v \(\text{CO}_2\) and 40% v/v \(\text{CH}_4\) (‘raw SNG’) in two methanation reactors with nickel catalysts. To investigate carbon partitioning, flue gas \(\text{CO}_2\) and raw SNG were sampled in gasbags. The \(\delta\(^{13}\)\)C and \(\delta\(^{14}\)\)C values were determined for flue gas \(\text{CO}_2\), raw SNG and for the separated \(\text{CO}_2\) and \(\text{CH}_4\) fractions of raw SNG. First, wood particles were used as input material to investigate the \(14\)C-homogeneity of the wood material and to investigate changes in carbon isotope signatures in the SNG production process for 100% biogenic carbon input. Then a 75% biogenic carbon mixture of wood and (fossil) lignite was used as input material.

The measured \(14\)C values were similar for all investigated wood-based samples. This demonstrated that the same carbon sources, from the same input material, end up in both flue gas \(\text{CO}_2\) and raw SNG during the applied SNG production process: no other materials used in the combustion process or in the production process had contributed to the carbon content in the flue gas and the raw SNG. The \(14\)C values of the flue gas \(\text{CO}_2\) and raw SNG with 75% biogenic carbon input were not similar: the biogenic carbon fraction of the flue gas \(\text{CO}_2\) was only 38%, whereas for the raw SNG and its \(\text{CO}_2\) and \(\text{CH}_4\) fractions it was 89%. This indicates bio-fossil carbon partitioning during the conversion of the specific input material (wood with lignite) to producer gas and char in the applied SNG production set up (specific gasification method). Because of differences in volatility between the biogenic and fossil input materials, relatively more biogenic carbon was converted into producer gas and more fossil carbon to char. This case demonstrates the usefulness of the applied \(14\)C-based method in quantifying the biogenic and fossil carbon composition at different stages of a production process.

The application of the \(14\)C-based methods for research and routine measurements

In the final chapter of this thesis (chapter 5), the current and future applications of \(14\)C-based methods for flue gases, fuels and also other materials are discussed. A new group of users of \(14\)C-based method can be identified who do not have experience with \(14\)C
research. New international standards implement $^{14}$C-based methods for these users as simple routine methods to quantify the biogenic carbon fraction for a wide range of sample materials. However, $^{14}$C-based methods are only at their best if sample-specific approaches are applied which take into account those factors influencing the biogenic carbon fraction determination. The new user group prefers accredited laboratories (ISO 17025), while almost all $^{14}$C laboratories experienced with $^{14}$C-based methods for bio-fossil carbon measurement are not. This gives an intriguing mixture of different interests: the interest of just knowing a number, not necessarily accurate but produced according to a standard procedure, or the use of a number that is as accurate as possible to get more insight into a product or process.

The final conclusion of the thesis is that $^{14}$C-based methods can also be used very well to identify and quantify biogenic carbon fractions in new bio-based products and to investigate (chemical) processes, especially if these methods are applied in their best mode. This “best” mode is described and illustrated in the chapters of this thesis.
Samenvatting

Introductie

De toename van het gebruik van materialen met fossiele koolstof, met name de verbranding van fossiele brandstoffen, heeft in de afgelopen eeuw geleid tot grote CO₂-emissies in de atmosfeer. De oceanen en de biosfeer hebben tot nu toe ongeveer vijftig procent van de toegevoegde CO₂ hoeveelheid uit de atmosfeer opgenomen. De andere hoeveelheid CO₂ is in de atmosfeer gebleven en zorgt daarvoor voor hogere CO₂ concentraties.

CO₂ is een broeikasgas, het absorbeert thermische infraroodstraling en houdt daarom warmte vast. De huidige gemiddelde temperatuurtoename zoals gemeten bij verschillende meetstations over de hele wereld, wordt dan ook gerelateerd aan toenames in de uitstoot van CO₂ en andere broeikasgassen. De wereldwijde opwarming van de aarde kan leiden tot klimaatveranderingen en verstoring van ecosystemen. Het bedreigt het leven op aarde zoals we dat vandaag kennen en heeft daardoor sterke invloed op de wijze waarop mensen (kunnen) samenleven.

Internationale beleidsmaatregelen proberen daarom een verdere stijging van de uitstoot van broeikasgassen te stoppen. Een van deze maatregelen, die gericht is op het afremmen van de CO₂-uitstoot, is de financiële stimulering van brandstoffen en producten uit biomassa. Het idee daarbij is dat de koolstof uit de biomassa, in tegenstelling tot de fossiele koolstof, onderdeel is van de mondiale koolstofcyclus en dat de gemiddelde opname van CO₂ door planten en de uitstoot van CO₂ door antropogene activiteiten (bijv. verbranding van biomassa) in evenwicht zijn: een CO₂-neutrale oplossing, met in de ideale situatie geen netto toename van de atmosferische CO₂ concentratie.

Vanwege deze beleidsmaatregelen wordt er in diverse regelgeving onderscheid gemaakt tussen biogene (van biomassa afkomstige) en fossiele koolstof. Doordat verschillende (financiële) belangen mee gemoeid zijn, is er bij overheden en producenten behoefte aan methoden om het aandeel biogene en fossiele koolstof vast te kunnen stellen in bijvoorbeeld brandstoffen, rookgassen en verschillende andere producten.

De meest specifieke tracer van biogene en fossiele koolstoffracties is het radioactieve koolstofisotoop 14C. Fossiele koolstof is miljoenen jaar oud en bevat geen 14C meer als gevolg van radioactief verval (de halveringstijd van 14C is 5730 jaar). Wanneer er 14C metingen worden uitgevoerd wordt er geen signaal in fossiele koolstof gemeten: dit nul-14C.