Characterization of chemical composition of fuel biofractions by different analytical techniques

Antto Pesonen
M.Sc. thesis
27.4.2012
University of Helsinki
Department of Chemistry
Laboratory of Analytical Chemistry
# Contents

Abbreviations ............................................................................................................................ 4

1. Introduction .................................................................................................................................. 6

I. Literary section ................................................................................................................................. 7

2. Radiocarbon, biofuels and radioanalytical techniques ................................................................. 7

2.1. Radiocarbon .................................................................................................................................. 8

2.2. Biofuels ........................................................................................................................................ 11

2.2.1. Environmental issues .................................................................................................................. 12

2.2.2. Fatty acid methyl ester ............................................................................................................... 14

2.2.2.1. Disadvantages of fatty acid methyl ester biodiesel ................................................................. 16

2.2.3. Hydrogenated renewable diesel ................................................................................................. 17

2.2.4. Fischer-Tropsch synthesis ......................................................................................................... 18

2.3. Accelerator Mass Spectrometry .................................................................................................. 20

2.4. Gas Proportional Counting .......................................................................................................... 30

2.5. Liquid Scintillation Counting ........................................................................................................ 32

2.6. Intracavity Optogalvanic spectroscopy ........................................................................................ 40

3. Characterization of fuel biofractions by other analytical techniques ............................................. 42

3.1. Infrared spectroscopy .................................................................................................................... 43

3.2. Fourier-transformation–Raman spectroscopy ................................................................................. 46

3.3. Nuclear Magnetic Resonance spectroscopy ................................................................................. 47

3.4. X-ray spectrometry ....................................................................................................................... 49

3.5. Fluorescence spectroscopy ............................................................................................................ 50

3.6. Gas Chromatography .................................................................................................................... 51

3.7. Liquid Chromatography ............................................................................................................... 53

3.8. Elemental Analyzer ....................................................................................................................... 55

3.8.1 The basis ...................................................................................................................................... 55

3.8.2. The sources of error and problems ........................................................................................... 58
4. Comparison of the different techniques ................................................................. 59

II. Experimental section............................................................................................ 61

5. Samples.................................................................................................................... 62

6. Modification of the Elemental Analyzer ............................................................ 62

7. Sample preparation.................................................................................................. 64

7.1. Closed-Tube-Combustion method................................................................. 65

7.2. Elemental Analyzer combustion method ....................................................... 67

7.3. Graphitization...................................................................................................... 69

7.4. Comparison of the methods ............................................................................. 71

8. Results .................................................................................................................... 71

9. Conclusions............................................................................................................ 78

10. References............................................................................................................. 81

11. Appendices........................................................................................................... 88
Abbreviations

AMS  accelerator mass spectrometry
ANN  artificial neural network
ATR  attenuated total reflectance
Bis-MSB  4-bis(2-methylstyryl)benzene
BP   before present
CTC  closed-tube combustion
DPM  disintegrations per minute
EA   elemental analyzer
EDXRF  energy-dispersive X-ray fluorescence spectrometer
ETBE  ethyl-\textit{tert}-butyl ether
ELSD  evaporative light scattering detector
F-T  Fischer-Tropsch
FAME  fatty acid methyl ester
FFA  free fatty acid
FTIR  Fourier transformation infrared (spectroscopy)
GC  gas chromatography
GCxGC  two-dimensional gas chromatography
GPC  gas proportional counting
HPLC  high performance/pressure liquid chromatography
ICOGS  intracavity optogalvanic spectroscopy
IRMS  isotope ratio mass spectrometer
LC  liquid chromatography
LN  liquid nitrogen
LOD  limit of detection
LOQ  limit of quantification
LSC  liquid scintillation counter
MLR/SPA  multiple linear regression – successive projections algorithm
MS  mass spectrometry
MTBE  methyl-\textit{tert}-butyl ether
NdYAG  neodymium-doped yttrium aluminum garnet
NExBTL  next generation biomass-to-liquid
<table>
<thead>
<tr>
<th>Acronym</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>NIR</td>
<td>near infrared</td>
</tr>
<tr>
<td>NMR</td>
<td>nuclear magnetic resonance</td>
</tr>
<tr>
<td>OGE</td>
<td>optogalvanic effect</td>
</tr>
<tr>
<td>PLS</td>
<td>partial least squares regression</td>
</tr>
<tr>
<td>pM</td>
<td>percent modern</td>
</tr>
<tr>
<td>pMC</td>
<td>percent modern carbon</td>
</tr>
<tr>
<td>ppq</td>
<td>parts per quadrillion</td>
</tr>
<tr>
<td>RID</td>
<td>refractive index detector</td>
</tr>
<tr>
<td>RSD</td>
<td>relative standard deviation</td>
</tr>
<tr>
<td>TCD</td>
<td>thermal conductivity detector</td>
</tr>
<tr>
<td>XRS</td>
<td>X-ray spectrometry</td>
</tr>
</tbody>
</table>
1. Introduction

This thesis is comprised of two distinct but related sections. In the literature review section a thorough review is given in the field of radiocarbon analytics and biofuel characterization. In the experimental section a new method for liquid fuel sample preparation for Accelerator Mass Spectrometric radiocarbon biofraction analysis is presented.

Biofuel analytics is a growing area of analytical chemistry. The production of biofuels has increased by 17 % from the year 2009 to 2010\textsuperscript{1}. Legislation of several countries promotes or dictates the increased use of biofuels.\textsuperscript{2-4} However, to date the actual biofractions of all the biofuels in the market can only be determined by radiocarbon analysis. With radiocarbon measurement it is possible to determine biofractions accurately and reliably. Radiocarbon enters living organisms from atmosphere via photosynthesis and the food chain. After an organism dies, the amount of radiocarbon reduces to half in every 5730 years (half-life) via radioactive decay\textsuperscript{5, 6}. Therefore, fossil material does not contain measurable amounts of radiocarbon, whereas young organic matter contains nearly the contemporaneous atmospheric level of it. By measuring the radiocarbon amount of a liquid biofuel mixture it is possible to calculate the fraction of biological carbon in the sample and therefore to determine the biofuel-fossil fuel mixing ratio.\textsuperscript{7}

Research has been conducted on simple and cheap methods, e.g. infrared spectroscopy, but these methods are limited in their applicability in the whole liquid biofuel range and are typically applicable only to fatty acid methyl ester (FAME) biodiesel or bioethanol determinations,\textsuperscript{8, 9} while radioanalytical techniques have no limitations.

Traditionally, liquid fuel samples for accelerator mass spectrometry have been prepared by the Closed-Tube-Combustion (CTC) method. This method is well known and reliable, but very time- and labor-consuming\textsuperscript{7, 10}. Packing and sealing the sample tubes often takes several hours, after which the sample tubes are combusted in 900 °C for four to ten hours. Actual work time for a preparation of a single sample is approx. 19 hours which usually means three working days, as some processes are performed automatically overnight.

In the experimental section of the thesis, an Elemental Analyzer (EA) sample combustion and collection system was established for liquid fuel sample preparation. The samples are
combusted in Elemental Analyzer and cryogenically collected using a customized sample collection line. Combusting a sample takes only few minutes, and the sample collection is easy and effortless. The actual work time is cut down to eight hours which, in turn, usually mean two working days when considering certain related work. This includes preparing the Elemental Analyzer for analysis, packing the reagents or cleaning the necessary instruments.

The results were compared with the traditional Closed Tube Combustion method and the newly established Elemental Analyzer method was demonstrated to be success. The Elemental Analyzer gave more accurate and repeatable results and the throughput of the system was vastly superior to Closed Tube Combustion, even though currently they both share the same bottleneck which is the graphitization. Also the user-friendliness of the Elemental Analyzer surpasses that of the Closed Tube Combustion.

The experimental work presented in this thesis was performed in the Laboratory of Chronology of the Finnish Museum of Natural History, University of Helsinki, under the guidance of the Laboratory Director, Markku Oinonen.

1. Literary section

2. Radiocarbon, biofuels and radioanalytical techniques

Measurement of radiocarbon contents is a process chain containing several phases. These can include possible sample pretreatment, physical and chemical cleaning, combusting or otherwise converting the sample into CO$_2$, purification of the combustion products, measurement of $\delta^{13}$C, graphitization of the sample, accelerator mass spectrometry (AMS) and finally data processing.

This section will describe the theory behind the radiocarbon, radiocarbon age and isotopic fractionation correction, the different biofuels, the radioanalytical techniques and the Elemental Analyzer. Sample preparation processes are described in section 7.
2.1. Radiocarbon

Carbon has three naturally occurring isotopes, $^{12}$C, $^{13}$C and $^{14}$C. $^{12}$C and $^{13}$C are stable isotopes and $^{14}$C, also known as radiocarbon or C-14, is radioactive with a half-life of 5730 ±30 years. $^{12}$C is by far the most common isotope accounting for 98.89 % of all atmospheric carbon on Earth. 1.1 % of the carbon is composed of $^{13}$C and $^{14}$C occurs in trace amounts with a fraction of approximately $1 \times 10^{-10}$ %.\(^5\)\(^,\)\(^11\)

Radiocarbon is created in the atmosphere indirectly by high-energy cosmic radiation. Cosmic radiation is absorbed by atmospheric molecules in nuclear reactions and this process creates several types of short-lived particles, including thermal neutrons. Thermal neutrons will react with atmospheric $^{14}$N resulting in the formation of $^{14}$C. Radiocarbon is quickly oxidized forming $^{14}$CO$_2$. These reactions are shown below.\(^6\)\(^,\)\(^12\)

$$n + ^{14}_7N \rightarrow ^{14}_6C + p$$

$$^{14}C + O_2 \rightarrow ^{14}CO_2$$

Radiocarbon enters the biosphere by photosynthesis. Photosynthetic plants take the CO$_2$ from the air and the radiocarbon eventually ends up in plant organic compounds and is transported to the rest of fauna and flora. The amount of radiocarbon in organic tissue remains in equilibrium as long as the animal or plant is alive because the decaying radiocarbon is continuously replaced by eating plant or animal tissue or directly by photosynthesis. When the animal or plant dies, this process stops and the radiocarbon stored in the tissues of the dead animal or plant begins to decay.\(^5\)\(^,\)\(^6\)

Radiocarbon analysis was pioneered by Willard Libby in the 1940s and 1950s. He postulated the formation of radiocarbon in atmosphere by cosmic radiation in 1946.\(^13\) After this it was quickly realized that radiocarbon will be detectable in animals and plants.\(^14\) Libby published several papers over the years and he was awarded the Nobel prize in chemistry for his work in this field in 1960.

The basis for modern radiocarbon data processing was laid out in 1977 by Minze Stuiver and Henry Polach. Although their paper is focused on old gas proportional counting, the basis remains the same as in the newer systems.\(^15\)
Latest radiocarbon data processing methods include Bayesian analysis which has been pioneered by Vesa Palonen and Pertti Tikkanen from University of Helsinki, Department of Physics.\textsuperscript{16}

In the field of radiocarbon analytics, the radiocarbon amount in a sample is usually expressed as percent modern carbon (pMC)\textsuperscript{15}. Alternatively, one could use expression of Fraction Modern (F)\textsuperscript{17}. In this work the unit of pMC is preferred, however.

Biofraction of the sample is obtained by $^{14}$C balance equation. Radiocarbon content of two-component mixture is defined as

$$pMC_{\text{mixture}} = F_{\text{bio}} pMC_{\text{bio}} + (1 - F_{\text{bio}}) pMC_{\text{foss}}$$  \hspace{1cm} (1)

where $pMC_{\text{mixture}}$ is the measured radiocarbon content of the sample, $F_{\text{bio}}$ is the biofraction of the sample, $pMC_{\text{bio}}$ is the radiocarbon content of biological component and $pMC_{\text{foss}}$ is the radiocarbon content of the fossil component. This equation is rearranged as

$$F_{\text{bio}} = \frac{pMC_{\text{mixture}} - pMC_{\text{foss}}}{pMC_{\text{bio}} - pMC_{\text{foss}}}$$  \hspace{1cm} (2)

and biofraction of the sample is obtained.\textsuperscript{7}

The traditional radiocarbon age of the sample using AMS measurements is defined as\textsuperscript{17}

$$C_{\text{uncorrected}} = -\tau \ln \left( \frac{\frac{14}{12}}{\frac{13}{12}} \left[ \frac{1950}{\frac{13}{12}} \right] \right)$$  \hspace{1cm} (3)

where the numerator is the $^{14}$C/$^{13}$C ratio measured from the sample and the denominator is the same ratio measured from a standard. $\tau$ is also known as Libby mean-life and it is the average lifetime of $^{14}$C atom, 8033 years (based on an old, inaccurate half-life of radiocarbon). The radiocarbon age is also corrected for isotopic fractionation by $\delta^{13}$C measurement. The measurement is performed typically by isotope ratio mass spectrometry (IRMS) and $\delta^{13}$C is defined as

$$\delta^{13}C_{\text{sample}} = \left[ \left( \frac{R_s}{R_{st}} \right) - 1 \right] \times 1000$$  \hspace{1cm} (4)

where $R_s$ and $R_{st}$ are the ratios of $^{13}$C/$^{12}$C in the sample and in the standard.\textsuperscript{18}
Radiocarbon age (corrected for fractionation) can also be defined as

\[
C_{\text{corrected}} = -\tau \ln \left( \frac{0.975}{(1 + \delta^{13}C_x)^{14}C/13C_x} \right) \]

where \((14C/13C)_x\) is the \(^{14}\text{C}/^{13}\text{C}\) ratio measured from the sample, \((14C/13C)_{\text{HOxII}[17,8]}\) is the \(^{14}\text{C}/^{13}\text{C}\) ratio measured from the Oxalic acid standard and \((\delta^{13}C)_x\) is the \(^{13}\text{C}\) value of the sample.\(^{19}\) This equation will give the age of the sample in years BP (Before Present). The year 1950 was agreed to be the “zero point” for radiocarbon age determinations and the age of the sample in years BP mean the difference from the “zero point”. For example the age 0 BP means the year 1950 and the age 100 BP means the year 1850 in radiocarbon years. It must be noted that the above equations (3) and (5) use the wrong, old half-life of radiocarbon (5568 years).

In addition, the amount of radiocarbon in the atmosphere has varied during the past years due to changes in the activity of the sun, composition of the atmosphere, industrialization and finally the atmospheric nuclear tests. Therefore a calibration is required to convert the radiocarbon age to calendar years.\(^{20}\) The calibration procedures have been implemented in various free software packages and one of the most popular calibration software is OxCal.\(^{21}\)

The actual radiocarbon amount during the Holocene period has been determined via dendrochronologically dated wood tree rings.\(^{22}\) Because of this variation one will usually not get an absolute age value or a Gaussian distribution. Instead the calibrated age has a certain kind of probabilistic distribution. An example of a calibrated sample is shown in figure 1.
Figure 1. An example of a calibrated age of an archaeological sample from 14\textsuperscript{th} century. OxCal software used in calibration.\textsuperscript{21} Two clear peaks (marked grey) of calendar year probability distribution are the result of the initial age (marked red) and its connection to the calibration curve (marked blue).

It can be seen in the figure that the radiocarbon calibration curve has a slight peak during the year 1385. This peak causes the initial calendar year probability distribution to be separated into two different peaks.

\section*{2.2. Biofuels}

The use of renewable liquid fuels in transportation has greatly increased during the last ten years due to eventual depletion of fossil fuels and the political pressure connected to this and to the climate change mitigation. Many governments pay subsidies or give tax reductions for biofuel production. There is a substantial political pressure in the European Union and in the United States for promotion of renewable energy sources. In the EU this is dictated by the EU Directive 2009/28/EC and in the USA by the Energy Policy Act of
On the other hand, some biofuels, especially FAME biodiesel and bioethanol, can even be harmful for the car engine in high concentrations. The most common liquid biofuels used in transportation are bioethanol, FAME biodiesels and NExBTL-type hydrogenated biodiesels. The fuel produced by transesterification is commonly called biodiesel and it is the first generation biodiesel. Fuels such as NExBTL which are produced by hydrogenation, are commonly called renewable diesel or green diesel to differentiate them from the FAME biodiesels. They are also called the second generation biofuel. Finally biofuels based on Fischer-Tropsch synthesis (F-T method) are third generation biofuels but they are not yet produced in large quantities. The energy-wastefulness of the biofuel production processes decrease as the generations increase. Bioethanol on the other hand is very widely used in gasoline fuel blends and is the most produced biofuel currently. Bioethanol can be produced from e.g. sugarcane or other biomass via fermentation. The following section will briefly describe the production processes and differences of the three biodiesel generations.

2.2.1. Environmental issues

It must be noted, however, that there is also significant controversy connected to the increased use of biofuels. It has been reported by several research groups that land use changes, when cropland, rainforest or peatland is converted into e.g. oil palm plantations, greatly increase the greenhouse gas emissions for several decades and this “carbon debt” is then slowly paid away. The payback time can be estimated to be as high as centuries. Another side effect from the land use changes is the increased food price, when food crops such as corn is converted into bioethanol instead of producing food for the population. The land use change effects are demonstrated in figure 2.
Figure 2. The carbon debt estimates of nine different scenarios. A. Carbon debt including aboveground and belowground CO₂ emissions, B. proportion of carbon debt connected to biofuel production, C. green house gas emission reductions from biofuels annually, D. total payback time of the carbon debt.²⁷

As can be seen from the figure, e.g. for Indonesian palm biodiesel produced from former tropical rainforest the carbon debt time is 86 years when considering the conversion of native ecosystems and the annual repayment.
2.2.2. Fatty acid methyl ester

FAME-type biodiesels were the first generation of biodiesels to go into wide production. The production process of a FAME biodiesel is shown in figure 3.

**Figure 3.** The flowchart of FAME production process.$^\text{34}$

FAME biodiesel is produced via transesterification reaction of fats and oils such as soybean or palm oil or used vegetable frying oil with alcohols, usually methanol (ethanol can also be used). The transesterification reaction is usually catalyzed by a suitable catalyst. Most common catalysts are either basic or acidic catalysts, such as NaOH, KOH and CH$_3$ONa or H$_2$SO$_4$, H$_3$PO$_4$ and CaCO$_3$. The transesterification reaction is shown in figure 4.$^\text{35}$
Other options for catalysts are biocatalysts such as an immobilized lipase enzyme or heterogeneous catalyst systems containing two catalysts and usually an additive co-solvent, or a non-catalyst system such as supercritical methanol transesterification process. All the different catalyst options have their advantages and disadvantages.\textsuperscript{34}

Usually the alkali catalytic method is applied. However, if the free fatty acid (FFA) concentration is high, they must first be removed via acid catalytic method. FFAs disturb the transesterification reaction and decrease the quality of the end product by forming soaps and water with basic catalysts. The amount of FFAs can vary depending on the feedstock used to produce biodiesel. If the FFA content is more than 1\% then the acid catalytic method is applied.\textsuperscript{34}

The catalysts are needed because methanol is not very soluble in oils. Using suitable catalysts one can increase the solubility of the methanol and therefore the reaction rate. The reaction rate is also affected by temperature. A temperature just below the boiling point of the alcohol is chosen, in the case of methanol usually 60 °C.\textsuperscript{34}

Recently it has also been discovered that ion exchange resins are very good heterogeneous catalysts. Especially when the ion exchange resin catalyst is coupled with microwave-assisted transesterification, instead of oil bath heating, the final yields can be up to 96.3\%. The resin is much easier to separate from the FAME by centrifugation. The resins can also be regenerated and used up to 7 times before conversion percentages start to drop.\textsuperscript{36}
2.2.2.1. Disadvantages of fatty acid methyl ester biodiesel

FAME biodiesel is a widely produced biofuel and the most common of the diesel biofuels. Unfortunately FAME fuel blends have their downsides. Firstly, the mixing ratios with FAME biodiesel are typically quite low. This is due to the fact that 100% FAME biodiesel is not a good fuel. The biodiesel causes engine degradation in long term. FAME fuels are not as resistant to oxidation as petrodiesel and increased oxidation can cause the fuel to precipitate. Sedimentation and oxidation promote the breakdown of fuel injection systems. In addition, the sedimentation and oxidation mean that the fuel must be used relatively quickly after its production and cannot be stored for long periods of time.

Since the chemical and physical properties of FAME biodiesel are different from the petrodiesel, there are certain differences in how the biodiesel combusts. This causes e.g. a so called “biodiesel NO\textsubscript{x} effect”. In 20% biodiesel blend a 2-4% increase in NO\textsubscript{x} emissions is detected. This increases so, that in 100% FAME biodiesel NO\textsubscript{x} emissions are increased by 10%. It must be noted, however, that the diesel particulate matter and soot emissions are decreased and are not as mutagenic as soot emissions from fossil diesel. Soot from biodiesel is more reactive and is therefore oxidized more efficiently into less harmful form.

It is a fact that not even 100% FAME is really 100% renewable. This is because FAME contains methyl group from methanol and the methanol is almost always originated from fossil sources due to a low production cost. This must be taken into account when calculating the final biofraction percentages. Furthermore, the production of methanol from natural gas is energy-consuming and this reduces the environmental friendliness of the end product.
2.2.3. Hydrogenated renewable diesel

Diesel made by hydrogenation is also called renewable or green diesel. One example of diesel fuels of this group is the Next Generation Biomass-to-Liquid (NExBTL) diesel fuel developed by Neste Oil Ltd. Despite that the fuel is called “biomass-to-liquid” the feedstock is vegetable oil, a refined product, not biomass.

Renewable diesel is produced from vegetable oil triglycerides. An example of the molecule structure of a triglyceride is shown in figure 5. In the FAME production the left-side carbon skeleton structure seen in figure 5 is converted into glycerol which has limited commercial use. However, in hydrogenation diesel production the glycerol is converted into propane which is a useful byproduct.\(^\text{39}\)

![Figure 5](image)

**Figure 5.** An unsaturated fat triglyceride. Red structure: glycerol, blue structure: palmitic acid, yellow structure: oleic acid, green structure: alpha-linolenic acid.

The production process of hydrogenated diesel fuel is shown in figure 6. Most common feedstocks are palm oil, rapeseed oil, waste oils, soybean oil, tallow, camelina oil and jatropha oil. Currently the most profitable feedstock is palm oil. Oil palm has the greatest yield of oil per hectare than any other feedstock. In addition the palm oil is suitable for diesel production due to low sulfur content and the composition of fatty acids.\(^\text{40}\)
Figure 6. The production process of hydrogenated renewable diesel.

Hydrogenated renewable diesel has several benefits over FAME biodiesel. Firstly, the chemical composition is much closer to petrodiesel. This allows for better performance of the engine. Secondly, the cetane number is very high. Cetane number for diesels is the same as octane number for gasoline; the higher, the better. It is a measure of the combustion quality of the fuel. For example, petrodiesel has a cetane number of 40, FAME biodiesel 50-65 and hydrogenated renewable diesel up to 90. In addition, hydrogenated diesel can be stored for long times, unlike FAME biodiesel. When combusted in an engine, hydrogenated diesel yields less harmful soot emissions, less nitric oxide emissions and less sulfur dioxide emissions compared to petrodiesel.

2.2.4. Fischer-Tropsch synthesis

The Fischer-Tropsch (F-T) is the third generation biodiesel production process. F-T synthesis was invented in Germany in 1920s by Franz Fischer and Hans Tropsch and it was extensively used in Germany during the World War 2 to produce fuel for the German military which suffered from the lack of fossil fuels at the time.
After World War 2 the research and production of F-T products was phased out in nearly all countries due to a cheap production of oil and high production costs of the F-T fuels. One exception to this was South Africa during its isolation due to apartheid, which turned to F-T to produce its fuel.\textsuperscript{42}

Fischer-Tropsch synthesis is a series of reactions which convert carbon monoxide and hydrogen into hydrocarbons. The carbon monoxide can be produced from several feedstocks, which can be either fossil, such as coal, or biological, such as vegetable oils or woodchips.\textsuperscript{43-45} The schematic of F-T synthesis reactor is shown in figure 7.

![Figure 7. The Fischer-Tropsch synthesis process; a. A F-T reactor system. b. Layout of the reactor tube.\textsuperscript{43}](image)

The carbon of the feedstock material is first converted into coke, impure carbon, via pyrolysis. After this, carbon monoxide is synthesized by gasification. Gasification is a reaction where the feedstock is subjected to high temperatures (approx. 700 °C) with excess steam but no oxygen.\textsuperscript{43} In these conditions, the CO is formed as by reaction:

\[
C + H_2O \rightarrow CO + H_2
\]
After this the synthetic gas, also called syngas or synthgas, the mixture of carbon monoxide and hydrogen, is converted into alkanes.\textsuperscript{43} The F-T synthesis reaction can be defined as:

\[ n\text{CO} + (2n + 1)\text{H}_2 \rightarrow C_n\text{H}_{(2n+2)} + n\text{H}_2\text{O} \]

The properties of the fuel produced by F-T synthesis are similar to that of the fuel produced by hydrogenation. This is due to the similarity of the molecular composition of the fuels.\textsuperscript{44, 45}

### 2.3. Accelerator Mass Spectrometry

Accelerator Mass Spectrometry (AMS) is a highly sensitive analytical method for the determination of analytes in parts per quadrillion (ppq) levels. These are extremely low concentration levels and effectively mean the concentration of one atom in $1 \times 10^{15}$ atoms.\textsuperscript{11, 14} C appears in living organisms in very low concentrations, usually under 1 ppt \textsuperscript{46}, and therefore the AMS is one of the few methods available for the accurate determination. Other methods include liquid scintillation counting (LSC), gas proportional counting (GPC) and Intracavity Optogalvanic Spectroscopy (ICOGS). LSC and GPC are radioanalytical methods and measure decay of the radioactive nuclei. AMS measures the atoms in a similar way as a common MS system.

The primary parts of the AMS are the ion source, the accelerator and the detector. The sample molecules are ionized and atomized in the ion source, after which they are accelerated into very high energies, usually into few million of electron volts. The accelerated ions are then filtered with different fields and counted in a detector. The comparison of MS and AMS systems is demonstrated in figure 8.\textsuperscript{11}
AMS is not only $^{14}$C-specific method. At least 30 different isotopes have been measured by AMS. Radiocarbon measurements are still the most common ones and different applications include archaeology, environmental sciences, atmospheric and aerosol studies, medical sciences and industrial power plant fuel monitoring.\textsuperscript{11}

There are different types of AMS equipment. Miniaturization of AMS equipment has been a rising trend in field. Most modern AMS equipment can fit into normal laboratory, while the older AMS such as the accelerator of University of Helsinki is a large three-storied device. The smaller machines are cheaper but the background levels are higher than in larger machines. The larger units also suffer from higher complexity.\textsuperscript{11} This section mainly focuses on similar units as the accelerator in Division of Material Physics, Department of Physics, University of Helsinki. The accelerator is of type TAMIA 5 MV Tandem Accelerator.

The more specific layout of Helsinki AMS is presented in figure 9. The ion source is the first component of the AMS. In the ion source, the sample is ionized via caesium sputtering. Positive caesium ions are bombarded in the graphite sample and carbon atoms
are sputtered out. Carbon atoms are ionized, are accelerated towards accelerator by electrostatic field and are injected into tandem accelerator.\textsuperscript{11}

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{ams_schematics.png}
\caption{Schematics of Helsinki AMS.\textsuperscript{11}}
\end{figure}

In the tandem accelerator the carbon ions are accelerated into energies of 2-3 MeV. Unwanted ions, molecules and atoms either will not enter the accelerator or will be
discarded by one of the many electrostatic or magnetic fields before the detector. Only chosen mass per charge ratio will end up to the detector. The detector is a high-resolution energy analyzer and ion-implanted silicon detector which the sample ions will hit.\textsuperscript{11}

Nowadays AMS is one of the two most popular methods for radiocarbon determination. The advantages of AMS in comparison to other methods are its sensitivity and accuracy. The disadvantages are labor-intensive sample preparation and large, complex and costly equipment. AMS has been used for radiocarbon measurements since 1977 and it has been applied to different research areas ranging from dating archaeological iron samples, soil studies and measuring $^{14}$C-labeled pharmaceutics from biological samples in cancer studies.\textsuperscript{47-49}

Research group of Reddy \textit{et al.} were the first to publish a radiocarbon measurement based method for determination of biodiesel blending ratios. The paper was published in 2008 in Environmental Science \& Technology.\textsuperscript{50}

Research group collected 44 different samples. In those samples three were fossil petrodiesel, 9 samples were commercial 99.9-100 % FAME biodiesels, four were blends made in laboratory, 19 were FAME biodiesel blends ranging from 2 to 20 % and four were blends made by the research group mixing petrodiesel and 100 % FAME biodiesel. The samples were collected from different distributors in 2006-2007. Reddy \textit{et al.} measured the fuel blends prepared in the laboratory and plotted a correlation curve from the results. The plot is shown in figure 10.\textsuperscript{50}

The samples were combusted into CO$_2$ which was in turn converted into graphite. The graphite samples were then sent to National Ocean Sciences Accelerator Mass Spectrometry (NOSAMS) facility for radiocarbon measurements\textsuperscript{51}.
Figure 10. a. Measured radiocarbon content vs. known biopercentages (V/V) of prepared fuel blends. b. Total propagated error in biopercantage (B*).\textsuperscript{50}

After this Reddy et al. determined how well the advertised biopercentages of commercial fuel samples matched the actual, measured values. Figure 11 demonstrates the advertised values vs. the measured values. The full results of Reddy et al. can be found in appendix 1.\textsuperscript{50}
Figure 11. Advertised biodiesel percentages vs. measured values. Only 2 – 20 % biodiesel samples are shown.\textsuperscript{50}

It was seen that blending errors occur with a large margin. The worst example was one 20 % biodiesel sample which was measured to have been blended into 74.4 % instead. In addition, there were several 20 % biodiesels which in truth had blending percentages below 20 %, down to 10.3 %. Reddy \textit{et al.} reported an error of 1 %.\textsuperscript{50}

When taken into account that high FAME biodiesel percentages can deteriorate the car engine\textsuperscript{23, 37}, this variability can be seen as vastly inaccurate and even irresponsible. The lower-than-reported –values on the other hand could even be seen to be in disagreement of current directives and laws.\textsuperscript{3, 4}

Oinonen \textit{et al.} measured the biopercentages of several NExBTL biodiesel blends in 2009.\textsuperscript{7} The samples were prepared according to ASTM D6866-06a standard.\textsuperscript{52} The sample preparation process is more thoroughly explained in section 7.1.

The biodiesel and gasoline samples were acquired from Neste Oil Ltd and on the biodiesels the blending percentages varied from 0 to 100 % of renewable diesel. The gasoline samples were blended with ethyl-\textit{tert}-butyl ether (ETBE) and bioethanol. The ETBE contained 1/3 of biobased carbon. The sample sizes were 1-4 mg of fuel and the radiocarbon content of the graphites was measured at Uppsala Tandem Laboratory.\textsuperscript{7} The
full results of Oinonen et al. can be found in appendix 2. The correlation of the measured biopercentages for 17 diesel samples vs. the weighed values is shown in figure 12.

![Figure 12](image.png)

**Figure 12.** The measured biopercentages vs. the weighed values of 17 diesel samples. The weighing was made by Neste Oil Ltd.  

Oinonen et al. also tried to develop a sample combustion line based on injection of the fuel sample into an oven. The line suffered from uneven combustion most likely due to the geometry of the oven chamber. The schematic of the combustion line is shown in figure 13.  

![Figure 13](image.png)

**Figure 13.** Schematics of the fuel combustion line used by Oinonen et al. 1. Molecular sieve tube, 2. oven, 3-7. valves, 8. water trap, 9. U-tube, 10, 11, 15. pressure meters, 12, 16. pressure meter central units, 13. connection for gas ampoule, 14. turbo pump.
Using the Closed-Tube-Combustion sample preparation method, Oinonen et al. reported an error of $< 0.5 \%$, good correlation, as seen in figure 12, and standard deviation below 0.2 \%.

In 2002, Buchholz et al. used AMS to determine emissions of a diesel engine from bioethanol-diesel blends. They monitored particulate matter, unburned hydrocarbons and carbon monoxide emissions from the engine and determined the origin or the carbon atoms by AMS radiocarbon measurements. The group reported a small elevation of radiocarbon levels in certain samples and noted that this was likely due to atmospheric CO$_2$ leaking into their collection bag.

The group concluded that AMS gave means to determine the origin of the monitored emissions. They noted that by knowing the origin of the emissions, combustion modelers were given better insight into the most emissive chemical structures in fuels.

In 2004, Buchholz et al. again determined particulate matter, unburned hydrocarbons, carbon monoxide and carbon dioxide emissions from diesel engines. They combusted bioethanol-diesel blends and fossil diesel fuel labeled with radiocarbon in diesel engine and collected the emissions. The radiocarbon labels were specifically bonded to different chemical groups in order to monitor their emissivity.

Buchholz et al. concluded that by labeling specific diesel components with radiocarbon it was possible to determine the behavior of different groups when combusted. Again, they noted that the data was valuable for combustion modelers and gave insights into most emissive chemical structures. In addition, the results of the diesel labeled with radiocarbon suggested that neighboring atoms influenced the formation of combustion products.

In addition to liquid biofuel determinations, AMS has been used to determine biofractions of several other sample materials. These include radiocarbon analyses of airborne particulate matter and aerosols, biocarbon determinations of different chemicals and flue gases.

Heal et al. measured radiocarbon levels of airborne particulate matter in 2011. The research group collected samples at an urban site in Birmingham, United Kingdom. The group measured $^{14}$C content in total carbon and in elemental and organic carbon fractions. The group reported that there was no seasonality in the data and the levels were constant throughout the year. The elemental and organic carbon fractions are shown in figure 14.
Heal et al. concluded that approx. 50% of UK particulate matter carbon was of contemporary origin. The group confirmed that soil organic carbon had a large presence especially in air masses passing over land.

In 2012, Sun et al. collected similar aerosols at a rural site in Beijing. The group measured contemporary carbon levels in total carbon and elemental carbon by AMS. The group reported that contemporary carbon fraction in total carbon ranged from 0.30 to 0.38 in winter and from 0.31 to 0.44 in summer.\(^56\)

The group compared their results to similar locations across the world and concluded that their site was more influenced by anthropogenic emissions. The group suggested that this was due to coal combustion in the nearby areas.\(^56\)

Funabashi et al. studied several chemical products in 2009. They determined the biomass carbon ratios of different polymers, starches, cellulose, calcium carbonate, charcoal,
ethanol and polymer blends by AMS. The group prepared their samples according the ASMT D6866 standard. An example of biomass carbon ratios of polymers and monomers is shown in table 1.\textsuperscript{10,57}

### Table 1. Biomass carbon ratios of monomers and polymers by Funabashi et al.\textsuperscript{57}

<table>
<thead>
<tr>
<th>Entry</th>
<th>Material</th>
<th>Origin</th>
<th>Shape</th>
<th>Δ^{14}C</th>
<th>pMC</th>
<th>Biomass carbon ratio</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>ethylene\textsuperscript{a)</td>
<td>petroleum</td>
<td>gas</td>
<td>$&lt; -390 \text{ }^{10} \text{C}$</td>
<td>$&lt; 0.13 \text{ }^{10} \text{C}$</td>
<td>$&lt; 0.12$</td>
</tr>
<tr>
<td>2</td>
<td>polyethylene\textsuperscript{b)}</td>
<td>petroleum</td>
<td>pellet</td>
<td>$&lt; -390 \text{ }^{10} \text{C}$</td>
<td>$&lt; 0.13 \text{ }^{10} \text{C}$</td>
<td>$&lt; 0.12$</td>
</tr>
<tr>
<td>3</td>
<td>propylene\textsuperscript{c)}</td>
<td>petroleum</td>
<td>gas</td>
<td>$&lt; -390 \text{ }^{10} \text{C}$</td>
<td>$&lt; 0.13 \text{ }^{10} \text{C}$</td>
<td>$&lt; 0.17$</td>
</tr>
<tr>
<td>4</td>
<td>polypropylene\textsuperscript{d)}</td>
<td>petroleum</td>
<td>pellet</td>
<td>$&lt; -390 \text{ }^{10} \text{C}$</td>
<td>$&lt; 0.13 \text{ }^{10} \text{C}$</td>
<td>$&lt; 0.12$</td>
</tr>
<tr>
<td>5</td>
<td>di-l-lactide\textsuperscript{e)}</td>
<td>biomass</td>
<td>powder</td>
<td>44.34</td>
<td>104.4</td>
<td>97.05</td>
</tr>
<tr>
<td>6</td>
<td>di-l-lactide\textsuperscript{f)}</td>
<td>biomass</td>
<td>powder</td>
<td>82.32</td>
<td>108.23</td>
<td>106.62</td>
</tr>
<tr>
<td>7</td>
<td>poly(lactic acid)\textsuperscript{g)}</td>
<td>biomass</td>
<td>solid</td>
<td>63.4</td>
<td>106.34</td>
<td>98.96</td>
</tr>
<tr>
<td>8</td>
<td>caprolactone\textsuperscript{h)}</td>
<td>petroleum</td>
<td>liquid</td>
<td>$&lt; -390 \text{ }^{10} \text{C}$</td>
<td>$&lt; 0.13 \text{ }^{10} \text{C}$</td>
<td>$&lt; 0.12$</td>
</tr>
<tr>
<td>9</td>
<td>poly(caprolactone)\textsuperscript{i)}</td>
<td>petroleum</td>
<td>pellet</td>
<td>$&lt; -390 \text{ }^{10} \text{C}$</td>
<td>$&lt; 0.13 \text{ }^{10} \text{C}$</td>
<td>$&lt; 0.12$</td>
</tr>
<tr>
<td>10</td>
<td>poly(butylen succinate)\textsuperscript{j)}</td>
<td>petroleum</td>
<td>pellet</td>
<td>$&lt; -390 \text{ }^{10} \text{C}$</td>
<td>$&lt; 0.13 \text{ }^{10} \text{C}$</td>
<td>$&lt; 0.12$</td>
</tr>
</tbody>
</table>

\textsuperscript{a) Ethylene, calibration gas, GL Sciences, Inc. \textsuperscript{b) Polyethylene, Mitsubishi Chemical Corporation. \textsuperscript{c) Propylene, calibration gas, GL Sciences, Inc. \textsuperscript{d) Polypropylene, Sigma-Aldrich. \textsuperscript{e) Di-l-lactide as received, Tokyo Chemical Industry Co., Ltd. \textsuperscript{f) Di-l-lactide purified by recrystallization, Tokyo Chemical Industry Co., Ltd. \textsuperscript{g) Poly(lactic acid) synthesized from di-l-lactide \textsuperscript{f). \textsuperscript{h) \textepsilon-Caprolactone, Tokyo Chemical Industry Co., Ltd. [measured in 2007]. \textsuperscript{i) Poly(caprolactone], Sigma-Aldrich [measured in 2007]. \textsuperscript{j) Poly(butylen succinate), Sigma-Aldrich [measured in 2007]. \textsuperscript{k) Less than detection limit of instrument.}

The research group concluded that by using AMS radiocarbon measurements it was possible to calculate biomass carbon ratios of different sample materials. The group reported the lowest biomass carbon ratio value measurable to be 0.12 %. In addition, the group tested the repeatability of AMS and measured the same sample material six times. The group reported a standard deviation of 0.36 % and noted that AMS evaluation method was adequate to determine biomass carbon ratios.\textsuperscript{57}

In 2007, Hämäläinen et al. determined the origin of power plant fuel by measuring the radiocarbon content of flue gases of the plant. By collecting flue gases and by measuring $^{14}$C values it was possible to calculate if the power plant had combusted fossil or biofuel and how much. The flue gases were collected directly from power plant chimneys by sampling rods and ten liter plastic bag. The samples were collected at five different power plants which used different fuels. The different fuel types are shown in table 2.\textsuperscript{58}
Table 2. Different fuel mixtures used at the different power plants.\textsuperscript{58}

<table>
<thead>
<tr>
<th>Power plant</th>
<th>Samples</th>
<th>Fuel</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>1–2</td>
<td>Natural gas (fossil methane)</td>
</tr>
<tr>
<td>2</td>
<td>3–10</td>
<td>Sawdust, wood chips</td>
</tr>
<tr>
<td>3</td>
<td>13</td>
<td>Bark, sludge from paper factory, peat, and wood chips</td>
</tr>
<tr>
<td>4</td>
<td>14–15</td>
<td>Plastics, paper, coal, peat, construction waste, and wood chips</td>
</tr>
<tr>
<td>5</td>
<td>16–17</td>
<td>Bark, bio sludge, plywood residue, and wood chips</td>
</tr>
<tr>
<td>5</td>
<td>18–19</td>
<td>Bark, bio sludge, plywood residue, wood chips, and peat</td>
</tr>
<tr>
<td>Test log</td>
<td>11–12</td>
<td>Wood</td>
</tr>
</tbody>
</table>

The collected carbon dioxide samples were then reduced into graphite in laboratory and their radiocarbon content measured by AMS. Hämäläinen \textit{et al.} reported that it was possible to determine the amount of the biofuel mixed with fossil fuel by radiocarbon measurement of flue gases. The group reported that atmospheric contamination was not a problem and could be taken into account in calculations.\textsuperscript{58}

However, the group noted that it was very difficult to estimate peat mixing ratios in fuel since the radiocarbon content in peat varies. Peat may be several thousands of years old and it does not anymore contain modern $^{14}C$ levels. The group noted that more research would be needed to reliably determine peat mixing ratios.\textsuperscript{58}

2.4. Gas Proportional Counting

Gas Proportional Counting (GPC) is one of the oldest techniques for radiation measurement. The basis of the technique is similar to a Geiger-Müller tube detector. The Geiger-Müller tube is shown in figure 15.
In the GPC the detector is a gas-filled tube. Usually the gas is Argon. When a radioactive nucleus decays via beta decay, it emits a beta particle. The beta particle hits a gas atom in the tube and an ion pair is formed. The ion pair separate and migrate to different electrodes. When the measurement is done in pulse mode, the computer records the electrode data from a certain amount of time after which the data collection is turned off. This is called a pulse.\(^59\)

The GPC takes advantage of an effect known as gas multiplication. This effect takes place when the electric field of the tube is raised to sufficiently high level. When the electric field is at high level, it is possible for a second ion pair to form when a beta particle hits the gas atom, forms an ion pair, migrates towards the anode, and hits another atom on the way. This requires that the kinetic energy of the collision of a free electron and gas atom is larger than the ionization energy of the gas atom. This secondary ionization releases another electron which can then hit another gas atom. So the reaction is a cascade reaction which is why it is also called a Townsend avalanche effect. The effect can be defined as

\[
\frac{dn}{n} = \alpha dx
\]  \((x)\)
in which $\alpha$ is the first Townsend coefficient for the gas. The Townsend coefficient is zero when electric field energies are lower than the gas multiplication threshold. As the avalanche advances, the density of electrons grows exponentially.\(^{60}\) The Townsend avalanche is shown in figure 16.

![figure 16. The Townsend avalanche effect.](image)

The downside of GPC is that the measurement times are very long. For a typical radiocarbon sample the measurement time is 48 hours. Also the GPC must be very efficiently isolated from background radiation, for example via lead shielding, and possibly a Faraday cage structure in the measurement laboratory. Another downside is that the sample sizes required are very large, which is unfortunate when considering precious samples such as ancient archaeological artifacts.\(^{60}\) Nowadays the GPC is considered outdated technology and it has been replaced practically everywhere by the Liquid Scintillation Counting and Accelerator Mass Spectrometry.

### 2.5. Liquid Scintillation Counting

Liquid Scintillation Counting (LSC) is a radioanalytical technique for determining radioactive substances. It is mainly used to measure beta decay and alpha decay but has certain applications to measure gamma or x-ray radiation or to measure samples which emit Auger electrons.\(^{60}\)

The detection in LSC is based on the detection of photons emitted by scintillation fluor. In beta decay, the beta particle hits a solvent molecule which is in turn excited to higher energy level. The excited solvent molecule eventually hits the scintillation fluor molecule and transfers its excess energy to it. The fluor molecule is specifically designed to release
the energy by emitting photons as efficiently as possible. The best fluors have an efficiency of almost 100 %. This means that the sample contains three major components: the radioactive sample, the solvent and the fluor. The simplified schematic of LSC is shown in figure 17.

The solvent must be chosen so that the sample and the fluors are soluble. Most used solvents are organic aromatic solvents such as xylene, toluene, benzene or cumene. Unfortunately many samples are aqueous which means that the solubility of the samples in pure organic solvents is very low. To compensate this, there are different fluor cocktails and some cocktails may contain water up to 50 % and aqueous sample is easily dissolved. Another aspect required of the solvent is that it transfers its excess energy efficiently to the fluor molecules.

Optimal fluor has several properties. The fluor must release the excitation energy by emitting detectable light as efficiently as possible. The intensity of emitted light must be proportional to the deposited energy and must be linear in a wide area. The fluor must not absorb light at the same wavelength as it emits. The response time of the fluor must be fast so that faster signals are more easily generated. The refraction index of the fluor must be close to that of the glass vial so that coupling it with photomultiplier tube is easier.

---

**Figure 17.** Simplified schematic of the LSC. Radioactive nucleus undergoes beta decay and the beta particle hits a solvent molecule. The excited solvent molecule hits a fluor molecule which emits a photon. The photon is detected and multiplied by photomultiplier tube and analyzed by analyzer.
The scintillators can be divided into organic, inorganic and other scintillators. Organic fluors are the most popular. In general, the organic fluors are not as efficient light emitters as inorganic but their response is much faster. Inorganic fluors on the other hand yield more light and their response is more linear, but their response time is slower. If the response time is slow, there is more time for the excited fluor molecule to hit other molecules and release the energy without emission. An example of an organic fluor, 2,5-diphenyloxazole (PPO) is shown in figure 18.

![Structure of 2,5-diphenyloxazole (PPO)](image)

**Figure 18.** The structure of 2,5-diphenyloxazole (PPO).

Very often, when the sample is added to the fluor, it is seen that the light output is somewhat reduced when compared to pure fluor. This is due to a phenomenon called quenching. Due to quenching one can’t add too much of the sample into the fluor since the effect is proportional to the amount of the sample. There are three types of quenching. The first is color-quenching and is caused by a change in optical properties of the sample-fluor mixture compared to pure fluor and means the absorption of the photons by pigment molecules in the sample. Second quenching type is called physical quenching where the beta particles travel through the vial without hitting the fluor molecules. The third type is chemical quenching which is the release of excitation energy by solvent or fluor molecules without emission of photons. 

The LSC is a very popular method for radiocarbon determination. It is relatively cheap and the equipment is widely available. The use of LSC is easy and does not require substantial training. The accuracy is good when analyzing samples with high radiocarbon content. However, the accuracy is not as good when analyzing low-concentration samples such as very old archaeological samples or liquid biofuel blends with low biofractions. The sample measurement time is often 6 hours for radiocarbon samples. With liquid biofuel samples the LSC has the major advantage that it doesn’t require sample preparation, since the fuel can be directly added to the fluor and measured.
Dijs et al. measured radiocarbon from fuel samples using both the LSC and AMS in 2006. The samples were ULG95 unleaded gasoline blended with bioethanol and fossil ethanol and were blended in the laboratory by the research group.\(^{62}\)

The LSC measurements were done in Turku, Wallac Low-Level Laboratory, using Quantulus\textsuperscript{TM} ultra low-level Perkin-Elmer LSC. The measurement time was 5.5 hours and the counting efficiency was determined using 2090 dpm [\(^{14}\text{C}\)]-cholesterol standard. The size of the fuel samples was 10 ml. The AMS samples were first converted into 2 mg graphite and then measured in Van de Graaff Laboratory, University of Utrecht.\(^{62}\)

The traditional method is converting the sample into CO\(_2\) or benzene but Dijs et al. used a so-called direct LSC method, where they mixed the liquid fuel directly into scintillant cocktail. The benzene synthesis and CO\(_2\) conversion were bypassed since the group did not detect any LSC quenching.\(^{62}\)

The research group reported accurate results and good correlation. The plot of known biopercentages vs. measured values is shown in figure 19. The full results of Dijs et al. can be found in appendix 3.

![Figure 19. Known bioethanol-gasoline biopercentages vs. the measured radiocarbon content. Count time 5.5 hours. \(R^2 = 0.9999\).](image)

Dijs et al. confirmed the LSC results by measuring the same samples with AMS. The research group reported same linear correlation with the AMS as with the LSC, \(R^2 = 0.9999\). The research group also reported an error up to 22% for fuel blend of bioethanol
content of 0.33%. The error was lower for samples of higher bioethanol percentages, e.g. for 6.22% bioethanol fuel the error was 6.3% and for 99% bioethanol fuel the error was 5.8%, which was the lowest error reported. Compared to measurements with AMS, the 0.33% bioethanol fuel had an error of 25%, the 6.22% fuel had an error of 1.8% and the 99% fuel had an error of 0.6%.

Yunoki et al. determined the bioethanol content in gasoline samples using LSC and two-step extraction method in 2009. The research group purchased gasoline from gas station and blended bioethanol with the gasoline in the laboratory. The samples were blended into 3% (E3) and 10% (E10).

Yunoki et al. had to perform a two-step extraction for the samples due to gasoline dyes which caused LSC quenching. They used a simple liquid-liquid extraction using water. The water phase or a portion of it was then mixed into scintillation cocktail making the whole volume 15 ml. They also tested direct LSC method for E3 gasoline. The bioethanol content (g/vial) was plotted vs. the dpm counts of LSC and the plots are shown in figure 20.

![Figure 20.](image)

Figure 20. a. Bioethanol content of 0.5 – 3.0 g vs. LSC dpm. b. Bioethanol content of 0.095 – 1 g vs. LSC dpm. For each sample 10 measurements of 50 minutes were performed (total 500 minutes) and the means are plotted here.
The E3 fuel prepared by Yunoki et al. had bioethanol content of 3.04 % and the E10 fuel had bioethanol content of 10.0 %. Using the extraction with LSC, they were determined to be $2.98 \pm 0.10 \%$ and $10.0 \pm 0.1 \%$. When the research group determined the E3 fuel using the direct LSC method, the sample was determined to be $0.00 \pm 0.1 \%$. The group speculated that the large error was due to LSC quenching, as the fuel contained dyes.\textsuperscript{26}

Norton et al. measured commercial bioethanol-gasoline blends acquired from local gas stations in 2009. The group employed the direct LSC method, where the fuel was directly added into scintillant fluor.\textsuperscript{63}

Norton et al. used a Packard Tri-Carb 3170 TR/SL LSC and Permafluor E\textsuperscript{+} fluor cocktail purchased from Perkin-Elmer. The group used a $^{133}\text{Ba}$ with activity of 1 Ci as external standard. The sample size was 10 ml + 10 ml fluor.\textsuperscript{63}

The group plotted a correlation curve where the LSC dpm was plotted vs. the ethanol content of the cocktail solution. This plot is shown in figure 21. The results of Norton et al. are shown in table 3.

![Figure 21](image.png)

**Figure 21.** LSC dpm vs. bioethanol content of the cocktail solution. Background subtracted. Measurement time varied between 300 and 1200 minutes depending on sample. Five replicate measurements per sample. Measurement range was 0-156 keV.\textsuperscript{63}
Table 3. The bioethanol concentrations in gasoline by Norton et al. using direct LSC and AMS.\textsuperscript{63}

<table>
<thead>
<tr>
<th>Sample</th>
<th>Measured by direct LSC method</th>
<th>Estimated from AMS pMC data</th>
</tr>
</thead>
<tbody>
<tr>
<td>E0 #1</td>
<td>0</td>
<td>—</td>
</tr>
<tr>
<td>E0 #2</td>
<td>0</td>
<td>—</td>
</tr>
<tr>
<td>E0 #3</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>E0 #4</td>
<td>0</td>
<td>—</td>
</tr>
<tr>
<td>E10 #1</td>
<td>9</td>
<td>—</td>
</tr>
<tr>
<td>E10 #2</td>
<td>10</td>
<td>—</td>
</tr>
<tr>
<td>E10 #3</td>
<td>8</td>
<td>10</td>
</tr>
<tr>
<td>E10 #4</td>
<td>11</td>
<td>10</td>
</tr>
<tr>
<td>E70–E75</td>
<td>72</td>
<td>—</td>
</tr>
<tr>
<td>E75</td>
<td>73</td>
<td>74</td>
</tr>
<tr>
<td>E10 “Standard”</td>
<td>10</td>
<td>10</td>
</tr>
<tr>
<td>E85 “Standard”</td>
<td>88</td>
<td>88</td>
</tr>
</tbody>
</table>

Norton et al. reported an error of 2%. They suggested that the error was due to pipetting errors. Gasoline is volatile liquid and has low viscosity. They suggested that the pipetting error might be minimized by using pipettes designed for volatile and low viscosity liquids. They also reported that LSC quenching was effectively compensated by the software (QuantaSmart\textsuperscript{TM}) they used.\textsuperscript{63}

In 2012, Norton et al. measured FAME biodiesels. Again, they bypassed the extraction, benzene synthesis and sample combustion and instead, they used the direct LSC method where the fuel sample was directly mixed into scintillant fluor.\textsuperscript{61}

Norton et al. compared their method with ASTM Method D7371 and into European Standard DIN EN 14078 which describe the determination of FAME concentration in fuel by infrared spectroscopy.\textsuperscript{61, 65, 66}

The research group estimated that with direct LSC method the sample preparation time and cost would drop by 90% when compared to AMS. The research group purchased petrodiesel from ConocoPhillips refinery in Borger, Texas, and prepared fuel blends by mixing it with 100% FAME biodiesel. The biodiesel percentage of the samples was blended to be between 2 and 20%. The group used 100% FAME biodiesels prepared from several feedstocks, including canola oil, soy oil, white grease and coconut oil.

The research group reported that color quenching was excessive in many fuel blends. However they noted that by diluting the samples the color quenching could be reduced, but advised against this, since diluting the $^{14}$C content will reduce count rates and therefore
accuracy and sensitivity. Instead of diluting the samples, the group decolorized 100% FAME biodiesels before blending. The decolorization was made by using activated alumina beds and Florisil over which the samples were passed.

Norton et al. noted that actual commercial fuel blends could not be decolorized prior to blending and therefore a suitable decolorization method for blended fuels would be needed which would not influence the carbon isotope ratios in the fuel.

The sample sizes were 18 ml of fuel and 2 ml of fluor in 20 ml scintillation vial. The composition of the fluor was PPO and bis-MSB mixed into xylene. Samples were measured three hours and six hours both in order to compare the effect of the counting time into the uncertainties and sensitivities. The FAME content measured by Norton et al. vs. the theoretical FAME content is shown in figure 22.

![Figure 22](image)

**Figure 22.** Measured FAME content vs. theoretical FAME content. Counting times displayed here were six hours. Method D7371 using FTIR determination is shown for comparison.\(^{61,65}\)

Norton et al. reported that the measurements made by method D7371 using FTIR had much higher errors, relative errors up to 55% in one case and in several cases the relative error was between 20 – 40%. When compared to the direct LSC method, the relative errors were usually under 10% and in few cases up to 15%. The coconut diesel especially was difficult to characterize since it had increased ester content which lead to positive error, as the FTIR detects the carbonyl bonds.
The research group concluded that direct LSC was more accurate and uncertainties were much lower when the decolorization was applied. Six hour counting times gave better results. Especially for coconut diesel the LSC was much more accurate since the increased carbonyl bonds do not affect LSC analysis. Still, color quenching remained a problem and a method for decolorizing the commercial fuel blends is still needed.\textsuperscript{61}

\section*{2.6. Intracavity Optogalvanic spectroscopy}

Intracavity Optogalvanic Spectroscopy (ICOGS) is a relatively new technique for determining radiocarbon contents. In ICOGS the detection of radiocarbon is based on molecule-specific resonances.\textsuperscript{67}

The basis of the detection is the change in electrical response of a gas discharge to an optical perturbation. This can be defined as\textsuperscript{68}

\[ S = \int_0^L dz \int_0^R r dr \int_0^{2\pi} d\theta [n(r, \theta)I(r, \theta, z, \theta)\sigma(\theta)K] \]  

where $S$ is the electrical response, $I$ is the laser intensity, $\nu$ is the frequency, $n$ is the density of interacting species, $\sigma(\nu)$ is the laser-species interaction cross section and $K$ is a optogalvanic proportionality constant.\textsuperscript{46} This equation can be simplified and redefined as

\[ S = nLI\sigma K \]  

where $n$ is the average molecular density of interacting particles, $L$ is the length of interaction region, $I$ is the laser intensity and $A$ the average area of the laser beam.\textsuperscript{46}

The detection of $^{14}$CO\textsubscript{2} from $^{12}$CO\textsubscript{2} is made possible by the fact that the laser resonances are strongly isotope-dependent. $^{14}$CO\textsubscript{2} has its lasing transition maxima at 11.8 and 11.3 µm which are longer wavelengths than stabile CO\textsubscript{2} lasing transition wavelengths. The difference between $^{14}$CO\textsubscript{2} and closest stabile CO\textsubscript{2} wavelengths is more than 500 linewidths.\textsuperscript{69} The schematics of ICOGS equipment is shown in figure 23.
Figure 23. The schematics of the ICOGS equipment. M1 is a high reflective mirror, M2 a 85% reflective output coupler, M3 a gold plate mirror, PS a pressure sensor, FC a flow controller and DAQ a data acquisition board.46

The ICOGS is not yet as accurate and sensitive as AMS. It is estimated that the $^{14}\text{C}/^{12}\text{C}$ ratio can be determined down to $10^{-15}$. ICOGS gives linear response in $^{14}\text{C}$ concentrations from 0 to 10 times “modern” level. On the other hand, the required sample size is a lot smaller in ICOGS. The AMS usually requires 0.5-1.0 mg of carbon, while the ICOGS can measure samples in µg range. Also, sample does not need to be graphitized, since pure CO$_2$ can be measured. Graphitization of the sample is a time-consuming phase and is more thoroughly explained in section 7. The linearity of the ICOGS is shown in figure 24. In the x-axis are the results from AMS and in the y-axis is the ICOGS signal.69
To date it seems that ICOGS is very well suitable e.g. in pharmaceutical studies where the samples are labeled with $^{14}$C or in other words when the $^{14}$C concentration in a sample is larger than the atmospheric $^{14}$C concentration. It seems that currently the ICOGS is not suitable for determining very small amounts of $^{14}$C. This is often the case in archaeological samples and in some cases in biofuels. However, it must be noted that the sensitivity of ICOGS has greatly increased from $^{14}$C/$^{12}$C ratio of $10^{-9}$ in 2004 to $10^{-12}$ in 2006 and to $10^{-15}$ in 2010.\textsuperscript{46, 67, 69}

3. Characterization of fuel biofractions by other analytical techniques

In addition to the radioanalytical techniques described previously, there are several other chromatographic and spectroscopic methods for determination of biodiesel blend ratios. These include Fourier transformation infrared spectroscopy (FTIR)\textsuperscript{70-72}, Raman spectroscopy\textsuperscript{73}, nuclear magnetic resonance spectroscopy (NMR)\textsuperscript{74-76}, x-ray spectroscopy\textsuperscript{77}, fluorescence spectroscopy\textsuperscript{78, 79}, gas chromatography (GC)\textsuperscript{80-84} and liquid chromatography (LC)\textsuperscript{85, 86}.

Biodiesel blend determinations using non-radioanalytical methods have especially been researched in Brazil due to the local legislation. In 2005, the law 11,097 was sanctioned. The law dictated that diesel fuels must contain 2 % of biodiesel during the years 2008-2013 and after 2013 the diesel fuels must contain 5 % of biodiesel.\textsuperscript{87}
What separates these techniques from the ones described section 2 is that they are most often suitable only for determination of FAME biodiesel or, in some cases, bioethanol in gasoline. Biofuels prepared by hydrogenation or F-T synthesis cannot be determined by these techniques. This due to the fact that all the techniques either directly detect the FAME carbonyl or methoxy group or separate the sample components based on the physicochemical properties of the group (figure 5). This group is completely absent in hydrogenated renewable diesel and in F-T biodiesel and the chemical composition of these fuels greatly resemble fossil petrodiesel. In addition, these techniques cannot actually determine whether the biofuel truly is biological in origin, this fact can only be determined by radiocarbon analysis. Because of these limitations these techniques are described in this section only shortly.

3.1. Infrared spectroscopy

In 2006 Oliveira et al. described a method for determination of FAME contents in biodiesel blends by Fourier transformation infrared spectroscopy – attenuated total reflectance (FTIR-ATR). The basis of the quantification with IR spectroscopy is the detection of the very intense carbonyl (C=O) peak in the area between 1700 – 1800 cm\(^{-1}\). Each FAME molecule contains one carbonyl group. The group also compared the FTIR-ATR with near-IR spectroscopy (NIR).\(^{71}\)

Oliveira et al. reported a precision of RSD \(\pm 0.02 \%\) and trueness of \(\pm 0.06 \%\) (w/w) for the NIR spectroscopy and reported that it was more accurate than FTIR-ATR. The trueness of FTIR-ATR was between \(\pm 0.2 – 0.4 \%\). An example of FTIR-ATR spectra is shown in figure 24.\(^{71}\)
Figure 24. FTIR-ATR for: a. diesel, b. soybean FAME, c. FAME from frying oil, d. dende FAME and e. babassu FAME.\textsuperscript{71}

Aliske \textit{et al.} applied mid-infrared spectroscopy and determined biodiesel blends in 0 – 100 % blend percentage range in 2007. For the blend percentage determination the research group used the same carbonyl peak as described earlier. A 3D carbonyl peak evolution in 0 – 100 % mixture area is shown in figure 25.\textsuperscript{70}

Figure 25. 3D carbonyl peak area evolution by biodiesel blend percentage by Aliske \textit{et al.}\textsuperscript{70}

Aliske \textit{et al.} reported a correlation factor (R) of 0.9995 and a standard deviation of 0.017 % for their fit made by peak area.\textsuperscript{70}
Cruz de Vasconcelos *et al.* used NIR spectroscopy in FAME determination in 2012. The group chose overtone NIR regions because of cheaper optical components and fewer number of spectral variations. The group measured a set of 132 samples in biodiesel blend levels from 0 – 5 %. The group compared several modeling algorithms, including partial least squares (PLS) and multiple linear regression – successive projections algorithm (MLR/SPA). An example of the wavelengths selected by MLR/SPA is shown in figure 26. The effect of long (50 mm) optical path length is seen in the figure as saturation is seen between 8000 – 8500 cm$^{-1}$.

![Figure 26. The wavelengths selected by MLR/SPA. Optical path lengths: a. 10 mm, b. 20 mm, c. 50 mm, d. 50 mm and e. 50 mm.](image)

The group reported that MLR/SPA was the most accurate modeling algorithm and that NIR spectroscopy was well applicable to FAME determination in the range of 0 – 10 % of biodiesel. The group also tried to quantify leftover vegetable oil in biodiesel blends with NIR but came to the conclusion that the overtone spectral regions were inferior to typical NIR and MIR regions.
3.2. Fourier-transformation–Raman spectroscopy

In 2007, Oliveira et al. used FT-Raman spectroscopy to measure leftover vegetable oils from FAME biodiesel. Leftover oils can cause problems with the engine. The research group measured total 182 samples with Equinox 55 Fourier transform instrument by Bruker. Each FT-Raman spectrum was an average of 128 scans. The FT-Raman spectra were measured with Equinox 55 Fourier transform instrument. Optical path was 0.5 cm and the signal was detected by liquid nitrogen cooled germanium detector. Excitation was done by neodymium-doped yttrium aluminum garnet (NdYAG) laser. The group used an artificial neural network (ANN) model which selected wavelengths depending on their standard deviation variations. FT-Raman spectrum with chosen wavelengths is shown in figure 27.

![Figure 27](image)

**Figure 27.** Standard deviation of first derivative vs. wavenumber. Vertical lines show the wavelengths selected by ANN model.

The group reported trueness better than 0.03 % (w/w) for the ANN chemometric model that they used and concluded that FT-Raman spectroscopy could be used to measure leftover oils from biodiesel.
3.3. Nuclear Magnetic Resonance spectroscopy

Diehl and Randel used NMR spectroscopy in 2007 to determine biodiesel blend levels. The group was especially interested in chemical shift range between 3 to 5 ppm, which includes the resonances of methoxy groups of FAME molecules. The $^1$H-NMR spectrum of 5% biodiesel is shown in figure 28.74

![Figure 28. $^1$H-NMR spectrum of 5% biodiesel. The methoxy group signal is clearly seen at $\delta = 3.5$ ppm.](image)

Diehl and Randel reported that FAME was efficiently quantified down to ppm values. Measurement time for one sample was one minute.74

In 2008 Mello et al. determined the esterification reaction yields by measuring the FAME contents by $^1$H-NMR. The feedstock was soybean oil. The research group developed a calibration curve from the ratio of the peak areas of methoxy ester group and olefinic proton peaks. The calibration curve developed is shown in figure 29.76
Mello et al. concluded that $^1$H-NMR was very well suitable for monitoring the esterification reaction yield. The group reported a prediction error of less than 2.45 % for the FAME concentration.\textsuperscript{76}

Monteiro et al. measured FAME contents from different diesel samples by $^1$H-NMR in 2009. The biodiesel was produced from soybean and castor oil. The biodiesels had different chemical composition due to different feedstocks. The group blended the biodiesels with different petrodiesels and measured total 120 samples and the blend levels ranged from 0.5 – 30 %. The group also measured 13 commercial 2 % biodiesels.\textsuperscript{75}

The research group reported that results did not vary by feedstock or different petrodiesels. The measured blend percentages for the commercial 2 % biodiesels varied between 1.6 – 2.4 % therefore giving an uncertainty of 20 %.\textsuperscript{75}
3.4. X-ray spectrometry

In 2011 Sitko et al determined FAME blend levels by X-ray spectrometry (XRS). The group used an energy-dispersive X-ray fluorescence spectrometer (EDXRF). The detection basis is the different intensity in X-ray radiation scattered from hydrocarbons and from FAME molecules. The difference of the X-ray spectra for diesel and FAME is shown in figure 30.

![Figure 30](image)

**Figure 30.** a. The X-ray spectra of fossil diesel and FAME, b. difference between the spectra.

The group reported a standard deviation of 0.46 % (v/v) of FAME and a detection limit of 1.2 % (v/v). The group noted that the sensitivity of low FAME concentration range could be improved by using more intensive primary radiation and by using higher input silicon drift detector and speculated that the standard deviation should drop to 0.20 % and the detection limit to 0.52 %. The plot of continuum scattered radiation vs. FAME concentration is shown in figure 31.
Figure 31. Continuum scattered radiation vs. FAME concentration. a. 45 kV, 700 µA with integration window 9.0-14.5 keV, b. 35 kV, 1300 µA with integration window 10.5-15.0 keV.77

3.5. Fluorescence spectroscopy

In 2011 Scherer et al. determined FAME blend percentages using fluorescence spectroscopy. The research group used a Cary Eclipse bench fluorescence spectrophotometer and a portable MM Optics spectrofluorimeter. The aim of the research was to find easy, cheap, low cost method for FAME determination that would work e.g. in situ analysis in gas stations.78

Peak area ratios vs. FAME percentages are shown in figure 32. δ is defined as $\delta = [(A-A_0)/A_0]*100\%$, where A is the area of biodiesel blend spectrum and A0 the area of fossil diesel spectrum.
Scherer et al. reported a $R^2$ (correlation coefficient) value of 0.9872 for their results. The group also compared the fluorescence spectroscopy to FTIR spectroscopy and concluded that the fluorescence spectroscopy was more sensitive. The group noted that more research would be needed to confirm whether the fluorescence spectroscopy would give accurate results when the FAME was produced from different feedstocks.

Kumar and Mishra measured bioethanol from gasoline samples and FAME from biodiesel blends using fluorescence spectroscopy in 2012. The focus of the research group was on finding optimal calibration models for fluorescence spectroscopy. They came to the same conclusion that the method was well applicable to determination of these fuels. They reported an error of the predictions of their models less than 2 %.

### 3.6. Gas Chromatography

Wawrzyniak et al. determined methyl esters from diesel by GC in 2005. The group used a HP5890 Series II GC with flame ionization detector and J&W INNOWAX capillary column. The group prepared three methyl ester standard solutions with varying mass percentages of lauric, myristic, palmitic and stearic acids in each. They reported a limit of
detection of $5 \times 10^{-4}$ mass-% for all esters. Relative standard deviation (RSD) was calculated separately for all standard solutions and it ranged between 1 – 5 %.\textsuperscript{81}

In 2007, Seeley \textit{et al.} reported the use of two-dimensional gas chromatography (GCxGC) system for FAME quantification. They analyzed petrodiesel, biodiesel and biodiesel-petrodiesel blends. The group used a 5 % phenyl dimethylpolysiloxane primary column which they coupled with polyethylene glycol secondary column. They reported that FAME peaks appeared in a same region with diesel hydrocarbon peaks but were much more intense which allowed for quantification.\textsuperscript{80}

In 2012, Seeley \textit{et al.} tested several different stationary phases in order to efficiently separate the FAME peaks from fossil fuel hydrocarbon peaks. The group used a mathematical model to go through 50 stationary phases and their 1225 different combinations. The model predicted most efficient pair to be poly(methyltrifluoropropylsiloxane) and poly(dimethyldiphenylsiloxane) phases. The group used this combination and an example of two-dimensional GCxGC chromatogram of diesel fuel is shown in figure 33.\textsuperscript{83}

\begin{figure}[h]
\centering
\includegraphics[width=0.8\textwidth]{figure33.png}
\caption{Two-dimensional GCxGC chromatogram of diesel fuel. Fuel contained 1 % of each fatty acid marked in the chromatogram.\textsuperscript{83}}
\end{figure}
Seeley et al. concluded that the FAMEs were efficiently separated from fossil fuel hydrocarbon peaks. The group noted that the selection of stationary phases went against the typical GCxGC principles where the phases are selected as opposites to each other in the matter of polarity. The group reported that FAMEs were able to be quantified in 2 ppm levels.\(^3\)

Prados et al. determined total esters, mono-, di- and triacylglycerides and free glycerol in methyl and ethyl biodiesel in 2012. The group compared their method to standards EN 14103 and 14105 and concluded that the results achieved with their method were consistent with the standards but sample preparation and analysis time was reduced.\(^4\)

### 3.7. Liquid Chromatography

In 2005, Foglia et al. used high performance liquid chromatography (HPLC) for determination of biodiesel blends. The group used a HP Hypersil silica column on two different LC systems. Another LC had evaporative light scattering detector (ELSD) and the another UV detector. An example of a chromatogram comparing the two detection methods is shown in figure 34.\(^5\)

![HPLC chromatograms](image)

**Figure 34.** HPLC chromatograms using a. ESLD and b. UV detector. The peaks: A: diesel, B: methyl esters, C: triacylglycerols. Isocratic mobile phase, consisting of 90% hexane and 10% methyl-tert-buty ether (MTBE).\(^5\)

Foglia et al. concluded that ESLD was superior to UV detector since it is a general detector and UV detector relies on unsaturated bonds for detection. Results of the group indicate
that UV detector has a large variation in the accuracy which is due to different feedstocks of biodiesel. Some feedstocks have more unsaturated bonds and some less and this reduces the accuracy whereas ELSD gave more repeatable results and was not influenced by the feedstock.\textsuperscript{85}

Kaminski \textit{et al.} determined aromatic hydrocarbons and FAMEs from diesel fuels by HPLC in 2006. The group used a LaChrom Merck-Hitachi LC with LiChrospehr NH\textsubscript{2} 5 µm column, a L-7490 refractive index detector (RID) and an UV-VIS diode array detector. The purpose of the research was to improve upon the standards EN 12916 and ASTM D6591 which described the proper analysis of aromatic hydrocarbons from diesel fuel. However, FAME contents made impossible to determine the aromatics as defined in the standards. Therefore the research group developed a method which allowed for determination of FAME contents and aromatic hydrocarbons from diesel fuel at the same time.\textsuperscript{86}

The group reported a detection limit for FAME to be 0.1 % and for polycyclic aromatic hydrocarbons to be 0.01 % for the UV detector and 0.3 % for the RID detector. An example of a chromatogram using RID detector is shown in figure 35.\textsuperscript{86}

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{bitmap.png}
\caption{LC-RID chromatogram. Mobile phase \textit{n}-heptane, flow rate 0.8 ml/min, temperature 20 °C, injection volume 20 µl, sample concentration 50 mg/ml. Peaks: 1. paraffins, naphthenes and olefins, 2. monoaromatic hydrocarbons, 3. diaromatic hydrocarbons, 4. polynuclear aromatic hydrocarbons, 5. FAME. BF = backflush. In (A) the detector has sensitivity lowered by a factor of eight.\textsuperscript{86}}
\end{figure}
3.8. Elemental Analyzer

3.8.1 The basis

An Elemental Analyzer (EA) is a laboratory device that allows determination of C, H, N and S, usually in mass-%, from plentiful amount of sample matrices. Oxygen can be determined too, with some minor modification. The EA is usually comparable to standard gas chromatograph or liquid chromatograph in size which means that the analysis is performed in laboratory, but the popular concept of miniaturization has not yet reached the EA and field-sized devices are not manufactured.

The internal layout of the EA differs somewhat depending on the manufacturer. The following section will mainly focus on the layout of Carlo Erba model EN1108 EA and similar systems. The basic operation principle is as follows: samples are packed in small metal cups. Size of the cup depends on the sample matrix. The cups come in two different varieties, ultra-clean and standard. Ultra-clean cups are more expensive but have certified and very low contaminant values. The most common material for the cups is tin but aluminum and silver are also widely used.

The samples are loaded into an autosampler which can contain from tens to hundreds of samples depending on the model. The autosampler will drop each sample in turn into the EA system.

The EA contains two quartz glass reactor tubes which are loaded with silvered cobaltous/cobaltic oxide, chromium oxide and pure copper rods. The specific layout of the reactor tubes is demonstrated in figure 36.
Once the sample is dropped by the autosampler into the reactor tube, the EA injects specified amount of pure oxygen to promote the decomposition and oxidation. The sample is very efficiently oxidized by the reagents in the first reactor tube which is heated into 1020 °C and practically the whole sample is converted into combustion products. Carbon is oxidized into CO$_2$, nitrogen into various nitric oxides and hydrogen into water. The tin reacts exothermically with oxygen and promotes a so called “flash combustion” reaction in which the temperature will rise up to 1800 °C for a short while. This is usually enough to decompose nearly all sample material.

The carrier gas, helium, transport the analytes into the second reactor tube in which the copper eliminates the extra oxygen by forming copper oxide. The various nitric oxides are converted into nitric gas and copper oxide. The second reactor tube is heated up to 650 °C.

After the reactor tubes, the analytes are carried into GC column which separates them. First analyte to exit the column is nitric gas, second carbon dioxide, third water and fourth sulfur dioxide. The analytes are detected by thermal conductivity detector (TCD) which compares
the thermal conductivity of the sample channel into reference channel. Computer software integrates the peaks and the elemental mass-% is calculated. The integrated area of the peak is directly proportional to the mass of the element.88

Usually when there is no need to determine sulfur or hydrogen, they are removed. A suitable reagent is added into the first reactor tube which eliminates the sulfur. In this case the silvered coboltous/cobaltic oxide will form silver sulfide. Water is removed before the GC column by magnesium perchlorate water trap.

The schematic of the Carlo Erba EA is shown in figure 37.

![Figure 37](image)

**Figure 37.** The schematic of the Carlo Erba EA. 1. Autosampler, 2. Oxidation reactor tube at 1020 °C, 3. Reduction reactor tube at 650 °C, 4. Water trap, 5. GC column at 50 °C, 6. thermal conductivity detector (filament at 180 °C).

After passing the detector, the gas flow will exit the EA via exit valves. It is very common to connect the EA into Isotope Ratio Mass Spectrometer (IRMS) when determining stable isotope ratios. EA-IRMS is a widely used method and has several applications, some examples being food chemistry18, environmental studies89 and medical studies90.
3.8.2. The sources of error and problems

The EA suffers from certain problems which must be noted by the analyst. Firstly, the connections of the EA must be thoroughly checked and secured. Any leak in the system will result in poor sample detection, strange oversized peaks (especially N₂) and vast consumption of the expensive carrier gas. All O-rings should be wiped clean of any dust or other particulate and the connections firmly connected.  

Secondly, ash will be formed in the top of the first reactor tube. The ash will eventually block the gas flows and even before that it will interfere with following combustions. Therefore the ash is to be removed at steady intervals. One option for ash removal is inserting ceramic crucible into the reactor tube. The ash will fill the crucible which is then removed and cleaned. Another option is scraping the somewhat hard ash into powder with suitable tool and removing it with vacuum. The maintenance interval varies but usually 200-300 combustions can be performed before cleaning the system. Since the EA reactor tubes contain solid chemical reagents, they are naturally consumed in certain time and need to be replaced by approx. every 500 samples. The condition of the water trap is also to be checked. The condition of the trap is clearly seen by naked eye as the magnesium perchlorate will solidify by use.

Thirdly, certain sample materials do not combust and decompose properly in the standard conditions of the EA. These sample materials include iron samples, some carbonates and graphite. This can be helped by changing the reagents of the first reactor tube. By filling the tube with Co₃O₄, Ag₂WO₄/ZrO₂/MgO mixture and Cr₂O₃ it is possible to determine carbon, hydrogen, nitrogen and sulfur from nearly all sample matrices.
4. Comparison of the different techniques

Several techniques were presented in sections two and three for biofuel characterization. In table 4 these techniques are compared by their applicability for all different biofuels currently in the market.

Table 4. Applicability of the different techniques by sample matrix. X marks applicability.

<table>
<thead>
<tr>
<th></th>
<th>Ethanol blends with gasoline</th>
<th>FAME biodiesel</th>
<th>Hydrogenated renewable diesel</th>
<th>Fischer-Tropsch biodiesel</th>
</tr>
</thead>
<tbody>
<tr>
<td>AMS</td>
<td>X</td>
<td>X</td>
<td>X</td>
<td>X</td>
</tr>
<tr>
<td>LSC</td>
<td>X</td>
<td>X</td>
<td>X</td>
<td>X</td>
</tr>
<tr>
<td>FTIR</td>
<td>X</td>
<td>X</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Raman</td>
<td>X</td>
<td>X</td>
<td></td>
<td></td>
</tr>
<tr>
<td>X-Ray</td>
<td>X</td>
<td>X</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Fluorescence</td>
<td>X</td>
<td>X</td>
<td></td>
<td></td>
</tr>
<tr>
<td>NMR</td>
<td>X</td>
<td>X</td>
<td></td>
<td></td>
</tr>
<tr>
<td>GC</td>
<td>X</td>
<td>X</td>
<td></td>
<td></td>
</tr>
<tr>
<td>LC</td>
<td>X</td>
<td>X</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

In table 5 the techniques are compared by their relative price, availability and training level of operating personnel.

Table 5. Comparison of the relative price, availability and personnel training for the different techniques.

<table>
<thead>
<tr>
<th></th>
<th>Price</th>
<th>Availability</th>
<th>Personnel training</th>
</tr>
</thead>
<tbody>
<tr>
<td>AMS</td>
<td>Very expensive</td>
<td>Limited</td>
<td>High training</td>
</tr>
<tr>
<td>LSC</td>
<td>Standard</td>
<td>Available</td>
<td>Normal training</td>
</tr>
<tr>
<td>FTIR</td>
<td>Cheap</td>
<td>Widely available</td>
<td>Normal training</td>
</tr>
<tr>
<td>Raman</td>
<td>Cheap</td>
<td>Available</td>
<td>Normal training</td>
</tr>
<tr>
<td>X-Ray</td>
<td>Standard</td>
<td>Available</td>
<td>Normal training</td>
</tr>
<tr>
<td>Fluorescence</td>
<td>Standard</td>
<td>Available</td>
<td>Normal training</td>
</tr>
<tr>
<td>NMR</td>
<td>Expensive</td>
<td>Available</td>
<td>Normal training</td>
</tr>
<tr>
<td>GC</td>
<td>Standard</td>
<td>Widely available</td>
<td>Normal training</td>
</tr>
<tr>
<td>LC</td>
<td>Standard</td>
<td>Widely available</td>
<td>Normal training</td>
</tr>
</tbody>
</table>
In table 6 the techniques are compared by their relative advantages and disadvantages.

**Table 6.** Advantages and disadvantages of the different techniques.

<table>
<thead>
<tr>
<th></th>
<th>Advantages</th>
<th>Disadvantages</th>
</tr>
</thead>
<tbody>
<tr>
<td>AMS</td>
<td>Accuracy, sensitivity, applicability</td>
<td>Price and size of the machine, poor availability, high personnel training, long sample preparation times</td>
</tr>
<tr>
<td>LSC</td>
<td>Applicability, cheap, accuracy in samples with high biofuel blend ratios</td>
<td>Quenching effects, higher uncertainties in samples with low biofuel blend ratios</td>
</tr>
<tr>
<td>FTIR</td>
<td>Simple and fast, cheap</td>
<td>Poor applicability, expensive optical parts for certain wavelengths</td>
</tr>
<tr>
<td>Raman</td>
<td>Fast, cheap</td>
<td>Poor applicability</td>
</tr>
<tr>
<td>X-Ray</td>
<td>Fast</td>
<td>Relatively high level of detection, poor applicability</td>
</tr>
<tr>
<td>Fluorescence</td>
<td>Easy, cheap, <em>in situ</em> determinations possible</td>
<td>Poor applicability</td>
</tr>
<tr>
<td>NMR</td>
<td>Fast, sensitive</td>
<td>Poor applicability, relatively high uncertainties</td>
</tr>
<tr>
<td>GC</td>
<td>Sensitive</td>
<td>Poor applicability</td>
</tr>
<tr>
<td>LC</td>
<td>Sensitive</td>
<td>Poor applicability</td>
</tr>
</tbody>
</table>
II. Experimental section

The Laboratory of Chronology in Finnish Museum of Natural History, University of Helsinki has been greatly exploring the feasibility of biofraction determinations by radiocarbon analysis since the year 2004. Previous research projects in the Laboratory of Chronology, funded by the Finnish Funding Agency for Technology and Innovation (TEKES) and Neste Oil Ltd have proved that radiocarbon analysis is indeed an accurate method for this. 7

This project, funded by the Magnus Ehrnrooth Foundation, was a natural continuation of the previous projects. As the previous project7 provided the reliable basis, the focus was shifted to enhancing the sample throughput and accuracy of the analysis and decreasing the work load.

ASTM standard D6866-10 is a standard that describes the proper preparation of radiocarbon samples. The standard describes the Closed-Tube-Combustion (CTC) method but the Elemental Analyzer combustion is not yet mentioned in the standard. One major goal of the research project was to go beyond the standard in the matters of reliability and accuracy as it was evident that EA combustion method was better than CTC method in nearly every respect. A scientific paper has been written on this work and it is hoped that once it is published in a media with sufficient impact factor, the EA combustion method would be integrated into the next evolution of D6866 standard.10

The Laboratory of Chronology has an increasing interest towards standardized laboratory operations and may at some point apply for accreditation from the Finnish Accreditation Service (FINAS) due to the increasing demand of commercial laboratory analytics especially in the field of biofraction analytics. The work presented was also a step forward in standardization of analytical processes and the increased automatization of sample preparation processes will greatly support the commercialization of the techniques.
5. Samples

The samples were supplied by a Finnish oil refining company Neste Oil Ltd. during the previous joint research project. The samples were NExBTL biodiesel mixtures and the biofractions of the samples varied from 0 to 100 % (w/w). The initial mixtures were weighed at the Neste Oil laboratory.

6. Modification of the Elemental Analyzer

The Elemental Analyzer used in this project was a Carlo Erba EN1108 EA model (section 2.8.). To obtain fast collection procedure for the combusted samples it was necessary to customize a sample collection line. Minami et al. had done similar modification previously but did not answer any queries by the author or by the laboratory director about the construct of their collection line. Evolution of the collection lines 1-3 is shown in figure 38. Cryotrap is cooled by liquid nitrogen (LN) (not shown in picture) into which CO$_2$ is trapped. Evacuated sample vial is connected to the collection line and carrier gas passes through the line. After trapping, valves around the collection line (not shown in picture) are closed and valve to the sample vial opened. Next, LN bath is moved from cryotrap to vial. In collection line type 3 two LN baths were used to increase the cryotrapping capabilities. The first three types of collection lines did not yield any CO$_2$. At first it was not understood why, but later it was realized that this was due to the much greater molecular weight of CO$_2$ compared to helium, used as carrier gas. Helium filled all the upper volume of the collection line and blocked the CO$_2$ to stay in the bottom of the cryotrap. Therefore the sample did not move to sample vial even when LN bath was removed from the cryotrap and moved to the sample vial, since at the time the volume was sealed to prevent air entering the line. As we aimed for a simple collection line without vacuum pumping, it was not possible to evacuate gaseous phase while cryogenically trapping the CO$_2$. 
After the problem was understood, it was solved by creating a customized part which acted as both the sample vial and the cryotrap. Original cryotrap and sample vial were replaced by the new parts. Before sample trapping, the vial/trap was evacuated and then connected to the sample collection line. The valve connected to the line was opened and the vial/trap was flushed by helium flow. After a while, a valve from vial to outside air was opened and constant helium flow passed through the vial. The vial was again flushed for several minutes and then cooled by LN bath just before combusting the sample in the EA. Final collection line, type 4, is shown in figure 39.
**Figure 39.** Sample collection line type 4 with customized sample vial. During sample collection both valves of the vial are kept open and upper right-side valve is kept closed. Carrier gas flows through the vial. LN bath (not shown in picture) is placed over the sample vial. Elemental analyzer is seen behind the sampling line.

### 7. Sample preparation

Radiocarbon sample preparation is often a very labor-intensive process which takes several days. This section is dedicated to describing this in detail and will also describe the difference between the older Closed Tube Combustion and the Elemental Analyzer combustion.
7.1. Closed-Tube-Combustion method

Traditionally fuel samples for radiocarbon analysis are prepared by old Closed Tube Combustion (CTC) method. In this method, 3 g of copper oxide grains is weighed and placed in quartz tube which is sealed from one end. Diesel sample is pipetted on the copper oxide grains and the quartz tube is placed inside another bigger quartz tube. This tube is then connected to sample preparation line and evacuated while cryogenically cooling the tube to prevent sample evaporation. The evacuated tube is then sealed by blowtorch. The sample is then combusted in 900 °C for at least 4 hours, as dictated by the standard ASTM D 6866 – 06a. This is usually done overnight. An example of sample preparation line with sample tubes is shown in figure 40 and an example of sealing the sample tubes is presented in figure 41.

Figure 40 Sample tubes connected to sample preparation line.

The sample tubes seen in figure 40 contain oxalic acid, a laboratory standard, which is seen as white material in tubes, mixed with copper oxide grains, grey material. A valve to a vacuum pump can be seen on the right upper corner of the sample preparation line.
Blowtorch-sealing process is one phase during the sample preparation where a loss of the sample is possible. If too intense torch is applied to a tube, it is possible to puncture the sample tubes and the sample is lost.

After the sealing, the sample tubes are combusted in an oven in 900 °C for four hours. After the combustion, the tube is taken to CO$_2$ purification line where the tube is cracked and the sample is cryogenically trapped with LN bath. Tube cracking is shown in figure 42.
Tube cracking is another phase where care must be taken not to destroy the sample. It is possible to crack the tube from the wrong place if the tube is not handled with care.

After trapping, the LN bath is replaced by cryogenic ethanol bath (~ -85° C). In this temperature the water remains trapped as ice but CO$_2$ is sublimed. The LN bath is moved to second trap where the CO$_2$ is deposited. The valve between the traps is closed and the line is evacuated. Finally the purified CO$_2$ sample is transferred to a sample vial which can be removed from the purification line and taken to $\delta^{13}$C measurement. Sample purification line is shown in figure 43.

![Figure 43. CO$_2$ purification line. Sample is being collected in a vial by liquid nitrogen bath on the right side of the picture.](image)

### 7.2. Elemental Analyzer combustion method

In the Elemental Analyzer combustion method, two µl of the sample is pipetted by Hamilton microsyringe in tin cup (Elemental Microanalysis D4019) which is then immediately sealed by a special sealing device. The sample is loaded in the autosampler of the EA, sample sequence created and the sample combusted in EA while collecting the sample as described in section 6. Since the EA is equipped with a water trap (magnesium perchlorate), no water will be collected with the CO$_2$ sample in the sample vial/trap. This eliminates the need of purification line. The sample vial is then evacuated and the sample
is ready for $\delta^{13}$C measurement. Special sealing device and the tin cups are shown in figures 44 and 45.

Figure 44. Tin cup sealing device.

Figure 45. Tin cups ready to be packed and sealed.

The diesel sample is carefully injected into the bottom of the cup by Hamilton microsyringe. After the injection, the cup is immediately sealed with sealing device to prevent evaporation. The cups are all the time handled with clean pincers to prevent contamination.
7.3. Graphitization

After δ¹³C measurement the sample is transferred into evacuated graphitization reactor. One tube of the reactor is loaded with purified zinc powder (~ 200-300 mg) and another tube is filled with 1.5 – 2.5 mg of iron powder. Graphitization reactor contains two movable ovens which are placed over the reactor tubes. The graphitization process consists of two phases. In the first phase, the oven over zinc powder is kept at 350 °C and the oven over iron powder is kept at 450 °C. This phase takes one hour and during this time the CO₂ is reduced to CO. Then the temperature of the zinc oven is increased to 450 °C and iron oven to 650 °C. During the second phase, CO is further reduced into solid graphite. Iron powder works as a catalyst during the reaction and the graphite is deposited on the powder. Zinc powder is oxidized in the reaction. This phase takes 4-12 hours depending on the sample size. Graphitization reactor is shown in figure 46.

![Graphitization reactor number G3. Oven number 10 is Zn-oven and oven number 11 is Fe-oven. Graphite sample is visible at the bottom of the lower tube.](image)

After this the graphite sample is pressed into an aluminum target. The target is loaded into a sample holder which is then sent to suitable AMS facility for radiocarbon measurement. AMS facilities used by Laboratory of Chronology are the Tandem Laboratory of University of Uppsala and the Accelerator Laboratory of University of Helsinki. The
sample pressing is shown in figure 47 and picture of the sample holder is shown in figure 48.

Figure 47. Graphite sample in the tube ready to be pressed into aluminum target.

Figure 48. Sample holder for pressed graphite targets ready to be sent to AMS.
7.4. **Comparison of the methods**

When using the CTC method, this whole process from a liquid fuel sample to a pressed graphite target ready for AMS measurement takes 19 hours of actual work time. Usually this means that sample packing and combusting takes the first day, purification and graphitization the second day and target pressing the third day. Usually the samples are prepared four at a time because the laboratory has only four graphitization reactors, which effectively is a bottleneck due to the long graphitization time.

With the use of the EA method, the actual work time is cut down to eight hours. Effectively this means that the sample preparation time takes two days. Still, the same graphitization reactors are used and, therefore, the same maximum of four samples at a time are prepared, but since the process takes one day less, more samples can be prepared in a week.

8. **Results**

After the EA was in working condition several tests were made to evaluate its performance since the EA was relatively old. At first, it was necessary to find optimal pipetting method for liquid samples. Liquid sample pipetting was tested on canola oil, since it was readily available at the laboratory, its properties were well known and evaporation was not a problem. At first, a F1 Finnpipette (1-10 µl range) was used but it was noticed that it was impossible to pipette the canola in the bottom of the tin cup. This was due to the capillary effects of the thin cup and the relatively thick head of the pipette tip which did not fit in the bottom of the cup. This caused an air bubble to stay stuck at the bottom and when sealing the cup some of the canola dripped out. The oily cup further stained the Sartorius M2P Microbalance which caused deviations in the weighing. After this, a Hamilton microsyringe was used and with its very thin tip it was possible to pipette the liquid sample all the way to the bottom of the cup. The sample masses were measured, samples combusted in EA and mass vs. peak area plot was made. Figure 49 demonstrates the two pipetting methods. It can be seen from the figure that Hamilton microsyringe is more
reliable in this case. It should also be noted that in the figure 1.5 µl of each sample was pipetted, and with Finnpipette the sample mass has large deviation (the x-scale). This is due to the fact that the canola drips out of the cup and/or does not properly enter the cup.

**Figure 49.** Sample mass vs. peak area plot by two different pipetting methods.

After finding the optimal pipetting method, the condition of the EA was tested by combusting different sample materials; caffeine, acetonilide and diesel. Samples were combusted and their carbon mass vs. peak area were plotted. This plot is shown in figure 50.
After the tests it was seen that EA still gave linear results despite the old age of the equipment and, despite the varying carbon percentages of the different samples matrices, there was no variation in the linearity.

Then several biodiesel samples were combusted and their $\delta^{13}$C values measured. $\delta^{13}$C is a value that can indicate possible contaminants and leaks in the system. $\delta^{13}$C value for atmospheric CO$_2$ is -8.0 ±0.5 ‰ and for fossil diesel the value is -30.0 ‰. Results are shown below in table 7.

**Figure 50.** Carbon mass of several sample materials vs. EA peak area.
Table 7. Measured $\delta^{13}$C values. 16 separate measurements were made from the same EN590 fossil diesel sample.

<table>
<thead>
<tr>
<th>sample</th>
<th>$\delta^{13}$C</th>
</tr>
</thead>
<tbody>
<tr>
<td>EN590 Hela 1264</td>
<td>-29.95</td>
</tr>
<tr>
<td>EN590 Hela 1264</td>
<td>-30.03</td>
</tr>
<tr>
<td>EN590 Hela 1264</td>
<td>-29.99</td>
</tr>
<tr>
<td>EN590 Hela 1264</td>
<td>-29.93</td>
</tr>
<tr>
<td>EN590 Hela 1264</td>
<td>-29.89</td>
</tr>
<tr>
<td>EN590 Hela 1264</td>
<td>-30.00</td>
</tr>
<tr>
<td>EN590 Hela 1264</td>
<td>-29.98</td>
</tr>
<tr>
<td>EN590 Hela 1264</td>
<td>-30.00</td>
</tr>
<tr>
<td>EN590 Hela 1264</td>
<td>-30.01</td>
</tr>
<tr>
<td>EN590 Hela 1264</td>
<td>-30.01</td>
</tr>
<tr>
<td>EN590 Hela 1264</td>
<td>-29.99</td>
</tr>
<tr>
<td>EN590 Hela 1264</td>
<td>-30.03</td>
</tr>
<tr>
<td>EN590 Hela 1264</td>
<td>-30.01</td>
</tr>
<tr>
<td>EN590 Hela 1264</td>
<td>-30.03</td>
</tr>
<tr>
<td>EN590 Hela 1264</td>
<td>-30.04</td>
</tr>
<tr>
<td>EN590 Hela 1264</td>
<td>-30.01</td>
</tr>
</tbody>
</table>

<p>| | |</p>
<table>
<thead>
<tr>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>Average</td>
<td>-29.99</td>
</tr>
<tr>
<td>St. deviation</td>
<td>0.04</td>
</tr>
<tr>
<td>Median</td>
<td>-30.00</td>
</tr>
<tr>
<td>RSD (%)</td>
<td>0.13%</td>
</tr>
</tbody>
</table>

These results were plotted with Origin and the plot is demonstrated in figure 51.

Figure 51. $\delta^{13}$C values of 16 separate measurements of EN590 diesel.
As can be seen from the figure 51, the \( \delta^{13} \)C values stayed at a constant level. The results were compared to previously measured biodiesel samples where the CTC method was applied. This comparison of delta values is shown in figure 52.

**Figure 52.** Comparison of \( \delta^{13} \)C values of the CTC and EA methods.

It was noticed that using the CTC method led to a certain kind of learning curve seen in the beginning. The CTC method requires more manual work and depending on several factors the analyst can influence the result. Some factors include the handling of the sample tubes, for how long the LN bath is applied or at what point the sample cooling is began, for instance. With the EA combustion there is significantly less factors where the analyst can influence the results as the process is more automated.

Based on the \( \delta^{13} \)C measurements it was seen that there were no leaks or contaminants in the system. In the next phase of the project several different biodiesel samples were combusted, collected and graphitized. The pressed graphites were sent to Uppsala AMS for radiocarbon measurements. Results are shown in table 8.
Table 8. AMS results compared to weighted results.

<table>
<thead>
<tr>
<th>Sample number</th>
<th>Weighed fossil (g)</th>
<th>Mass fractions %</th>
<th>AMS results</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>bio (g)</td>
<td>fossil</td>
<td>bio</td>
</tr>
<tr>
<td>D2_0209 98/2</td>
<td>79.55</td>
<td>1.52</td>
<td>98.1</td>
</tr>
<tr>
<td>D3_0209 98/2</td>
<td>79.55</td>
<td>1.52</td>
<td>98.1</td>
</tr>
<tr>
<td>D4_0209 98/2</td>
<td>79.55</td>
<td>1.52</td>
<td>98.1</td>
</tr>
<tr>
<td>D3_0216 98/2</td>
<td>79.55</td>
<td>1.52</td>
<td>98.1</td>
</tr>
<tr>
<td>D1_0217 95/5</td>
<td>77.19</td>
<td>3.57</td>
<td>95.6</td>
</tr>
<tr>
<td>D2_0209 95/5</td>
<td>77.19</td>
<td>3.57</td>
<td>95.6</td>
</tr>
<tr>
<td>D3_0209 95/5</td>
<td>77.19</td>
<td>3.57</td>
<td>95.6</td>
</tr>
<tr>
<td>D2_0210 90/10</td>
<td>73.15</td>
<td>7.35</td>
<td>90.9</td>
</tr>
<tr>
<td>D3_0210 90/10</td>
<td>73.15</td>
<td>7.35</td>
<td>90.9</td>
</tr>
<tr>
<td>D4_0216 90/10</td>
<td>73.15</td>
<td>7.35</td>
<td>90.9</td>
</tr>
<tr>
<td>D1_0210 70/30</td>
<td>56.62</td>
<td>22.65</td>
<td>71.4</td>
</tr>
<tr>
<td>D2_0210 70/30</td>
<td>56.62</td>
<td>22.65</td>
<td>71.4</td>
</tr>
</tbody>
</table>

These results were compared to previous results\(^7\) where the CTC method was applied. The comparison of EA combustion and CTC is shown in figure 53.

![Figure 53](image_url)

**Figure 53.** Comparison of EA combustion and CTC. Upper graph demonstrates the EA combustion and lower graph the CTC.
While both methods give linear results, it was noticed that EA combustion was more accurate than the CTC method.

One initial cause of concern was whether the EA system would suffer from memory effects and if a very modern sample would contaminate the following fossil sample. This was tested by combusting the samples in a series with varying biofractions, e.g. first 30% biodiesel was combusted, then 2% etc. The results were plotted and are shown in figure 54.

**Figure 54.** Sample biofraction vs sample order.

As can be seen from the figure, no memory effects were detected during the tests within the timescale used in our sampling. At fastest two consecutive samples were combusted within half an hour.

Finally the results were compared to the uncertainties allowed by the ASTM D6866-10 standard. The plot is shown in figure 55.
Figure 55. The results of the CTC and EA methods compared to the uncertainties allowed by the ASTM D6866-10 standard.\textsuperscript{7,10}

The figure demonstrates that while both methods are within the allowed uncertainties of ASTM D6866, EA gives slightly better results.

9. Conclusions

In the literary section of this thesis a review on the field of radiocarbon analytics and biofuel characterization was given. During the past few years, significant research has been conducted on the field of liquid biofuel characterization. In several countries, such as Brazil and United States and in the European Union, this is driven by legislation connected to promotion of biofuel use.

Especially in Brazil, several easy, cheap and relatively accurate methods have been used to characterize FAME biodiesel blends. These include IR spectroscopy, X-ray spectroscopy, fluorescence spectroscopy, NMR, GC and LC. Some of these methods, such as NMR or GCxGC, can quantify FAME contents down to ppm levels. On the other hand, some
methods have higher levels of detection, e. g. for X-ray spectrometry the level of detection is 1.2 % (v/v). The uncertainties of these methods vary, but there can be a deviation up to ± 20 % such as with NMR. Nevertheless, all these methods are promising in their cost-effectiveness and accuracy.

It must be noted, however, that all the methods described above are limited in their ability to be applied to other biofuel types, such as NExBTL –type hydrogenated biodiesels and biodiesels produced by the Fischer-Tropsch synthesis. This is because the chemical compositions of these fuels are very different from the FAME biodiesels. The hydrogenated renewable diesels and F-T biodiesels are very similar to petrodiesel. In addition, the methods described above are completely unable to differentiate e.g. fossil ethanol from bioethanol. To date, the difference of biological vs. fossil origin can only be determined by radiocarbon analysis.

Two of the most popular methods for measuring radiocarbon contents are Liquid Scintillation Counting and Accelerator Mass Spectrometry. LSC is cheaper and the equipment is more readily available and easy to use. On the other hand, when dealing with samples with very low radiocarbon content the accuracy is not as good as with AMS. The LSC can also suffer from color quenching as some FAME biodiesels have a yellowish tint, intensity of which depends on the feedstock. A method for decolorization of the biodiesel blends without effecting the carbon isotope ratios is still under research. The correlation of biodiesel blend ratios vs. measured values are usually linear, with $R^2$ values up to 0.9999. Relative errors of under 10 % have been reported, usually so that the smaller the biodiesel percentage, the larger the error. In the worst cases the error was up to 15 %. Despite that, the lower cost of the LSC compensates effectively the smaller accuracy and sensitivity when compared to the AMS. LSC is still accurate especially for more modern samples containing near-atmospheric levels of radiocarbon.

AMS is by far the most accurate and sensitive method for radiocarbon determination but is very expensive. Furthermore, the AMS requires a very well trained personnel to operate. This increases the cost of a single sample. When compared to the LSC, the errors are usually under 6 % for biodiesels of higher blend percentage, even down to 0.1 % for 30 % biodiesel as presented by this work. As with the LSC, the errors grow larger when analyzing biodiesels with smaller blend percentages, reaching up to 14 % for 2 % biodiesel. Still, the AMS method remains the most accurate and sensitive. When
considering radiocarbon determinations from a larger perspective, such as in the case of archaeological samples, the radiocarbon contents can be so low on some samples that the only reasonable method for determination is the AMS.

Based on the results shown in this work it could be claimed that the superior method for measuring modern samples is, at the moment, the LSC, and in the case of very old samples, the AMS. It can be recommended for radiocarbon laboratories to keep access to both methods.

An interesting new method for radiocarbon measurement is laser spectroscopy. This method is not yet widely used and therefore there is not much data available. However, it is likely that the sensitivity and the accuracy of the method will increase as more research and development is conducted on it. The method is promising, and the laser spectroscopy equipment could, for instance, be coupled with an Elemental Analyzer and Isotope Ratio Mass Spectrometer allowing for simple sample combustion and immediate radiocarbon measurement.

Sample preparation for radiocarbon analysis can often be very labor-intensive process which can take several days. The experimental section of the thesis describes a new method for sample preparation for AMS measurements using an Elemental Analyzer instead of traditional Closed-Tube-Combustion method.

The first tests showed that the EA gave repeatable results and that the peak area vs. the mass of carbon in the sample was quite linear even though the carbon percentages were not of interest in this project.

The δ\(^{13}\)C measurements of the diesel samples suggested that there were no leaks in the system and the sample collection system did not leak air into the sample vial. This was proved by AMS measurements as the fossil diesels gave fossil values and the biofractions of the biodiesel samples were more accurate than with CTC method. Furthermore, it was seen that EA gave acceptable results when compared to the uncertainties allowed by the ASTM D6866-10 standard.

The user-friendliness of the EA greatly surpasses that of the CTC method. The CTC method is very labor-intensive and the packing of the quartz tubes, sealing them with blowtorch and cracking them open are all phases that are prone to human error. It is very easy to puncture the tubes by too intense blowtorch flame and it is easy to break the quartz
tube from the wrong place when cracking the tube. There is also the risk of breaking the sample purification line itself while cracking the tube as the glass line does not withstand excessive force and, indeed, much force is required for cracking the very hard and rather thick tubes. In addition, the continuous use of blowtorch equipment can be stressful and is an obvious fire hazard. Furthermore, the combustion takes quite a lot of time but is usually done overnight.

All this is eliminated with the use of the EA combustion method. Packing the samples is fast and effortless, combustion takes 200 seconds and after quick evacuation of the vial the sample can be taken to $\delta^{13}$C measurement and graphitized.

With the EA combustion method the actual sample preparation work time is dropped from 19 to eight hours. This is quite significant decrease in working time and it allows more samples to be prepared or alternatively the efforts of the personnel to be focused on other tasks. It is foreseen that the EA combustion could be implemented within the future standardization of biofraction measurements.

10. References


2. European Commission, Communication from the Commission to the European Parliament, the Council, the European Economic and Social Committee and the Committee of the Regions. A Roadmap for moving to a competitive low carbon economy in 2050, European Commission, Brussels, 2011.


66. DIN, DIN EN 14078:2010 Liquid petroleum products - Determination of fatty methyl ester (FAME) content in middle distillates - Infrared spectrometry method; German version EN 14078:2009 (Foreign Standard), German Institute for Standardization, Germany, German Institute for Standardization.


### 11. Appendices

Appendix 1. Radiocarbon contents of the samples analyzed by Reddy _et al._

Appendix 2. NExBTL renewable diesel samples and the measured biofractions by Oinonen _et al._

Appendix 3. $^{14}$C LSC analysis of bioethanol-gasoline blends and AMS results by Dijs _et al._
Appendix 1. Radiocarbon contents of the samples analyzed by Reddy et al. Table 1. Radiocarbon (Δ¹⁴C) Content and B* (from 10) of Samples Analyzed in This Study (All Samples Acquired in 2006 unless Noted Otherwise)

<table>
<thead>
<tr>
<th>sample source</th>
<th>month acquired</th>
<th>Δ¹⁴C (‰)</th>
<th>biodiesel (v/v)</th>
<th>calculated B* (v/v)</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Fat Source endmembers</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>used vegetable oil (N. Carolina restaurant)</td>
<td>April</td>
<td>59.1</td>
<td>NA²</td>
<td>NA²</td>
</tr>
<tr>
<td>new fry oil (Massachusetts restaurant A)</td>
<td>May</td>
<td>54.6</td>
<td>NA</td>
<td>NA</td>
</tr>
<tr>
<td>used fry oil (Massachusetts restaurant A)</td>
<td>May</td>
<td>73.5</td>
<td>NA</td>
<td>NA</td>
</tr>
<tr>
<td>bacon grease (Massachusetts restaurant B)</td>
<td>June</td>
<td>58.8</td>
<td>NA</td>
<td>NA</td>
</tr>
<tr>
<td>new Crisco soybean (store bought)</td>
<td>Sept</td>
<td>62.2</td>
<td>NA</td>
<td>NA</td>
</tr>
<tr>
<td><strong>Petrodiesel endmembers</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Bouchard 65 barge®</td>
<td>Oct 1974²</td>
<td>−999.9</td>
<td>0²</td>
<td>0.01 ± 0.02</td>
</tr>
<tr>
<td>Massachusetts distributor A</td>
<td>Nov</td>
<td>−1000</td>
<td>0²</td>
<td>0.00 ± 0.02</td>
</tr>
<tr>
<td>removed from truck driving petrodiesel only</td>
<td>March 2007</td>
<td>−999.5</td>
<td>0²</td>
<td>0.05 ± 0.02</td>
</tr>
<tr>
<td><strong>Commercial B99.9s and B100s</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>California distributor A</td>
<td>June</td>
<td>−10.1</td>
<td>99.9²</td>
<td>98.6 ± 0.9</td>
</tr>
<tr>
<td>Massachusetts distributor A</td>
<td>Nov</td>
<td>−1.71</td>
<td>99.9²</td>
<td>99.4 ± 0.9</td>
</tr>
<tr>
<td>California distributor B</td>
<td>July</td>
<td>8.29</td>
<td>99.9²</td>
<td>100 ± 0.9</td>
</tr>
<tr>
<td>California distributor B</td>
<td>July</td>
<td>10.3</td>
<td>99.9²</td>
<td>101 ± 0.9</td>
</tr>
<tr>
<td>California distributor B</td>
<td>August</td>
<td>11.6</td>
<td>99.9²</td>
<td>101 ± 0.9</td>
</tr>
<tr>
<td>Indiana distributor A</td>
<td>April</td>
<td>−31.2</td>
<td>100³</td>
<td>96.7 ± 0.9</td>
</tr>
<tr>
<td>Massachusetts distributor A</td>
<td>June</td>
<td>9.88</td>
<td>100³</td>
<td>100 ± 0.9</td>
</tr>
<tr>
<td>Massachusetts distributor A</td>
<td>Sept</td>
<td>−4.92</td>
<td>100²</td>
<td>99.1 ± 0.9</td>
</tr>
<tr>
<td>California distributor C</td>
<td>June</td>
<td>15.3</td>
<td>100²</td>
<td>101 ± 0.9</td>
</tr>
<tr>
<td><strong>Blends we prepared by mixing Bouchard 65 with Massachusetts distributor A B100; June (see above)</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>known laboratory mix</td>
<td>NA</td>
<td>−983</td>
<td>2.00²</td>
<td>1.9 ± 0.2</td>
</tr>
<tr>
<td>known laboratory mix</td>
<td>NA</td>
<td>−956</td>
<td>4.97²</td>
<td>4.8 ± 0.2</td>
</tr>
<tr>
<td>known laboratory mix</td>
<td>NA</td>
<td>−818</td>
<td>20.0²</td>
<td>19.4 ± 0.6</td>
</tr>
<tr>
<td>known laboratory mix</td>
<td>NA</td>
<td>−331</td>
<td>69.8²</td>
<td>68.5 ± 1</td>
</tr>
<tr>
<td><strong>Commercial biodiesel blends ranging from B2 to B20</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Minnesota distributor A</td>
<td>June</td>
<td>−979</td>
<td>2³</td>
<td>2.3 ± 0.2</td>
</tr>
<tr>
<td>Minnesota distributor B</td>
<td>June</td>
<td>−980</td>
<td>2³</td>
<td>2.2 ± 0.2</td>
</tr>
<tr>
<td>Minnesota distributor C</td>
<td>June</td>
<td>−981</td>
<td>2³</td>
<td>2.0 ± 0.2</td>
</tr>
<tr>
<td>Minnesota distributor D</td>
<td>June</td>
<td>−976</td>
<td>2³</td>
<td>2.6 ± 0.2</td>
</tr>
<tr>
<td>Indiana distributor A</td>
<td>April</td>
<td>−954</td>
<td>5³</td>
<td>4.9 ± 0.2</td>
</tr>
<tr>
<td>North Carolina</td>
<td>April</td>
<td>−953</td>
<td>5³</td>
<td>5.1 ± 0.2</td>
</tr>
<tr>
<td>Massachusetts distributor B</td>
<td>June</td>
<td>−968</td>
<td>5³</td>
<td>3.5 ± 0.2</td>
</tr>
<tr>
<td>Indiana distributor B</td>
<td>April</td>
<td>−869</td>
<td>15³</td>
<td>14.0 ± 0.5</td>
</tr>
<tr>
<td>Massachusetts distributor A</td>
<td>May</td>
<td>−855</td>
<td>20³</td>
<td>15.5 ± 0.6</td>
</tr>
<tr>
<td>Massachusetts distributor A</td>
<td>June</td>
<td>−901</td>
<td>20³</td>
<td>10.7 ± 0.4</td>
</tr>
<tr>
<td>Massachusetts distributor A</td>
<td>Sept</td>
<td>−269</td>
<td>20³</td>
<td>74.4 ± 1</td>
</tr>
<tr>
<td>Massachusetts distributor A</td>
<td>Nov</td>
<td>−904</td>
<td>20³</td>
<td>10.4 ± 0.4</td>
</tr>
<tr>
<td>Massachusetts distributor B</td>
<td>June</td>
<td>−840</td>
<td>20³</td>
<td>17.2 ± 0.6</td>
</tr>
<tr>
<td>Massachusetts distributor C</td>
<td>April</td>
<td>−843</td>
<td>20³</td>
<td>16.8 ± 0.6</td>
</tr>
<tr>
<td>Massachusetts distributor C</td>
<td>June</td>
<td>−795</td>
<td>20³</td>
<td>21.8 ± 0.7</td>
</tr>
<tr>
<td>Massachusetts distributor C</td>
<td>Sept</td>
<td>−796</td>
<td>20³</td>
<td>21.8 ± 0.7</td>
</tr>
<tr>
<td>Massachusetts distributor C</td>
<td>Nov</td>
<td>−810</td>
<td>20³</td>
<td>20.3 ± 0.7</td>
</tr>
<tr>
<td>Tennessee (replicate i)</td>
<td>May</td>
<td>−852</td>
<td>20³</td>
<td>15.8 ± 0.6</td>
</tr>
<tr>
<td>Postretail “Personal user” blends</td>
<td>May</td>
<td>$-851$</td>
<td>$20^c$</td>
<td>$15.9 \pm 0.6$</td>
</tr>
<tr>
<td>-----------------------------------</td>
<td>-----</td>
<td>--------</td>
<td>--------</td>
<td>----------------</td>
</tr>
<tr>
<td>Tennessee (replicate $ii$)</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Massachusetts personal A self-mixed from retail endmembers of petrodiesel and B100</td>
<td>May</td>
<td>$-900$</td>
<td>$20^c$</td>
<td>$10.7 \pm 0.4$</td>
</tr>
<tr>
<td>Massachusetts personal B self-mixed from retail endmembers of petrodiesel and B100</td>
<td>May</td>
<td>$-424$</td>
<td>$70^c$</td>
<td>$59.5 \pm 1$</td>
</tr>
<tr>
<td>Massachusetts personal A supply (stored in owners supply jug and purchased from a retailer)</td>
<td>May</td>
<td>$-3.43$</td>
<td>$100^c$</td>
<td>$99.3 \pm 0.9$</td>
</tr>
<tr>
<td>Massachusetts personal B (collected from tank of vehicle and purchased from a retailer)</td>
<td>March 2007</td>
<td>$-862$</td>
<td>$20^c$</td>
<td>$14.8 \pm 0.5$</td>
</tr>
</tbody>
</table>

\(a\) Not applicable.

\(b\) This oil was collected from a hold in the barge *Bouchard 65* after it spilled product in Buzzards Bay, MA in October 1974.

\(c\) Expected biodiesel content.

\(d\) Advertised biodiesel content.

\(e\) Known biodiesel percentage based on laboratory preparations.
Appendix 2. NExBTL renewable diesel samples and the measured biofractions by Oinonen et al.\(^7\)

Table 1. Results obtained by combusting torch-sealed diesel samples. All the mixed samples are EN590/NExBTL blends (fossil/bio). Note the extremely consistent $\delta^{13}$C values indicating high reproducibility.

<table>
<thead>
<tr>
<th>Hela-#</th>
<th>Blending % (foss/bio) + details</th>
<th>$\delta^{13}$C (‰)</th>
<th>pMC (‰)</th>
<th>±</th>
<th>$F_{bio}$ (wt.%) ±</th>
<th>Theor. (wt.%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>840</td>
<td>100 EN590, foss</td>
<td>-29.6</td>
<td>0.3</td>
<td>±0.1</td>
<td>0.1</td>
<td>±4.4</td>
</tr>
<tr>
<td>894</td>
<td>100 EN590, foss</td>
<td>-29.5</td>
<td>0.5</td>
<td>±0.1</td>
<td>0.1</td>
<td>±4.4</td>
</tr>
<tr>
<td>1267</td>
<td>100 NExBTL, bio</td>
<td>-30.4</td>
<td>106.5</td>
<td>±0.5</td>
<td>±0.1</td>
<td>±4.4</td>
</tr>
<tr>
<td>1551</td>
<td>100 NExBTL, bio</td>
<td>-30.1</td>
<td>106.4</td>
<td>±0.4</td>
<td>±0.1</td>
<td>±4.4</td>
</tr>
<tr>
<td>1631</td>
<td>95/5, top, 520 °C/10 h</td>
<td>-30.1</td>
<td>4.6</td>
<td>±0.1</td>
<td>4.3 0.1</td>
<td>±4.4</td>
</tr>
<tr>
<td>1634</td>
<td>95/5, bottom, 520 °C/10 h</td>
<td>-30.2</td>
<td>4.8</td>
<td>±0.1</td>
<td>4.5 0.1</td>
<td>±4.4</td>
</tr>
<tr>
<td>1632</td>
<td>70/30, top, 520 °C/10 h</td>
<td>-30.1</td>
<td>30.4</td>
<td>±0.2</td>
<td>28.6 0.2</td>
<td>±28.6</td>
</tr>
<tr>
<td>1633</td>
<td>70/30, bottom, 520 °C/10 h</td>
<td>-30.1</td>
<td>30.9</td>
<td>±0.2</td>
<td>29.0 0.2</td>
<td>±28.6</td>
</tr>
<tr>
<td>1643</td>
<td>70/30, 520 °C/10 h (-90 °C)</td>
<td>-30.1</td>
<td>30.5</td>
<td>±0.1</td>
<td>28.6 0.1</td>
<td>±28.6</td>
</tr>
<tr>
<td>1644</td>
<td>70/30, quartz, 720 °C/10 h</td>
<td>-30.1</td>
<td>30.5</td>
<td>±0.1</td>
<td>28.7 0.1</td>
<td>±28.6</td>
</tr>
<tr>
<td>1645</td>
<td>70/30, quartz, 720 °C/1 h</td>
<td>-30.1</td>
<td>30.5</td>
<td>±0.1</td>
<td>28.6 0.1</td>
<td>±28.6</td>
</tr>
<tr>
<td>1668</td>
<td>95/5, 520 °C/10 h</td>
<td>-30.1</td>
<td>4.5</td>
<td>±0.1</td>
<td>4.2 0.1</td>
<td>±4.4</td>
</tr>
<tr>
<td>1669</td>
<td>95/5, 520 °C/10 h</td>
<td>-30.1</td>
<td>4.7</td>
<td>±0.1</td>
<td>4.4 0.1</td>
<td>±4.4</td>
</tr>
<tr>
<td>1670</td>
<td>95/5, 520 °C/10 h</td>
<td>-30.1</td>
<td>4.7</td>
<td>±0.1</td>
<td>4.4 0.1</td>
<td>±4.4</td>
</tr>
<tr>
<td>1671</td>
<td>95/5, 520 °C/10 h</td>
<td>-30.1</td>
<td>4.6</td>
<td>±0.1</td>
<td>4.3 0.1</td>
<td>±4.4</td>
</tr>
<tr>
<td>1676</td>
<td>95/5, 520 °C/10 h</td>
<td>-30.1</td>
<td>4.8</td>
<td>±0.1</td>
<td>4.5 0.1</td>
<td>±4.4</td>
</tr>
<tr>
<td>1672</td>
<td>98/2, 520 °C/10 h</td>
<td>-30.1</td>
<td>1.8</td>
<td>±0.1</td>
<td>1.7 0.1</td>
<td>±1.9</td>
</tr>
<tr>
<td>1673</td>
<td>98/2, 520 °C/10 h</td>
<td>-30.1</td>
<td>2.1</td>
<td>±0.1</td>
<td>1.9 0.1</td>
<td>±1.9</td>
</tr>
<tr>
<td>1674</td>
<td>98/2, 520 °C/10 h</td>
<td>-30.1</td>
<td>1.9</td>
<td>±0.1</td>
<td>1.8 0.1</td>
<td>±1.9</td>
</tr>
<tr>
<td>1675</td>
<td>98/2, 520 °C/10 h</td>
<td>-30.1</td>
<td>1.9</td>
<td>±0.1</td>
<td>1.8 0.1</td>
<td>±1.9</td>
</tr>
<tr>
<td>1677</td>
<td>98/2, 520 °C/10 h</td>
<td>-30.1</td>
<td>2.2</td>
<td>±0.1</td>
<td>2.1 0.1</td>
<td>±1.9</td>
</tr>
</tbody>
</table>
Appendix 3. $^{14}$C LSC analysis of bioethanol-gasoline blends and AMS results by Dijs et al.\textsuperscript{62}

Table 2 $^{14}$C LSC analysis, 5.5 hr counting.

<table>
<thead>
<tr>
<th>Sample</th>
<th>$C_b$ (mol/L)</th>
<th>$C_b/(C_b + C_f)$</th>
<th>Net activity</th>
<th>%M $^a$</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td>(Bq/L)</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>Err. (%)</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>Err. (%)</td>
<td></td>
</tr>
<tr>
<td>1</td>
<td>0.00</td>
<td>0.00</td>
<td>0.00 0.12</td>
<td>0.00 0.10</td>
</tr>
<tr>
<td>2</td>
<td>34.39</td>
<td>100.0</td>
<td>106.6 0.81 0.8</td>
<td>108.1 6.25 5.8</td>
</tr>
<tr>
<td>3</td>
<td>0.00</td>
<td>0.00</td>
<td>0.00 0.12</td>
<td>0.00 0.20</td>
</tr>
<tr>
<td>4</td>
<td>0.00</td>
<td>0.00</td>
<td>0.00 0.12</td>
<td>0.00 0.20</td>
</tr>
<tr>
<td>5</td>
<td>3.29</td>
<td>6.22</td>
<td>9.32 0.25 2.7</td>
<td>6.53 0.41 6.3</td>
</tr>
<tr>
<td>6</td>
<td>1.70</td>
<td>3.15</td>
<td>4.90 0.19 3.8</td>
<td>3.37 0.23 6.8</td>
</tr>
<tr>
<td>7</td>
<td>0.65</td>
<td>1.20</td>
<td>1.91 0.18 4.7</td>
<td>1.31 0.14 11</td>
</tr>
<tr>
<td>8</td>
<td>0.33</td>
<td>0.61</td>
<td>1.08 0.17 5.3</td>
<td>0.74 0.12 16</td>
</tr>
<tr>
<td>9</td>
<td>0.18</td>
<td>0.33</td>
<td>0.79 0.17 5.5</td>
<td>0.54 0.12 22</td>
</tr>
<tr>
<td>10</td>
<td>17.26</td>
<td>50.16</td>
<td>51.7 0.58 1.1</td>
<td>55.6 3.24 5.8</td>
</tr>
<tr>
<td>11</td>
<td>33.72</td>
<td>98.04</td>
<td>99.2 0.89 0.9</td>
<td>106.5 6.18 5.8</td>
</tr>
<tr>
<td>12</td>
<td>34.05</td>
<td>99.00</td>
<td>99.9 0.89 0.9</td>
<td>107.3 6.23 5.8</td>
</tr>
<tr>
<td>13</td>
<td>34.22</td>
<td>99.50</td>
<td>100.4 0.89 0.9</td>
<td>107.9 6.26 5.8</td>
</tr>
</tbody>
</table>

$^a$Corrected for $^{13}$C isotope fractionation ($\delta^{13}$C data taken from AMS analysis, see text).

$^b$C$_b$ = carbon from biofuel; C$_f$ = carbon from fossil fuel. (See Table 1 for the bioethanol content of samples 1–13).

The error in %M differs from the error in $^{14}$C activity per liter as a result of the Gauss law of propagation of errors and because of both the spreading of 0.79 dpm in the specific $^{14}$C activity for carbon and an error of 2.5% in the determination of the carbon content by GC-MS and NMR.

Table 3 AMS results of gasoline-ethanol samples.

<table>
<thead>
<tr>
<th>Sample</th>
<th>$C_b/(C_b + C_f)$ $^b$</th>
<th>Err. $^c$</th>
<th>$\delta^{14}$C $^c$ $^d$</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>(% atom/atom)</td>
<td>(%)</td>
<td>(‰ atom/atom)</td>
</tr>
<tr>
<td>4</td>
<td>0.00</td>
<td>0.0</td>
<td>-27.3</td>
</tr>
<tr>
<td>5</td>
<td>6.22</td>
<td>6.8</td>
<td>-27.1</td>
</tr>
<tr>
<td>6</td>
<td>3.15</td>
<td>3.4</td>
<td>-27.2</td>
</tr>
<tr>
<td>7</td>
<td>1.20</td>
<td>1.2</td>
<td>-27.6</td>
</tr>
<tr>
<td>8</td>
<td>0.61</td>
<td>0.7</td>
<td>-27.4</td>
</tr>
<tr>
<td>9</td>
<td>0.33</td>
<td>0.4</td>
<td>-27.0</td>
</tr>
<tr>
<td>11</td>
<td>98.04</td>
<td>103.8</td>
<td>-25.6</td>
</tr>
<tr>
<td>12</td>
<td>99.00</td>
<td>105.7</td>
<td>-26.0</td>
</tr>
<tr>
<td>13</td>
<td>99.50</td>
<td>106.8</td>
<td>-25.9</td>
</tr>
</tbody>
</table>

$^a$Measured percent Modern, normalized to $\delta^{14}$C = -25 ‰ (atom/atom) (Higman 1999).

$^b$C$_b$ = carbon from biofuel; C$_f$ = carbon from fossil fuel. (See Table 1 for the bioethanol content of samples 1–13.)

$^c$Abundance of $^{14}$C relative to $^{12}$C with respect to the VPDB reference (Higman 1999).