

Methodologies for Biogenic Carbon Determination when Co-Processing Fast Pyrolysis Bio-Oil



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Summary

This paper describes the different methodologies that are available for tracing biogenic carbon when a renewable feedstock is co-processed with conventional (fossil) feedstock in a refinery. Specifically, it looks into the situation of co-processing Fast Pyrolysis Bio-Oil (FPBO) in Fluidized Catalytic Cracker units, in order to determine which methods are potentially suitable for regulatory purposes.

It can be concluded that the analytical method based on radiocarbon (a.k.a. “C14”) analysis with Accelerated Mass Spectroscopy (AMS) is not a suitable method, because it is not sensitive enough to reliably determine the biogenic carbon content at the concentrations that apply when co-processing FPBO. Since AMS is the most sensitive technique that currently exists for radiocarbon analysis, unfortunately there are no analytical techniques available for biogenic carbon content determination in this context.

Several bookkeeping methods are available for this purpose, such as mass or energy balance methods. These are shortly described in this paper as they provide a feasible alternative. Important factors for choosing the right method is that on the one hand they have to be fair and transparent so that the biofuel production is not over- nor underestimated, and on the other hand they have to be practically implementable so that economic operators can comply with the method.

A case study was performed on the various bookkeeping methods that are known, thereby using pilot plant data reported in literature. Two of these methods would be the most suitable bookkeeping methods for co-processing low percentages of FPBO in FCC units. The first is the observed yields method in an adapted form, for those refiners that have a steady longer-term operation and are able to reliably determine the CO, CO₂ and water being formed in the unit. For those refiners that are unable to comply with the requirements of the observed yields method, we believe the energy balance method would be most suitable, as it is the most universally applicable method and it strikes an appropriate balance between fairness, applicability and transparency.

1. Introduction

Fast Pyrolysis Bio-oil (FPBO) is an advanced biofuel that can be used directly as a renewable heating fuel, to replace heating oil or natural gas, and that can also be converted into a drop-in fuel for transportation. The associated greenhouse gas savings are very high (up to 93 %).¹ FPBO is produced by fast pyrolysis of lignocellulosic biomass (residues from forestry, agriculture and related industries), which is a process that converts biomass into a dark brown liquid in just seconds. While it bears a visual resemblance to crude oil and is therefore referred to as a bio-oil, the properties of raw FPBO make it immiscible with fossil fuels.

Co-processing FPBO in conventional oil refinery units, and specifically in fluidized catalytic cracker (FCC) units, is one of the most cost-effective routes to produce advanced biofuels. It provides a very direct way to replace fossil feedstocks, meaning less crude oil is needed to meet the demand for transportation fuels, and more oil reserves can stay untouched. A complication with using oil refineries to produce advanced biofuels is that they are extremely well-integrated and complex, and the scale is much greater than the scale of biofuels production. To illustrate this complexity, Figure 1 shows a scheme of a typical oil refinery, with the FCC unit at the heart of it. The blue arrows indicate the streams feeding the FCC, while the red arrows indicate the product streams of the FCC.

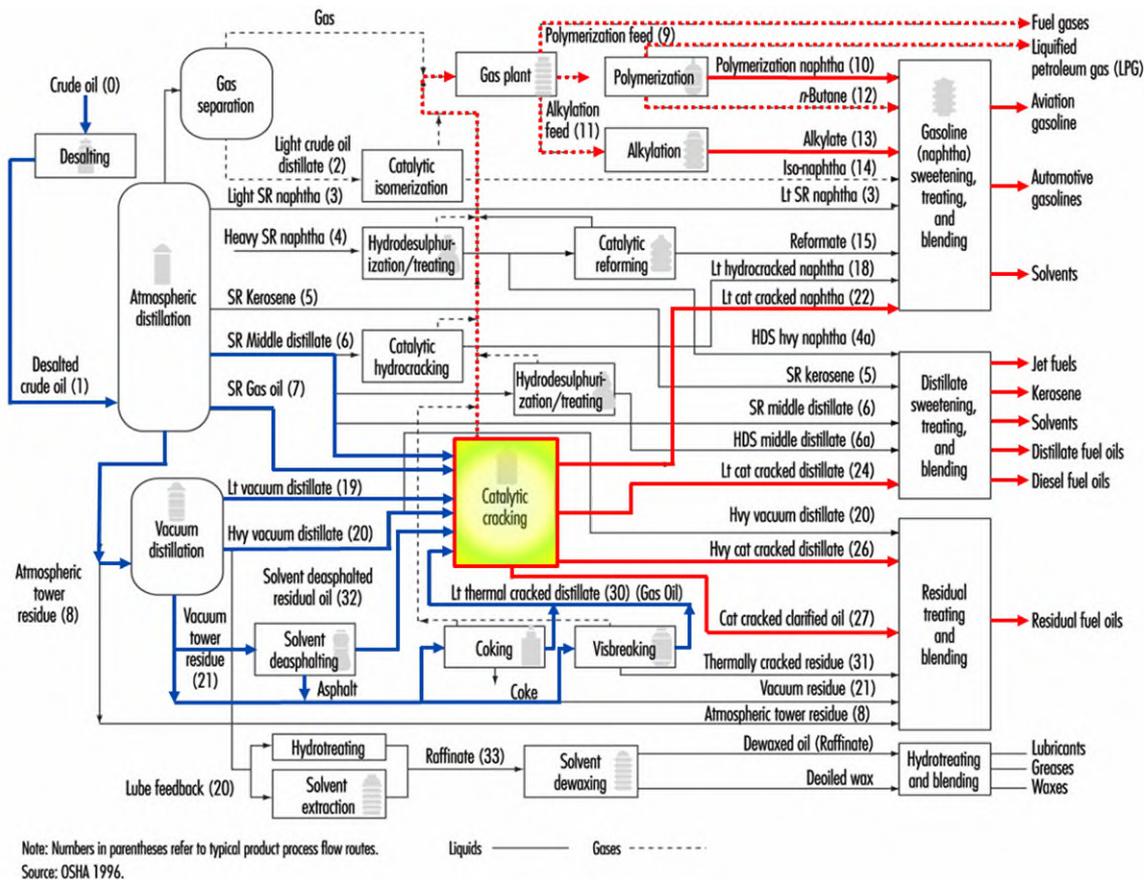


Figure 1. A typical complex refinery scheme highlighting the various inputs and outputs of the FCC unit.

The FPBO volume that is produced by a typical production plant such as Empro in the Netherlands is equal to about 1 % of the total feedstock of an average-sized European FCC. The combination of these

¹ Empro, audits for NTA8080 in 2017 and 2018.

two factors (complexity and scale-difference) pose a severe challenge for tracing biogenic carbon through an oil refinery.

There are two types of methods for tracing biogenic carbon: analytical and bookkeeping methods. The analytical method that is the most commonly applied is radiocarbon (a.k.a. “carbon-14”) analysis, because it is the most sensitive and accurate analytical method. Bookkeeping methods that are commonly applied are those based on mass or energy balances, for example the methods defined by the ISCC.

The purpose of this paper is to describe both types of methods and assess their suitability for tracing biogenic carbon when co-processing FPBO, in order to come to a conclusion on what would be the most suitable method for regulatory purposes, especially in the context of the implementation of the Recast of the Renewable Energy Directive (RED2) in Europe.

2. Radiocarbon analysis

Radiocarbon dating is a method for determining the age of an object containing organic material by using the properties of radiocarbon, a radioactive isotope of carbon.

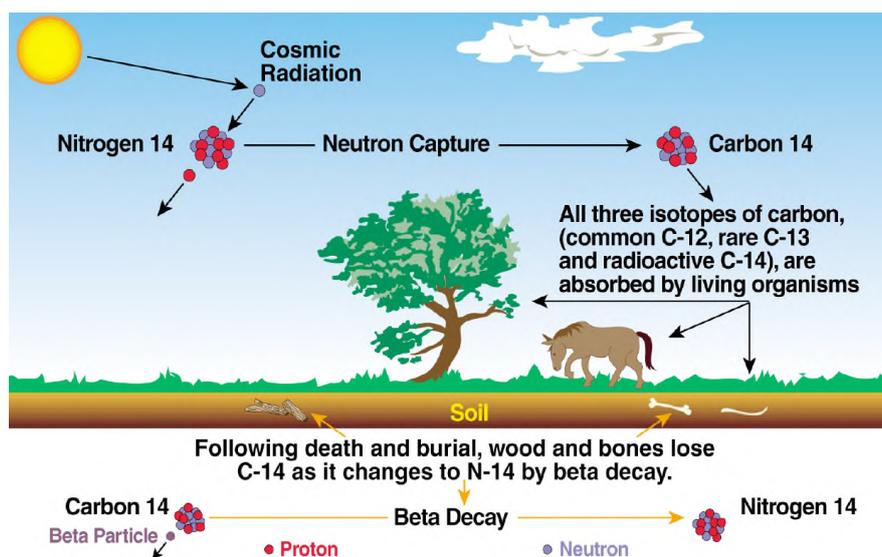


Figure 2. The way in which radiocarbon forms and decays.²

In nature, carbon exists as two stable, non-radioactive isotopes: carbon-12 (¹²C), and carbon-13 (¹³C), and as an unstable radioactive isotope, carbon-14 (¹⁴C), also known as "radiocarbon". The half-life of radiocarbon (the time it takes for half it to decay) is 5,730 years, yet ¹⁴C is constantly being produced in the atmosphere by cosmic radiation. Radiation generates neutrons that in turn create radiocarbon when they strike nitrogen atoms in the air. The radiocarbon immediately combines with oxygen in the air to form ¹⁴CO₂. This carbon dioxide diffuses in the atmosphere, is dissolved in the oceans, and is taken up by plants via photosynthesis. Figure 2 shows the overall process. During its lifetime, a plant exchanges carbon with the atmosphere and will therefore have the same ratio between ¹⁴C and ¹²C as the atmosphere has, which is roughly one to one trillion. Once it dies, it ceases to acquire ¹⁴C, and so the ratio of ¹⁴C to ¹²C in its remains will gradually decrease.³ Because fossil resources are in fact ancient

² Buchholz 2018, "[Quantifying Biologically Derived Carbon in Refinery Products Using AMS](#)"

³ Wikipedia 2019, "[Radiocarbon dating](#)"

plant remains, they do not have any radiocarbon left. That is why the percentage of biogenic carbon in a product can be calculated by determining the amount of radiocarbon in it. As such it has become a popular method to determine the bio-based carbon content of biofuels and bio-based products.

2.1 Detection of radiocarbon and biogenic carbon in products

The main method of ^{14}C analysis is by Accelerator Mass Spectrometry (AMS), which is a form of mass spectrometry that accelerates ions to extraordinarily high kinetic energies before mass analysis.⁴ The special strength of AMS among the mass spectrometric methods is its power to separate a rare isotope from an abundant neighbouring mass, such as ^{14}C from ^{12}C . AMS is required over other forms of mass spectrometry because other instruments give insufficient suppression of molecular isobars to resolve ^{13}CH and $^{12}\text{CH}_2$ from radiocarbon. AMS instruments are complex and expensive spectrometers, and there are not many laboratories that are equipped with one.



Figure 3. Accelerator mass spectrometer at the Lawrence Livermore National Laboratory in the USA.⁵

A typical method for sample preparation is to chemically separate the carbon from the original sample by turning it into CO_2 , which is cryogenically purified and then converted into graphite. The graphite is pressed into a sample holder, which is placed into a sputter ion source of an accelerator.⁶

The analytical measurement is cited as “percent modern carbon (pMC)”. As mentioned above, the ratio between radiocarbon and normal carbon atoms in a living plant is about one to one trillion. Based on that ratio and a modern reference standard (NIST 4990C), the pMC is calculated from the ^{14}C measurement. The biogenic carbon content is subsequently calculated from the pMC, by multiplying the pMC with an “atmospheric adjustment factor”, which corrects for the average ^{14}C content of carbon dioxide in the air today. Such a correction is necessary because the radiocarbon content of the atmosphere changed over the years. This is further described in paragraph 2.2.

The statistical limit of detection of this type of analysis is 0.44 % pMC, equal to 4.4 parts per quadrillion (10^{-15}) of radiocarbon. This is the level that should almost always generate a measurement above the critical level and thus yield a statistically significant value.⁷ In other words: below that limit of detection a measured pMC value is not reliable.

⁴ Another method is with Liquid Scintillation Counters (LSC), but this is less precise than by AMS.

⁵ Wikipedia 2019, “[Accelerator mass spectrometry](#)”

⁶ Beta Analytic 2019, “[Introduction to Radiocarbon Determination by the AMS Method](#)”

⁷ Rocke 2018, “[Measurement error in percent modern carbon analysis by \$^{14}\text{C}\$](#) ”

2.2 Variations in atmospheric radiocarbon

Coal and oil began to be burned in large quantities during the 19th century. As a result, the CO₂ released substantially diluted the atmospheric ¹⁴C/¹²C ratio. Dating an object from the early 20th century hence gives an apparent date older than the true date. For the same reason, radiocarbon concentrations in the neighbourhood of large cities are lower than the atmospheric average. This fossil fuel effect would only amount to a reduction of 0.2% in radiocarbon activity if the additional fossil carbon was immediately distributed throughout the entire carbon exchange reservoir (oceans, plants, atmosphere), but because of the long delay in mixing with the deep ocean, the actual effect is a 3% reduction. Translating that effect into biogenic carbon content, means the apparent biogenic carbon content is a little lower than the actual biogenic carbon content.

A much larger effect comes from above-ground nuclear testing, which released large numbers of neutrons and created radiocarbon. From about 1950 until 1963, when atmospheric nuclear testing was banned, it is estimated that several tonnes of radiocarbon were created. If all this extra radiocarbon had immediately been spread across the entire carbon exchange reservoir, it would have led to an increase in the ¹⁴C/¹²C ratio of only a few per cent, but the immediate effect was to almost double the amount of radiocarbon in the atmosphere, with the peak level occurring in 1964 for the northern hemisphere, and in 1966 for the southern hemisphere. The level has since dropped, as this bomb pulse or "bomb carbon" as it is sometimes called percolates into the rest of the reservoir.³ This is shown in figure 4.

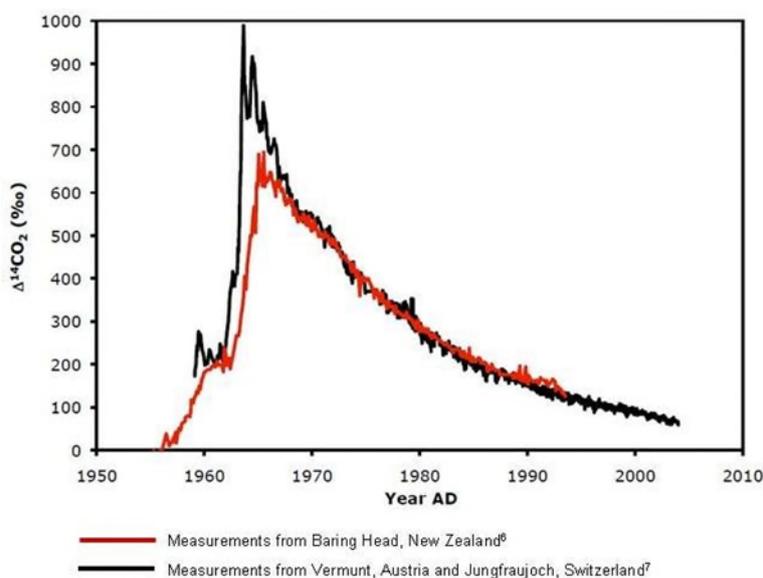


Figure 4. Atmospheric ¹⁴CO₂ concentrations in the northern and southern hemispheres.⁸

The bomb carbon effect means that based on the location and age of a tree, the same amount of wood can result in a higher or in a lower apparent biogenic carbon content. For example, sawdust from Scandinavian sawmills will likely contain much older wood (with boreal forest rotation lengths in the order of 100 years) than residues from a eucalyptus plantation in Portugal that has rotation lengths of less than 10 years, or agricultural residues from a one-year crop such as wheat straw. In a single forest there will be different radiocarbon concentrations in residues from thinning versus in residues from fully grown trees. Even in a single tree the radiocarbon content will vary between different year rings. This means that different batches of sawdust are likely to have a different radiocarbon content.

⁸ US National Oceanic & Atmospheric Administration 2019, "[The Bomb Spike](#)"

2.3 Accuracy, Precision, Uncertainty

The variations of radiocarbon in the atmosphere (over time and in location) have an impact on the accuracy with which the biogenic carbon content of a product can be determined. In this context it is important to distinguish between accuracy and precision. Accuracy is the closeness of a value (or average) to the true value, while precision is the closeness of values obtained by independent measurements under identical conditions to each other. This is graphically represented in Figure 5.⁹

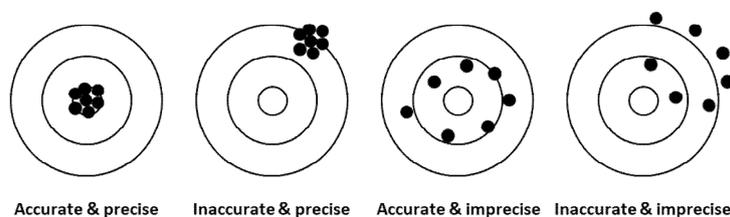


Figure 5. Graphic representation of accuracy and precision. Accurate means hitting a target on average; precise means all samples give the same value. Accuracy and precision are both required for a reliable result.

When a pMC measurement yields a small error margin, it means that the measurement is precise. Yet it does not automatically mean that the measurement is accurate. The variations in atmospheric radiocarbon may result in precise yet inaccurate measurements, if the adjustment factor that is used for converting pMC to biogenic carbon is inaccurate for a certain biomass sample. Therefore, the ASTM method for determining biogenic carbon content prescribes an absolute uncertainty of $\pm 3\%$.

2.4 Radiocarbon analysis in the context of FPBO co-processing

Co-processing FPBO with a crude oil-based feedstock in fluidized catalytic cracking (FCC) units can be done up to a volume of 5 wt-% FPBO, without a major impact on the process yields.¹⁰ A typical European FCC unit processes in the order of 2.5 million tons of feedstock per year. Co-processing 1 wt-% FPBO in an FCC thus requires 25 kton FPBO per year, which is the output of a single fast pyrolysis plant. This means that the first FCC's that will start co-processing FPBO commercially, will probably start with co-processing 1 wt-% FPBO, increasing that percentage when more FPBO capacity comes online.

In order to assess the feasibility of using radiocarbon analysis to determine the biogenic carbon content of the products from co-processing FPBO, samples were prepared from FCC gasoline and FCC diesel (a.k.a. LCO or cat cracked distillate) that were produced in an FCC demo-plant, using 5 and 10 wt-% FPBO as feedstock.¹¹ The product samples were analysed for their radiocarbon content and subsequently diluted with fossil product in order to mimic the radiocarbon concentrations that would be present in FCC products when co-processing between 0.5 and 3 wt-% FPBO.¹² The diluted samples

⁹ Scott 2007, "[Error and Uncertainty in Radiocarbon Measurements](#)", also cited by Talmadge 2016, "[Analysis for co-processing fast pyrolysis oil with VGO in FCC units for second generation fuel production](#)"

¹⁰ Pinho 2015, "[Co-processing raw bio-oil and gasoil in an FCC Unit](#)"; Pinho 2017, "[Fast pyrolysis oil from pinewood chips co-processing with vacuum gas oil in an FCC unit for second generation fuel production](#)"

¹¹ These products were prepared in 2017 in the Petrobras SIX-plant, using FPBO produced by Empyro.

¹² Experimental procedure: 2 gram of diesel product sample from 5 wt-% FPBO co-processing was mixed with 2 gram of diesel product sample from 0 wt-% co-processing. The resulting mixture was sampled for analysis and 2 gram of it was further diluted with 2 gram of diesel product sample from 0 wt-% co-processing, etc. In this way the amount of biogenic carbon is diluted by a factor 2 each time (blue points in figure 6). The same procedure was done with a diesel sample from 10 wt-% FPBO co-processing (orange points in figure 6).

were then submitted to a reputable laboratory for analysis of their radiocarbon content, following the AMS method described in paragraph 2.1.^{6,13}

Figure 6 shows the percentage Modern Carbon (pMC, see paragraph 2.1 for the definition) that was measured for 11 FCC diesel samples (the blue and orange points). The blue points represent the samples in the dilution range starting from 5 wt-% FPBO and the orange points represent the samples in the dilution range starting from 10 wt-% FPBO. The error bars represent the error margins provided by the lab for individual measurements, based on background noise, etcetera. The blue and orange lines in Figure 6 represent the actual pMC that can be calculated for diluting the product samples (from either the 5 wt-% or the 10 wt-% product sample). If the ¹⁴C measurements are precise the blue points should overlap with the blue line and the orange points should overlap with the orange line.

The original product samples from co-processing 5 and 10 wt-% FPBO were each submitted for analysis twice, on different dates. What can be noticed from the analyses of these identical samples (the blue points at 5 wt-% and the orange points at 10 wt-% in Figure 6), is that the actual variation in measured values is larger than the error margins provided by the lab. This means that although the measurement appears precise from the small error margins of a single measurement, multiple measurements of the same sample indicate less precision. Furthermore, it is clear from figure 6 that measurements around the statistical limit of detection (below 3 wt-% FPBO co-processing) are indeed very unreliable, as some points fit the lines quite nicely, while others are far off. For these low FPBO concentrations it can be concluded that the ¹⁴C method is fairly imprecise.

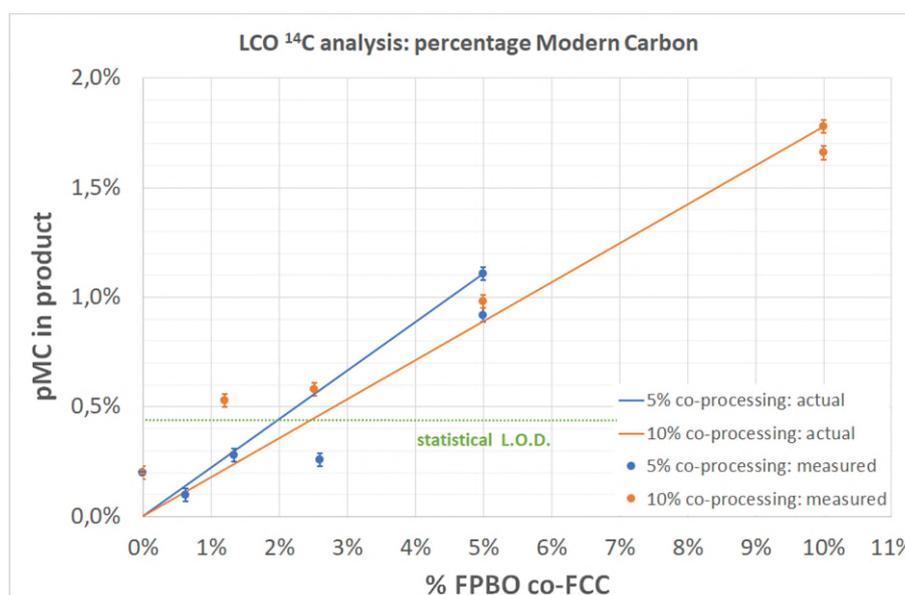


Figure 6. Results of the pMC analysis of FCC diesel samples from FPBO co-processing. Blue points represent the ¹⁴C analyses of samples prepared by diluting diesel product from 5 wt-% FPBO, while orange points represent ¹⁴C analyses of samples prepared by diluting diesel product from 10 wt-% FPBO. The blue line is the line which the blue points should follow if they are precise, while the orange line is the line which the orange points should follow if they are precise. The statistical limit of detection is indicated with a green dotted line.

Then, in order to assess the accuracy of this method when applying it to FPBO co-processing, an assessment was made of the accuracy of the atmospheric adjustment factor that is applicable for converting the percentage Modern Carbon into percentage biogenic carbon (see paragraph 2.2 for the background on this). To do this, FPBO prepared from sawdust from a Scandinavian sawmill was

¹³ ASTM D6866-18 Method B, using Accelerator Mass Spectroscopy

analysed for its pMC concentration. Neat FPBO has a biogenic carbon content of 100 %.¹⁴ The measured pMC value for this sample was 115 %, so it was a factor 1.15 too high. FPBO samples that were diluted with known quantities of a fossil alcohol (yielding mixtures with known biogenic carbon contents of 28 %, 53 % and 76 %) were also analysed and consistently showed a pMC that was a factor 1.15 higher than the actual biogenic carbon percentage. It is likely that the “bomb carbon” that was described earlier (see figure 4) is responsible for this inaccuracy, as trees that are harvested for timber in Scandinavia, from which the sawdust was used to produce FPBO, are typically around 75-100 years old. These trees accumulated more radiocarbon in their lifetime than the current atmospheric average. In theory one could compensate for this inaccuracy by measuring the pMC of the FPBO feedstock. That is possible for lab or pilot experiments, but at commercial scale the variations in radiocarbon content between different batches of sawdust would mean that every single batch of FPBO as delivered to a refinery by e.g. a tank truck would have to be analysed for its pMC.

The analytical results that are shown above indicate that the pMC measurements of these samples are both imprecise and inaccurate. The ASTM norm for determining biogenic carbon content deals with this imprecision and inaccuracy by prescribing an absolute uncertainty of $\pm 3\%$. Figure 7 shows the results of these analyses, when the ASTM norm is followed and the pMC concentrations that are shown in Figure 6 are converted to the biogenic carbon content of these samples, including the prescribed error margin. It is obvious from Figure 7 that the high uncertainty of the biogenic carbon content makes the radiocarbon analysis method unsuitable for determining the biogenic content of co-processing FPBO at these low concentrations.

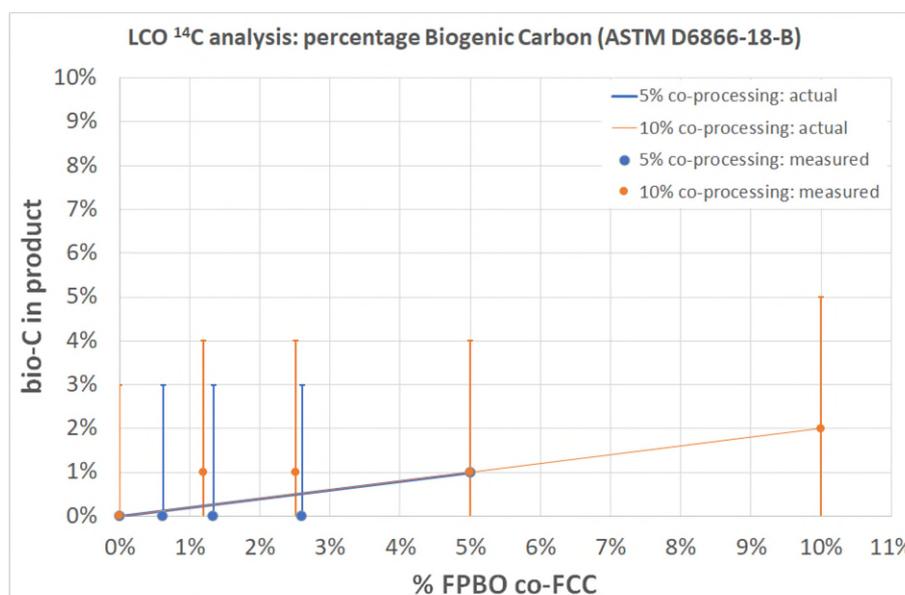


Figure 7. Biogenic carbon content of FCC diesel samples from FPBO co-processing. The error margins indicated in this graph are those that are prescribed by the ASTM method.

2.5 Conclusion on the suitability of radiocarbon analysis

It can be concluded that while radiocarbon analysis is a very suitable technique for determining the biogenic carbon content of products that have a high bio-based content, it is neither accurate nor precise enough for reliably determining the biogenic carbon content of products from FCC co-processing of FPBO at quantities of 5 wt-% FPBO or less.

¹⁴ Actually, 100% of the carbon in FPBO is biogenic; the total carbon content of this FPBO sample was 44 wt-%.

3. Mass or energy balance approaches

Ecofys recently prepared an overview of the various methods that have been developed regarding mass and energy balances, including their advantages and disadvantages.¹⁵ Mass and energy balance methods are administrative (“bookkeeping”) methods, which are based on the principle that in any system the total inputs of mass or energy are equal to the respective outputs. The assumption is that all the renewable feedstock which enters a refinery unit (e.g. an FCC) has to end up in the various products. The various methods differ in the way how the distribution of the renewable feedstock across the various products is calculated.

Figure 8 shows the principle of FCC co-processing of FPBO and the various products, with typical yields, across which the renewable feedstock is distributed.

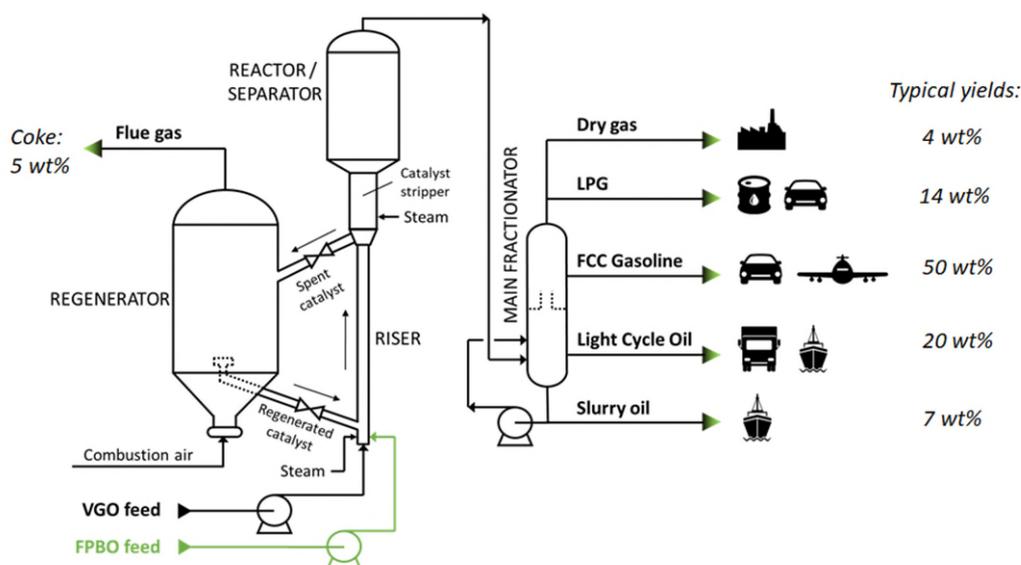


Figure 8. Principle of FCC co-processing of FPBO, with the various products and typical yields.

Typically, about 95 wt-% of the feedstock becomes the various FCC products, and 5 wt-% becomes coke, which is burned to provide the energy for the catalytic cracking process. Dry gas is used elsewhere in the refinery as a fuel, while LPG, gasoline, light cycle oil (LCO, a.k.a. FCC diesel) and slurry oil (a.k.a. bottoms) are further refined into final products. Further refining can encompass upgrading (e.g. sulphur removal), separation (e.g. isolating propylene from LPG), blending (e.g. mixing LCO with diesel or marine fuel), etcetera. When a feedstock such as FPBO is added to an FCC unit, the product yields will slightly change. That is due to the nature of FPBO, which contains about 50% oxygen, of which about half is water, and the other half of the oxygen is chemically bound to organic molecules in the FPBO. The oxygen mainly ends up as CO, CO₂, and water. This means that not all the mass of the FPBO is converted into fuel, but rather half of it (the carbon and hydrogen), minus some carbon that is removed together with the chemically bound oxygen. A bookkeeping approach should keep this in mind in order not to overestimate the amount of fuel that is produced from the FPBO.

In its report, Ecofys describes three mass balance methods that are applied or under development, as well as one energy balance method. These three mass balance methods are based on: 1) observed yields, 2) a carbon mass balance, or 3) a total mass balance. In fact, there is one more method that is in use, by ISCC PLUS, which is a voluntary scheme for bio-based chemicals. This mass balance method is based on free attribution. All of them will be shortly described here.

¹⁵ Ecofys, “[Determining the renewability of co-processed fuels](#)”, BIENL Final Report, 2018, for EC DG Energy

3.1 Observed yields mass balance

A mass balance on the basis of observed yields starts from a baseline scenario without any renewable feedstock, and allocates any observed differences in yield when co-processing a renewable feed to the renewable products. The ISCC refers to this method as “determination through efficiency / losses”.¹⁶ For this method you look at all the products and label the differences in yields as renewable.

For example: if 90 kg fossil feedstock would yield 90 kg products, and 90 kg fossil feedstock plus 10 kg renewable feedstock would yield 97 kg products, the volume of renewable products produced with this method would be 7 kg. When one unit produces multiple outputs, such as the FCC (see figure 8), the yield effect for all the different outputs needs to be calculated independently.

A challenge with this method would be that it starts from a baseline of yields from only fossil feedstock, which means that when an operator would switch from one fossil feedstock to another, which is rather common in the refinery industry, the baseline would need to be re-established.

3.2 Carbon mass balance

The carbon mass balance method is somewhat simpler than the observed yields method. It does not consider all the yields of the different products, but rather takes the produced CO and CO₂ into consideration as a production loss that should be subtracted from the renewable carbon input, on the basis of the assumption that fossil feedstock does not lead to the production of any CO or CO₂. The remaining renewable carbon input is considered as being completely converted into all the different products, in equal ratios. So, when the FCC produces 50% gasoline, 50% of the remaining renewable carbon input (the mass of carbon present in the FPBO minus the mass of carbon in the produced CO and CO₂) is considered to be converted into bio-gasoline.

3.3 Total mass balance

The total mass balance approach takes the produced CO, CO₂ and water into consideration as production losses that should be subtracted from the total renewable mass input (including oxygen). This is based on the assumption that fossil feedstocks do not produce any CO, CO₂, or water. The remaining renewable mass input is considered as being completely converted into all the different products, in equal ratios. So, when the FCC produces 50% gasoline, 50% of the remaining renewable mass input (the mass of FPBO minus the total mass of the produced CO, CO₂ and water) is considered to be converted into bio-gasoline.

3.4 Free attribution

When applying the free attribution method, the operator can freely choose to which products stream the renewable carbon input is attributed. This is the simplest mass balance method that exists, as it ignores any yields of different outputs. For example, 100% of the renewable carbon input of the FPBO could then be considered as being converted into bio-gasoline. This could also be done on the basis of energy content rather than on the basis of carbon content. This method should not be applied on the basis of the total renewable mass input, because then the mass of the oxygen present in FPBO would also be considered to be converted into fuel, which would lead to a significant overestimation of the actual biofuel production volume.

¹⁶ ISCC, 203-01, [Guidance for the Certification of Co-Processing](#), 2016.

3.5 Energy balance

The energy balance method considers the difference in energy content of different feedstocks and products. FPBO typically has a lower heating value (LHV) of 16 MJ/kg, which is less than regular oil products that have an LHV around 40 MJ/kg. The reason for the lower LHV of FPBO is its oxygen content. When applying the energy balance method, the renewable energy content of the FPBO is considered to be completely converted into all the different products, in equal ratios. As this method is based on energy content it does take into account the oxygen content of FPBO that will not be converted into usable products. Therefore, in terms of complexity, this is a method that can be considered as being in between free attribution and the other mass balance methods. It is easier to implement but less precise.

3.5 Conclusion on mass and energy balance methods

Here the different options for mass and energy balance methods have shortly been described. All have their merits and their disadvantages. When implementing a bookkeeping method in a regulatory framework it should be fair, transparent, and executable. It is important that a method is chosen which does justice to the actual amount of biofuel that is produced when co-processing FPBO in an FCC, so also to the fact FPBO contains oxygen and is not completely converted into biofuel. Some methods require analyses of the different products and of CO and CO₂ that may be formed, which may or may not be achievable in practice for a certain operator. Especially determining the amount of water being formed in an FCC may pose a challenge, as steam is used for introducing feedstocks into an FCC unit. It would be important to get a clear view from the operators that are planning to implement FPBO co-processing in refinery units on which methods would be achievable in practice and which would not, in order to make sure a method is chosen to which they can comply in a transparent fashion.

A case study on the basis of literature data was performed, in order to compare and evaluate the various bookkeeping methods that are available. The case study is available as an appendix to this paper, while Figure 9 summarizes the main results.

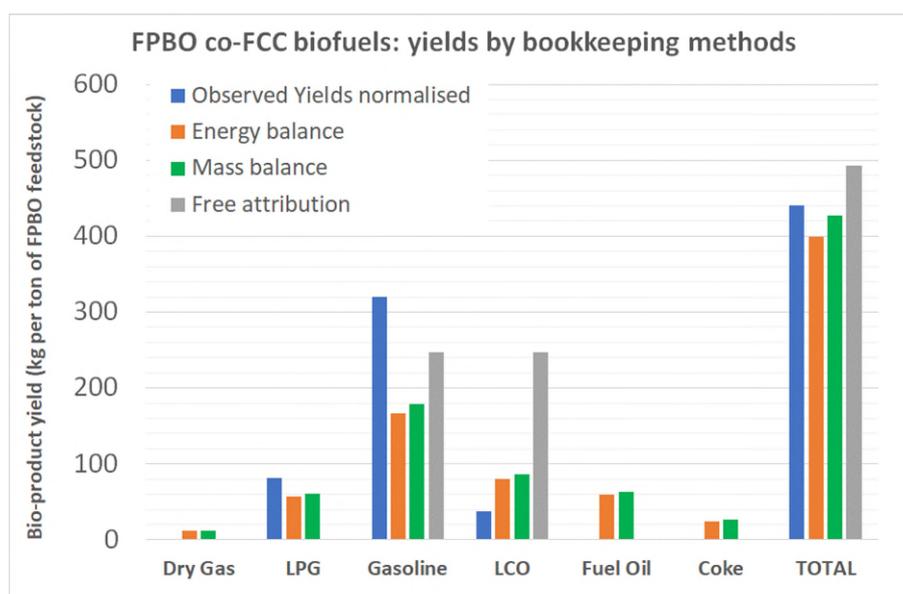


Figure 9. Yields (wt-%) of advanced biofuels from FPBO by the various bookkeeping methods

4. Conclusions

The complexity and size of conventional oil refineries pose a significant challenge for tracing biogenic carbon in refinery products. Several methods have been discussed in this paper, based on both analytical tools and on bookkeeping.

An assessment was made of the suitability of analytical methods when co-processing Fast Pyrolysis Bio-Oil (FPBO) in an FCC unit. For this a set of product samples from FPBO co-processing in a demo FCC unit was submitted for radiocarbon analysis using the ASTM method based on Accelerated Mass Spectroscopy, which is known to be the most sensitive and precise analytical method. Unfortunately, our data showed that this technique is neither accurate nor precise enough when employed at the radiocarbon concentrations that are relevant when co-processing 5 wt-% FPBO or less. This means that actual tracing of biogenic carbon atoms through a refinery by C14 analysis is impossible at these concentrations.

Another approach for tracing biogenic carbon is based on bookkeeping methods such as mass or energy balances. Several options were described, and it is clear that some methods are more precise than others, at the penalty of being more difficult to implement. Our preference would be that a method would be applied which is fair in the sense that it does not over- nor underestimate the actual biofuel volume that is produced from FPBO. Therefore, the method would have to take into account any losses that occur due to the presence of oxygen in the bio-oil. On the other hand, it has to be feasible for operators to comply with the chosen method, for which they will have to do more analyses (for example of baseline yields or produced CO, CO₂ and water). Therefore, it would be important to get a clear view from economic operators that are planning to co-process FPBO on which bookkeeping methods would be achievable in practice.

A case study was performed in order to evaluate and compare the various bookkeeping methods. In conclusion, we believe that from the methods that were discussed in this paper two methods would be the most suitable bookkeeping methods for co-processing low percentages of FPBO in FCC units. The first is the observed yields method in the proposed (adapted) form, for those refiners that have a steady longer-term operation and are able to reliably determine the CO, CO₂ and water being formed in the unit. For those refiners that are unable to comply with the requirements of the observed yields method, we believe the energy balance method would be most suitable, as it is the most universally applicable method and it strikes an appropriate balance between fairness, applicability and transparency.

APPENDIX:

Case-study evaluation of Mass and Energy balance approaches

A1. Introduction

An overview of the various methods that have been developed regarding mass and energy balances was recently prepared by Ecofys, including their advantages and disadvantages.¹⁷ Mass and energy balance methods are administrative (“bookkeeping”) methods, which are based on the principle that in any system the total inputs of mass or energy are equal to the respective outputs. The assumption is that all the renewable feedstock which enters a refinery unit (e.g. an FCC) has to end up in the various products. The various methods differ in the way to calculate the distribution of the renewable feedstock across the various products.

Figure A1 shows the principle of FCC co-processing of FPBO and the various products, with typical yields, across which the renewable feedstock is distributed.

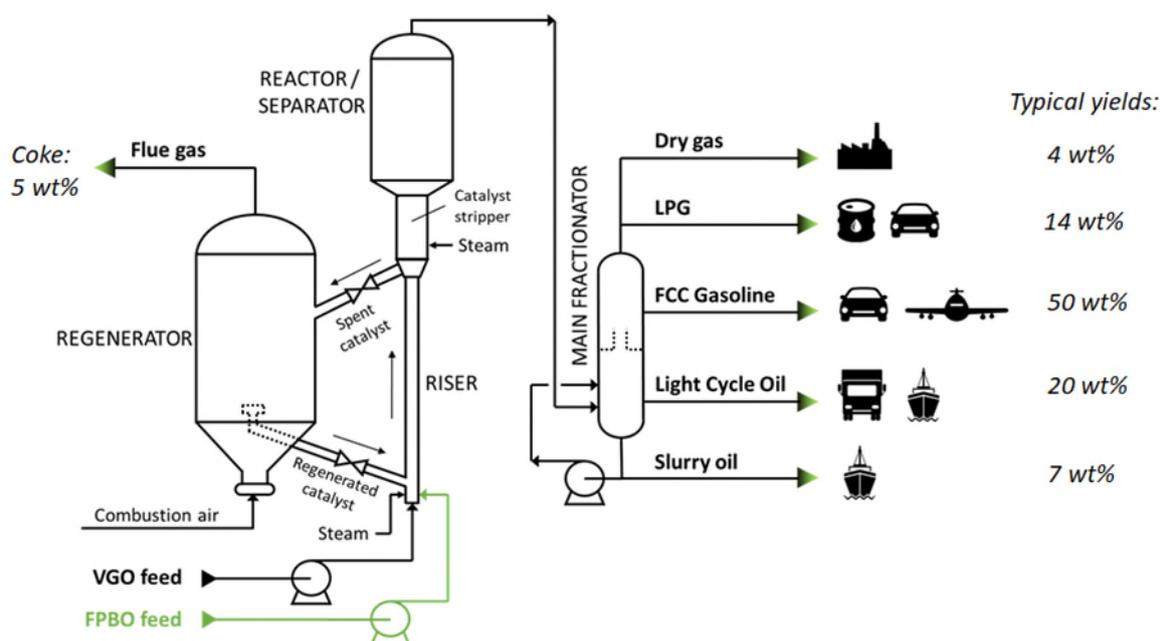


Figure A1. Principle of FCC co-processing of FPBO, with the various products and typical yields.

Typically, about 95 wt-% of the feedstock becomes the various products, and 5 wt-% becomes coke, which is burned to provide the energy for the catalytic cracking process. Dry gas is used elsewhere in the refinery as a fuel, while LPG, gasoline, light cycle oil (LCO, a.k.a. FCC diesel) and slurry oil (a.k.a. heavy fuel oil or bottoms) are further refined into final products. Further refining can encompass upgrading (e.g. sulphur removal), separation (e.g. separating propylene from LPG), blending (e.g. mixing LCO with diesel or marine fuel), etcetera. When a feedstock such as FPBO is added to an FCC unit, the product yields will slightly change. That is due to the nature of FPBO, which contains about 50% oxygen, of which about half is water, and the other half is bound to organic molecules in the FPBO. The oxygen mainly ends up as CO, CO₂, and water. This means that not all the mass of the FPBO is converted into fuel, but rather half of it (the carbon and hydrogen), minus some carbon and hydrogen that is removed together with the organically bound oxygen. A bookkeeping approach should keep this in mind in order not to overestimate the amount of fuel that is produced from the FPBO.

¹⁷ Ecofys, “[Determining the renewability of co-processed fuels](#)”, BIENL Final Report, 2018, for EC DG Energy

In their report, Ecofys describe three mass balance methods that are applied or under development, as well as one energy balance method. These three mass balance methods are: 1) on the basis of observed yields, 2) on the basis of a carbon mass balance, or 3) on the basis of a total mass balance. In fact, there is one more method that is in use, by ISCC PLUS, which is a voluntary scheme for bio-based chemicals. This mass balance method is based on free attribution. In paragraph 2 all these methods will be described and analysed in a case study on the basis of actual co-FCC pilot plant data reported in scientific literature, by Petrobras.¹⁸ This will show significant differences between the various methods. Then in paragraph 3 each method will be adapted in order to come to improved and more harmonised results. Finally, some conclusions will be drawn on what would be the two most suitable methods in practice.

The reason to perform this analysis in the form of a case study is that it provides concrete input data that can be used to compare the different methods. However, this means that the results of this analysis in terms of the actual numbers depend on the specific conditions of the pilot plant test that was used as input, and they cannot be generalised. A specific example of that is that for the pilot plant test a rather heavy vacuum gasoil was used as fossil feedstock, which results in a decrease in gasoline yield and an increase in bottoms yield compared to the yields that are indicated in figure A1 as being typical. Therefore, these numbers may be representative for some FCC units that operate with a heavy fossil feedstock, while others may operate with a lighter feedstock and may observe different yield effects upon co-processing FPBO.

The yields that form the basis of this case study evaluation are shown in Figure A2.

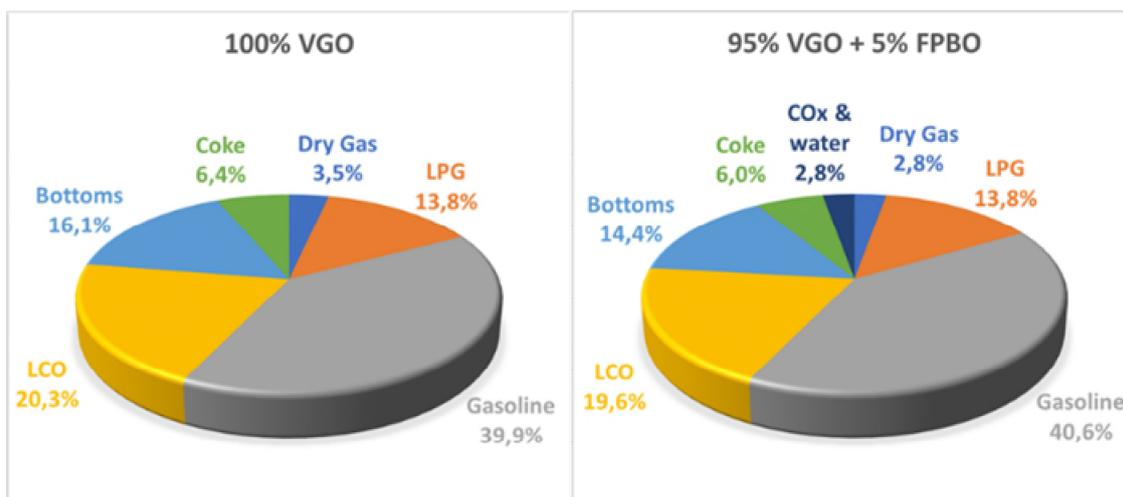


Figure A2. FCC yield distribution without and with 5 wt-percent FPBO

¹⁸ Chum 2015, [“DOE Bioenergy Technologies Office \(BETO\) 2015 Project Peer Review 2.4.2.303 Brazil Bilateral: Petrobras-NREL CRADA”](#)

A2. Case study analysis of various book-keeping methods

A2.1 Observed yields mass balance method

A mass balance on the basis of observed yields starts from a baseline scenario without any renewable feedstock, and allocates any observed differences in yield when co-processing a renewable feed to the renewable products. The ISCC refers to this method as “determination through efficiency / losses”.¹⁹ For this method you look at all the products and label the differences as renewable. This calculation was applied for data reported by Petrobras (Figure A2).¹⁹ 100% fossil feedstock was taken as baseline, and the effect of adding 5 wt-% FPBO on the yields was calculated.²⁰ Figure A3 shows the impact of adding 5 wt-% FPBO to the overall yields of the FCC. It results in increased yields of LPG, gasoline and LCO, in the formation of 2.8 wt-% CO, CO₂, and water (loss), and in a reduction of dry gas, bottoms and coke production. The latter has been reported in literature as possibly being due to “synergistic effects” in the FCC.

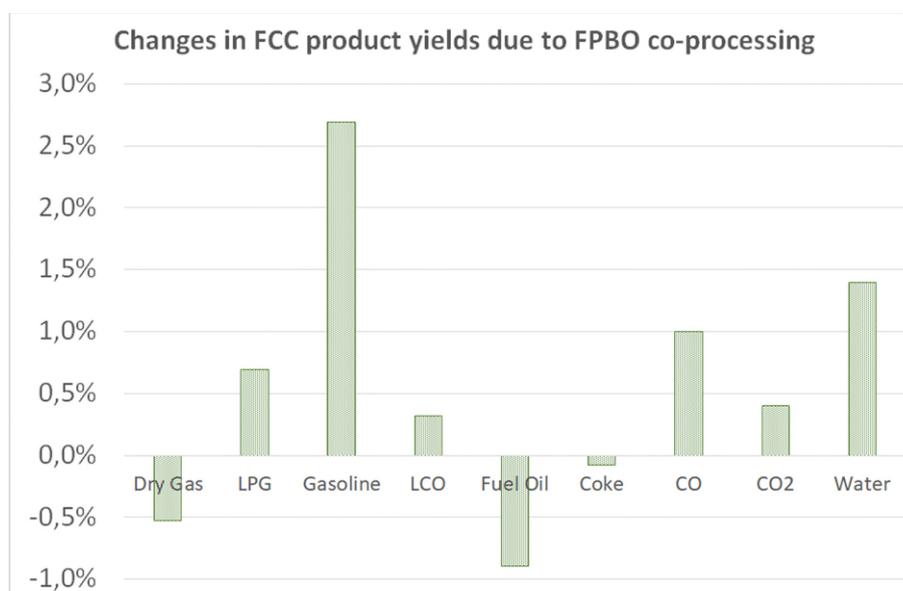


Figure A3. Impact of co-processing 5 wt-% FPBO on the observed FCC yields.

When applying this calculation method, the co-processing of 1000 ton of FPBO results in the production of 539 ton bio-gasoline, 138 ton bio-LPG, and 63 ton bio-LCO, as well as in negative production values of dry gas, bottoms and coke (biofuel yields from FPBO are separately shown in Figure A4). Adding all the positive and negative yields together and subtracting the CO, CO₂ and water results in an overall yield of 440 ton of products from 1000 ton of FPBO. How would be accounted for the negative yields is unsure, as it is not considered yet in the methods that have been developed. Just looking at the LPG, gasoline and diesel yields, together they would amount to 74 wt-% yield of renewable products from FPBO, which is excessive given the fact that about 50 wt-% of the FPBO is oxygen.

¹⁹ ISCC, 203-01, [Guidance for the Certification of Co-Processing](#), 2016.

²⁰ To measure the effect of the FPBO, the baseline yields from 100% fossil were multiplied by 0.95 in order to establish the baseline of only fossil for 95% fossil + 5% FPBO. These baseline yields were subtracted from the yields of 95% fossil + 5% FPBO in order to establish the nett effect of the FPBO, which is shown in the graph.

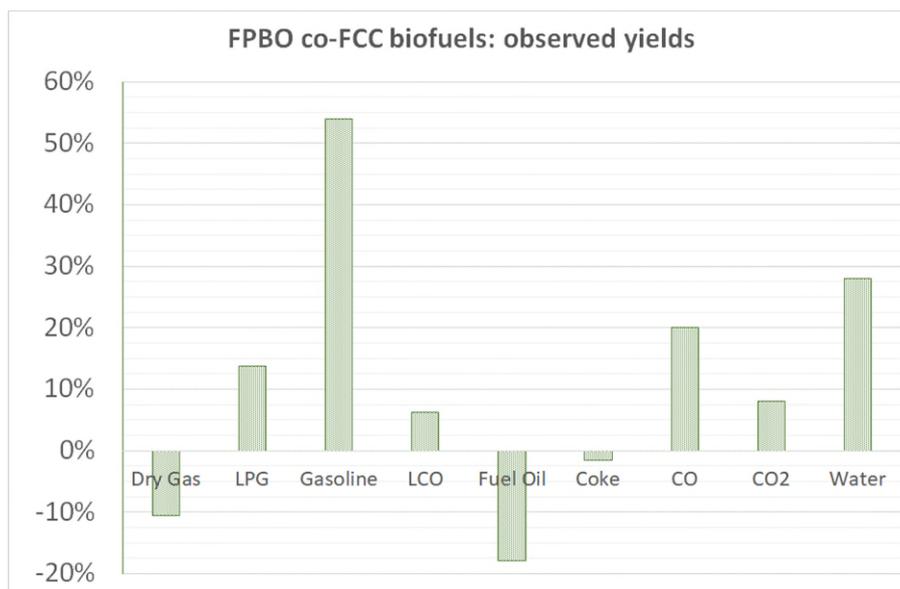


Figure A4. Yields (wt-%) of advanced biofuels from FPBO by the observed yields method.

A logical way of accounting for the negative product yields would be to subtract them equally from the positive product yields (“products” here exclude CO, CO₂, water). The reason for this is that while the yield shift that occurs here would be interesting from a refinery perspective (more valuable products), it leads to an over-estimation of the biofuels yield. Such accounting can be done by introducing a “zero-normalisation factor”, which is calculated by dividing the sum of both the positive and negative product yields by the sum of only the positive product yields. By multiplying the positive product yields with this factor and setting the negative product yields to zero, the overall yield stays the same, and a more realistic total yield of bio-products emerges (Figure A5). Using this method, the co-processing of 1000 ton of FPBO results in the production of 320 ton bio-gasoline, 82 ton bio-LPG, and 37 ton bio-LCO. The overall product yield stays the same at 440 ton.

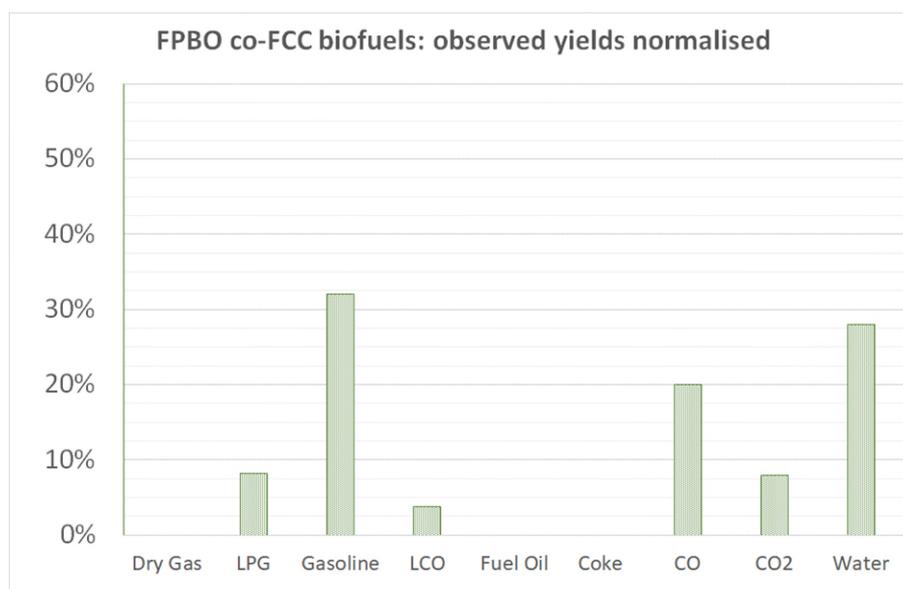


Figure A5. Yields (wt-%) of advanced biofuels from FPBO by the adapted observed yields method.

A2.2 Carbon mass balance method

The carbon mass balance method is somewhat simpler than the observed yields method. It does not consider all the yields of the different products, but takes the produced CO and CO₂ into consideration as a production loss that should be subtracted from the renewable carbon input. When applying the same yield data as above to these methods, the carbon mass balance method results in a total carbon yield of 69% of renewable fuels from FPBO (the “renewable carbon correction factor”), the rest of the FPBO being lost as CO and CO₂.²¹ The co-processing of 1000 ton of FPBO then results in the production of 280 ton bio-gasoline, 95 ton bio-LPG, and 135 ton bio-LCO (Figure A6). The overall product yield is 670 ton. This again appears excessive, and is probably the result of no taking into account the water that is formed from the oxygen present in the FPBO.

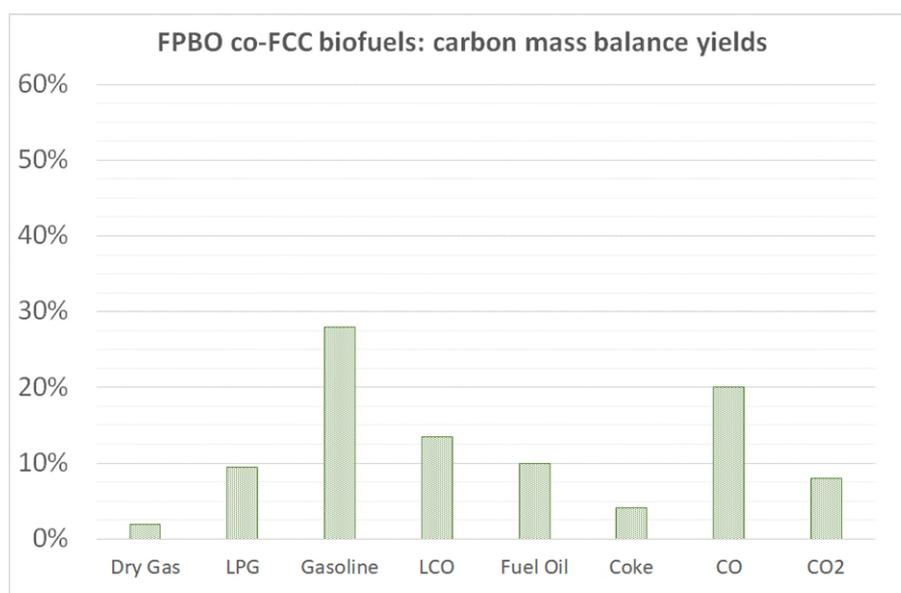


Figure A6. Yields (wt-%) of advanced biofuels from FPBO by the carbon mass balance method.

A2.3. Total mass balance method

The total mass balance approach takes the produced CO, CO₂ and water into consideration as production losses that should be subtracted from the total renewable input. Using again the same yield data, co-processing 1000 ton of FPBO results in the production of 179 ton bio-gasoline, 61 ton bio-LPG, and 86 ton bio-LCO (Figure A7). The total yield of products in this case is 428 ton of renewable products from the FPBO, which is better in line with the overall result of the observed yields method.

²¹ Following the CARB method published here:
https://ww3.arb.ca.gov/fuels/lcfs/lcfs_meetings/053017draft_discussion_paper_coprocessing.pdf.

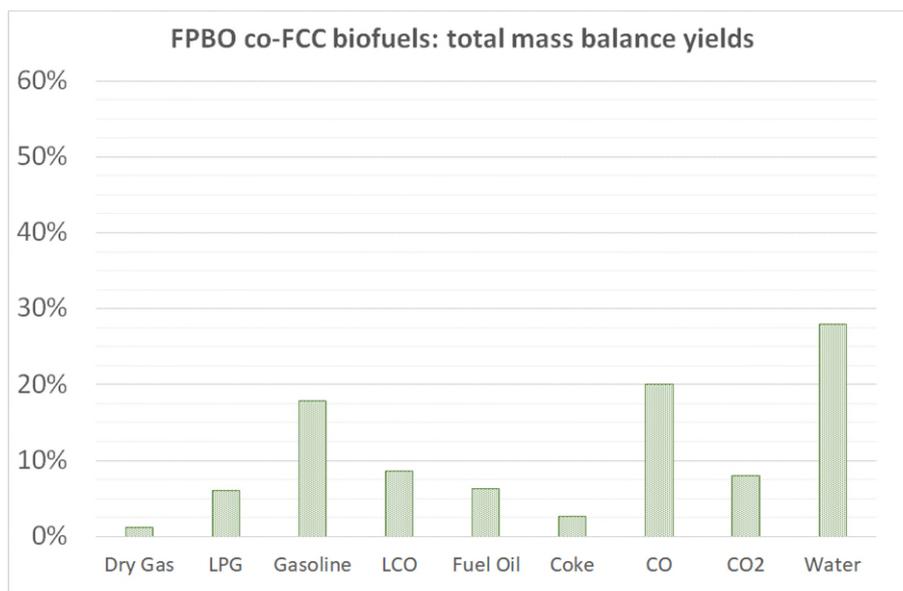


Figure A7. Yields (wt-%) of advanced biofuels from FPBO by the total mass balance method

A2.4. Free attribution method

When applying the free attribution method, the operator can freely choose to which products stream the renewable carbon input is attributed. This is the simplest mass balance method that exists, as it ignores any yields of different outputs. For example, 100% of the renewable carbon input of the FPBO could then be considered as being converted into bio-gasoline. This could also be done on the basis of energy content rather than on the basis of carbon content. This method should not be applied on the basis of the total renewable mass input, because then the mass of the oxygen present in FPBO would also be considered to be converted into fuel, which would lead to a significant overestimation of the actual biofuel production volume. In a (arbitrary) case where half of the weight of the FPBO feedstock, excluding the oxygen, would be attributed to the gasoline product, and the other half to the LCO product, that would result in the production of 247 ton of bio-gasoline and 247 ton of bio-LCO per 1000 ton of FPBO (Figure A8). The total product yield is now 493 ton.

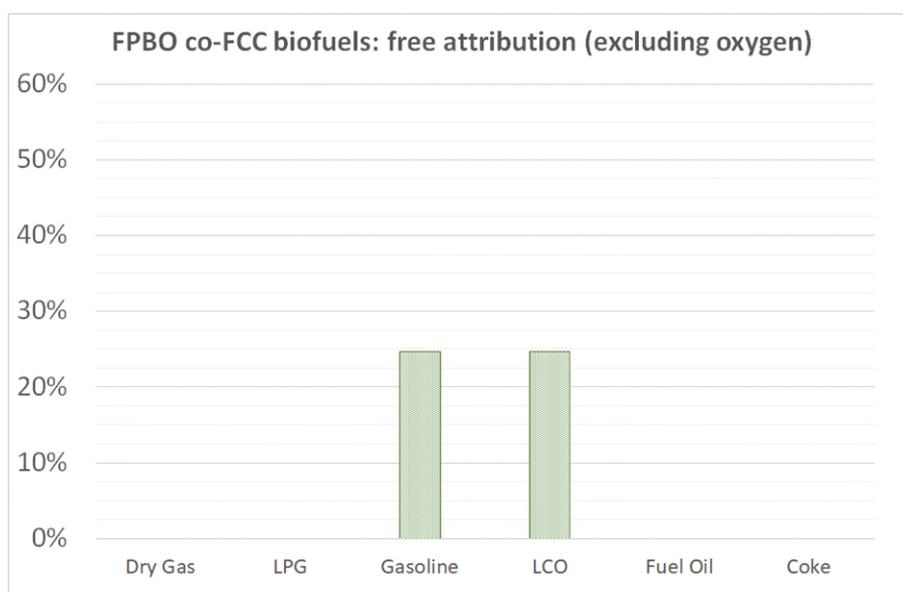


Figure A8. Yields (wt-%) of advanced biofuels from FPBO by the free attribution method

A2.5. Energy balance method

The energy balance method considers the difference in energy content of different feedstocks and products. FPBO typically has a lower heating value (LHV) of 16 MJ/kg, which is less than regular oil products that have an LHV around 40 MJ/kg. The reason for the lower LHV of FPBO is its oxygen content. When applying the energy balance method, the renewable energy content of the FPBO is considered to be completely converted into all the different products, in equal ratios. As this method is based on energy content it does take into account the oxygen content of FPBO that will not be converted into usable products. It also takes into account some other losses, such as the loss of carbon to CO₂, due to the thermodynamics involved. The conversion of biogenic carbon atoms from FPBO into CO₂ within the FCC unit are exothermic reactions that release (bio-)energy in the process. That energy is incorporated into the other products (during a steady state operation the nett energy balance of a heat-balanced FCC unit is zero). The same is the case for the conversion of biogenic hydrogen to water within the process. When calculating the product yields on an energy basis this effect is automatically incorporated through the lower heating values of water and CO₂, which are by definition zero, meaning that no bio-energy ends up in those two products.

Because of the relatively simple energy-based calculation method, this is a bookkeeping method that can be considered as being in between free attribution and the other mass balance methods in terms of complexity. In theory it is a little less precise than a mass balance method but it is much easier to implement and it does not depend on the accurate monitoring of the amounts of water and CO₂ being formed, although it does depend on accurate data on the energy content of all the products. In practice it may actually be more accurate than mass balance methods.

Co-processing 5 wt-% FPBO gives a bio yield factor (or energetic weighting factor) of about 2 %. Based on that factor and the LHV (energy content) of each FCC product, the mass yield of each product from FPBO was calculated. This calculation method yields per 1000 ton of FPBO 167 ton bio-gasoline, 57 ton bio-LPG, and 80 ton bio-LCO (Figure A9). The total product yield is 399 ton.

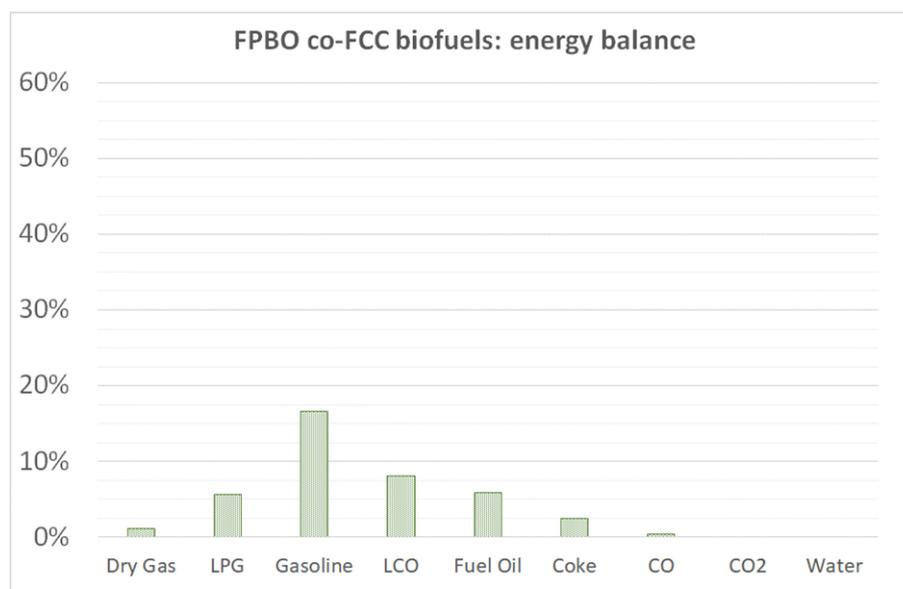


Figure A9. Yields (wt-%) of advanced biofuels from FPBO by the energy balance method

A3. Overview of results of the mass and energy balance methods

The table below shows a translation of the mass yields reported above into energy yields of the various products for each method. The overall bio-yield as calculated on an energy basis might imply that except for the energy balance method each of these methods results in an overestimation of the biofuel yields. This effect could be due to the difference in heating values between FPBO and oil products, as well as an incomplete mass balance closure in the experiments (not all the oxygen in the FPBO was accounted for in the used literature).

| Overview of product yields on energy basis (as GJ bio-product per ton FPBO input) | | | | | | | |
|---|-------------|--------------------|---------------------------|-------------------|-----------------|-------------------|---------------------|
| | LHV GJ/t | Observed yields | Obs. yields normalised | Carbon balance | Mass balance | Energy balance | Free attribution |
| Dry Gas | 49.7 | -5.2 | 0.0 | 1.0 | 0.6 | 0.6 | 0.0 |
| LPG | 45.5 | 6.3 | 3.7 | 4.3 | 2.8 | 2.5 | 0.0 |
| Gasoline | 42.0 | 23.4 | 13.9 | 12.1 | 7.8 | 7.0 | 10.7 |
| LCO | 39.5 | 2.7 | 1.6 | 5.8 | 3.7 | 3.3 | 10.6 |
| Fuel oil | 39.0 | -7.0 | 0.0 | 3.9 | 2.5 | 2.2 | 0.0 |
| Coke | 29.5 | -0.5 | 0.0 | 1.2 | 0.8 | 0.7 | 0.0 |
| Bio output (GJ/t) | | 19.7 | 19.2 | 28.3 | 18.1 | 16.4 | 21.4 |
| Bio input (GJ/t) | | 16.3 | 16.3 | 16.3 | 16.3 | 16.3 | 16.3 |
| Overall bio-yield | | 115% | 115% | 169% | 108% | 100% | 123% |

A way to correct the overestimation in bio-yield due to incomplete oxygen mass balance closure would be to introduce an “energy yield correction factor” that assumes the total bio-output to be equal to the total bio-input on an energy basis. The overall bio-yield is then set to 100% and the product yields corrected to add up to that 100%. However, as it is uncertain where the inaccuracy comes from and whether it is the mass or the energy-based method that is more accurate, such a correction has not been performed here. All yields on a weight basis are shown below, to enable a comparison.

| Overview of product yields on weight basis (as ton bio-product per 1000 ton FPBO input) | | | | | | |
|---|--------------------|---------------------------|-------------------|-----------------|-------------------|---------------------|
| | Observed yields | Obs. yields normalised | Carbon balance | Mass balance | Energy balance | Free attribution |
| Dry Gas | -105 | 0 | 19 | 12 | 11 | 0 |
| LPG | 138 | 82 | 95 | 61 | 57 | 0 |
| Gasoline | 539 | 320 | 280 | 179 | 167 | 247 |
| LCO | 63 | 37 | 135 | 86 | 80 | 247 |
| Fuel oil | -179 | 0 | 99 | 63 | 59 | 0 |
| Coke | -16 | 0 | 41 | 26 | 25 | 0 |
| Total yield (t/kt) | 440 | 440 | 670 | 428 | 399 | 493 |
| Biofuels* yield (%) | 56% | 44% | 61% | 39% | 36% | 49% |

*) Biofuels are here defined as the LPG, gasoline, LCO and fuel oil, not dry gas and coke. Dry gas and coke are refinery fuels and cannot be sold, but they do reduce the GHG footprint of the refinery.

The total product yields are all within the range of 400-500 ton per 1000 ton of FPBO feedstock, except for the carbon balance method, that clearly gives an overestimation of the product yields. Looking at just the biofuels, excluding the dry gas and the coke, the range is a little wider, between 36 and 49 %. Here the unmodified observed yields method is the outlier, because of the negative coke and dry gas yields. Also the free attribution method gives relatively high yields, because it does not take into

account the carbon or hydrogen losses to CO, CO₂ and water. If free attribution were to be discarded for that reason, the obtained range of biofuel yields is between 36 and 44 wt-%.

A4. Discussion and Conclusions

Various bookkeeping methods that are in use or have been proposed have been evaluated here in the context of FPBO co-processing in FCC units, as a case study on the basis of pilot plant data that were published by Pinho *et al.*

In essence there are three different ways of determining the biogenic content of the co-refined products through bookkeeping. The first method is to look at the actual yield shift that follows the introduction of the FPBO in the FCC; the second method is to equally distribute the biogenic content that is fed into the unit across the various products, either on the basis of mass, carbon mass, or energy basis; and the third method is to distribute the biogenic content freely across the preferred products.

The observed yields method showed positive as well as negative yield effects for this case study. Currently the method as employed by ISCC does not account for this possible effect. Therefore, this method was adapted with a normalisation factor, in order to avoid overestimating the biofuels production.

The carbon, mass and energy balance methods showed quite different results, although their approach is rather similar. The carbon balance method appears to seriously overestimate the biofuel yields, as compared to the total mass and the energy balance method. This is probably caused because water formation is ignored in that method. The mass balance method also gives a slightly higher yield than the energy balance method. This could be due to an incomplete oxygen mass balance closure for the pilot plant tests, or it could be due to inaccuracies in the values that were assumed here for the energy content of the fuels. Therefore it is likely that the 'real' mass balance yields are somewhere in between those provided by the total mass and the energy balance methods.

The free attribution method was applied on the basis of carbon and hydrogen content rather than complete weight of the FPBO feedstock, because of the large amount of oxygen present in the FPBO. Still, this resulted in an overestimation of the biofuel yield.

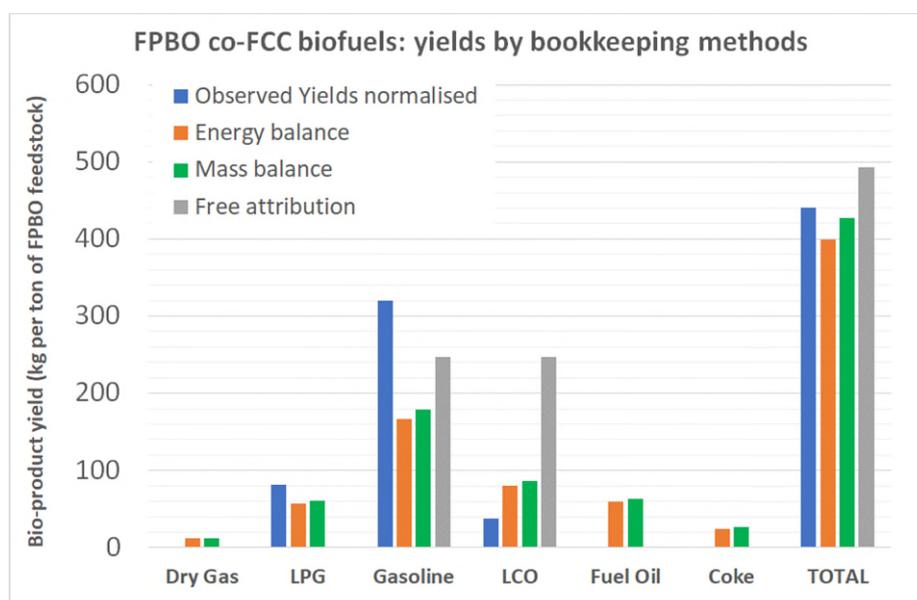


Figure A10. Yields (wt-%) of advanced biofuels from FPBO by the various bookkeeping methods

When the carbon balance and the unmodified observed yields method are not taken into account, the overall biofuels yield slate finally appears quite realistic. Only the distribution between the different products varies significantly across the methods, while the total product yield is in the same range for the remaining methods. This is shown in Figure A10.

For this case study the easiest method that gave credible results was the Energy Balance method. Although this method does not say much about what is actually happening inside the unit, it does take into account the large difference in energy content between FPBO and fossil fuels. It also avoids the introduction of errors by using an incomplete mass balance such as in the pilot plant data that were used for this case study. In a refinery context it may also be difficult to get to total mass balance closure, because it is hardly possible to determine the amount of water that is formed in the process. It is probably more easy to get reliable energy content data of all the products.

The observed yields method is the only bookkeeping method that takes into account what is actually happening in the FCC unit as a consequence of FPBO co-processing. That is a large benefit for the credibility of that method. Nevertheless, the observed yields method comes with a few challenges. First of all, if the refinery modifies a parameter that influences the FCC yield slate, for example the operational conditions or FCC feedstock, a new baseline would need to be established in order to determine the real impact of FPBO co-processing on the yields. This may or may not be an issue from an operational point of view, depending on how often the situation occurs. Secondly, this case study showed that the observed yields method can lead to negative yields for some products, and thus an overestimation of the biofuel yields for some other products. That effect is probably due to synergistic effects that occur between the FPBO and the fossil feedstock in this specific case and does not necessarily happen in other cases, as it would depend on the feedstock and operating conditions. From the perspective of a refiner this effect may be positive in the case of an increased production of gasoline and a decreased production of coke, for example, or negative if the situation would be the other way around, but in either case it does not say anything about the actual amount of biofuel being produced. Currently the observed yields method as described by ISCC does not have a way to deal with this effect, therefore a proposition was made in paragraph 2 how this could be taken into account, namely by subtracting the negative yields from the positive ones. The third challenge with this method is that it depends on reliable measurements of the CO, CO₂ and water being formed, as with the mass balance methods that were discussed earlier. Especially the water balance could be challenging to determine.

The free attribution method as derived from the ISCC+ certification system for bio-based chemicals would be the easiest to apply but is not allowed under the current Renewable Energy Directive. Applying this method could be a defensible option for low percentages FPBO co-processing (below 5 wt-%) in order to incentivise this new technology pathway. However, such implementation would likely be prone to criticism by various stakeholders that could claim the creation of a non-level playing field for advanced biofuels production by other forms of processing (e.g. hydrotreatment) or for example at higher percentages of vegetable oil co-processing.

In conclusion, we believe that from the methods that were discussed in this paper two methods would be the most suitable bookkeeping methods for co-processing low percentages of FPBO in FCC units. The first is the observed yields method in the proposed (adapted) form, for those refiners that have a steady longer-term operation and are able to reliably determine the CO, CO₂ and water being formed in the unit. For those refiners that are unable to comply with the requirements of the observed yields method, we believe the energy balance method would be most suitable, as it is the most universally applicable method and it strikes an appropriate balance between fairness, applicability and transparency.