ABSTRACT
The reliance on petroleum derivatives and the increasing trend of fuel consumption in the transport sector have brought attention to biofuels as a measure to reduce greenhouse gas (GHG) emissions, enhance energy security and boost economic development. The incentive for utilizing biofuels is their potential to reduce carbon dioxide (CO2) emissions compared to fossil fuels. Biofuels are considered to be carbon-neutral, regarding the direct CO2 emissions associated with their combustion, on the grounds that the carbon dioxide absorbed by the plants through photosynthesis is equivalent to the CO2 released during their combustion. However, a part of the carbon of biofuels may have a fossil origin and therefore, it is responsible for “non-neutral” CO2 emissions. This was recognized by the Intergovernmental Panel on Climate Change (IPCC) in its guidelines for greenhouse gas inventories. Nevertheless, specific guidance of how to estimate fossil CO2 emissions per each type of biofuel, in order to facilitate the work of emission inventory compilers and practitioners, is neither available in the IPCC guidelines nor in the scientific literature. The purpose of this paper is to define a higher tier method to estimate the associated CO2 emissions with the fossil carbon content of biofuels, aiming to cover all possible biofuel types that are mainly used nowadays to replace diesel and gasoline.

Introduction
The continuing, even increasing, trend of change in the global climate is the greatest danger that humanity is facing and is likely to face in the coming decades. Impacts on natural and human systems from global warming have already been observed and are expected to be more widespread and rapid in the future [1]. Climate and weather extremes are more intense and frequent compared to recent past. The ice in the polar regions is melting and the sea level is rising. Some areas are more frequently affected by extreme rainfalls, while others are affected by high temperatures and droughts, and such effects are expected to intensify in the coming decades [2].

CO2 produced by human activities is the main GHG contributing to global warming. In 2019, its concentration in the atmosphere was 148% of the pre-industrial levels (period before 1750) [3].

Reducing greenhouse gas emissions is the main target of the United Nations Framework Convention on Climate Change (UNFCCC), which was signed by 197 countries, and of subsequent protocols and agreements, i.e. the Kyoto Protocol and the Paris Agreement. The mitigation of GHG emissions requires accurate, reliable and consistent...
measurement or estimation of emissions by the international community because “if you cannot measure it, you cannot improve it” [4,5]. Therefore, in accordance with the decisions of the Parties to the UNFCCC, a set of requirements for reporting national GHG inventories have been established, which is based on IPCC Guidelines for National GHG Inventories. At present, national inventories need to comply with 2006 IPCC Guidelines [6]. In addition, the IPCC has approved the “2019 Refinement to the 2006 IPCC Guidelines for National Greenhouse Gas Inventories” [7]. The 2019 Refinement does not substitute the 2006 IPCC Guidelines, but supplements it with data and methodologies in cases where gaps have been identified.

The transport sector is responsible for a significant part of CO₂ emissions worldwide. In the European Union, for example, transport is responsible for almost 30% of the total carbon dioxide emissions, while 72% of CO₂ emissions from the transport sector come from road transport activities. Of these emissions, 60.7% was emitted by passenger cars, 11.9% from light commercial vehicles, 26.2% from heavy duty vehicles and 1.2% from motorcycles [8].

A frequently applied mitigation policy to reduce CO₂ emissions in the road transport sector is the replacement of fossil fuels with biofuels. Biofuels are considered to be carbon-neutral, regarding the direct CO₂ emissions associated with their combustion, on the grounds that the carbon dioxide absorbed by the plants through photosynthesis is equivalent to the CO₂ released into the atmosphere during their combustion. It should be clarified that the term “carbon-neutral,” which is used hereinafter in this paper to characterize biofuels, refers only to the direct CO₂ emissions that are associated with the combustion of the biogenic part of biofuels’ carbon content. It does not cover any life cycle GHG emissions prior to their final use, such as emissions from their production (e.g. cultivation of energy crops and transformation of crops into fuel) and distribution, or any consideration as to whether the biofuels were produced within the country or imported. The assessment of the life-cycle emissions of biofuels prior to their final use is outside the scope of this work.

The IPCC confirmed the need for incorporating enhanced production and use of biofuels in the mitigation pathways in order to limit or return global mean warming to 1.5 °C, either as simple replacement of fossil fuels, or as part of Bio-Energy with Carbon Capture and Storage (BECCS) [1]. BECCS is a Negative Emissions Technology (NET), which remove CO₂ from the atmosphere through photosynthesis of plants and store it in geological reservoirs [9]. A number of BECCS technologies have been presented in the international literature, including Hydrogen Bio-Energy with Carbon Capture and Storage (HyBECCS) [10]. HyBECCS focuses on the production of bio-hydrogen from biogenic material through electrolysis, using renewable electricity. Furthermore, a potential feedstock for biofuel production, which could address the limitations of land-based biofuel sources and cover the global transport fuel requirements in the future, are algae. However, they are still in an early stage of advancement and further work is required in order to enhance the economic feasibility of the algae biofuel sector [11]. Another rapidly evolving area of international research is the production of biofuels through engineered cyanobacterial development [12].

Currently, biofuels are produced from vegetable oil, sugar, and starch yields (first generation), and waste oils, agricultural and woodland residues (second generation) [12]. Despite their biological origin, some of their carbon may have a fossil source, depending on their production method, and therefore is associated with “non-neutral” CO₂ emissions [13]. This was recognized in the 2006 IPCC Guidelines for National Greenhouse Gas Inventories, which stress the importance of assessing the origin of biofuel specifically for the purpose of distinguishing between fossil and biogenic feedstock. The 2006 IPCC Guidelines provide some examples of the fossil origins associated with biofuels [6]:

- Biodiesel can be non carbon-neutral when made from coal methanol with animal feedstock;
- With few exceptions (e.g. due to use of fossil-fuel derived methanol), the biogenic ethanol produced through agricultural product fermentation is carbon neutral;
- Products that have undergone further chemical transformation may contain substantial amounts of fossil carbon ranging from about 5–10 percent in the fossil methanol used for biodiesel production upwards to 46 percent in ethyl-tertiary-butyl-ether (ETBE) from fossil isobutene.

However, the exact fossil carbon part per biofuel type is not explicitly provided in the guidelines. The 2019 Refinement of the 2006 IPCC Guidelines [7] did not provide any additional
guidance, either. As a result, there is confusion among GHG inventory compilers and other practitioners about how to estimate the respective emissions.

Some information about this issue can be found in the scientific literature. The fossil part of Fatty Acid Methyl Ester (FAME), a biodiesel type, is reported in the literature. Reddy et al. [14] estimated the ratio of bio per total carbon of B100 biodiesel fuel, and the Ofgem e-serve (Great Britain’s independent energy regulator) provided guidance for the estimation of the biomass content of FAME biodiesel [15]. However, there is no detailed analysis and method of how to estimate the fossil origin part of CO2 emissions from biofuel combustion, covering all types of biofuels.

The objective of this article is to facilitate GHG compilers and practitioners by providing a higher tier method on how to estimate the direct CO2 emissions associated with the combustion of the fossil carbon content of biofuels, covering all possible biofuel types used nowadays to replace diesel and gasoline. The term “tier” represents the level of methodological complexity [6]. The proposed method is considered “higher tier,” as it is based on detailed data about the type and origin of biofuels.

Materials and methods

Fossil carbon content of biofuels that replace fossil diesel

The main biofuels used nowadays to replace fossil diesel are Hydrotreated Vegetable Oil (HVO) and Fatty Acid Methyl Esters (FAME). Due to the different chemical composition of these fuels, a separate method has been developed for each fuel, described in detail in the following subsections.

Hydrotreated vegetable oil (HVO)

HVO is produced through the hydro-treatment of triglyceride-containing feedstock (vegetable oil or animal fat). All carbon in these sources can be considered of biogenic origin, i.e. there is no fossil part. For the production of HVO, vegetable oil or animal fat reacts only with hydrogen, without the use of other chemicals that contain fossil carbon. Most likely, hydrogen is produced from fossil sources (e.g. by steam reforming of natural gas). The associated CO2 emissions from hydrogen production should be estimated and reported under the category “petroleum refining” or “chemical industry” of the national GHG inventory.

The hydro-treatment of vegetable oil or animal fat follows three distinct pathways (Figure 1): decarboxylation (DCX), decarbonylation (DCN) and deoxygenation (DEOX). All pathways produce long chain normal paraffin molecules with a number of carbon atoms close to the corresponding range of diesel fuel (16–20 carbon atoms) [16].

Fatty acid methyl esters (FAME)

Vegetable oil or animal fat reacts with methanol in the presence of catalysts to form glycerol and fatty acid methyl esters. The FAME is the desired component of biodiesel and the glycerol is separated as a by-product.

The use of fossil-derived methanol in the production of biodiesel means that the fossil and the biogenic parts within the biodiesel are chemically bonded. Figure 2 shows the chemical reaction that occurs in the typical biodiesel (FAME) manufacturing process. As we can see from the chemical reaction, FAME molecules (ROOCH3) contain the carbons of the triglyceride fatty acids (R- part), and one carbon from the methyl group (CH3-) of methanol. Therefore, the fossil carbon of FAME originates from the methyl group of methanol, i.e. 1 mole carbon per mole of FAME (ROOCH3).

The fossil part of the carbon content of FAME ranges from 5.3 to 5.5% and depends on the type of vegetable oil or animal fat that was used for FAME production. The carbon content of FAME biodiesel (both biogenic and fossil origin) ranges from 76 to 77% and also depends on the type of vegetable oil or animal fat that was used for FAME production. The estimation of the carbon content and its fossil part for various types of vegetable oil and animal fat is presented in Tables 1 and 2, respectively.

Step-by-step method to estimate fossil CO2 emissions from biodiesel

In order to estimate the fossil CO2 emissions from biodiesel, the following higher tier step-by-step approach is proposed (Figure 3):

Step 1: Obtain data on the amount of biodiesel used (in kt) within the country (source: national energy balance). Identify which proportion of the reported quantities is FAME and which is HVO, by using country specific information. This is necessary, because HVO is not associated with fossil CO2 emissions. If country specific information about the
FAME/HVO ratio is not available, consider that all biodiesel is FAME.

**Step 2**: Estimate the total carbon content (CC) of FAME (both bio and fossil origin). If country specific information is available about the vegetable oil and animal fat feedstock of FAME, use it to estimate the weighted average CC of FAME. The carbon content per FAME type could be obtained from Table 1, or any other well documented source. If country specific information is not available, use 77% kgC/kgFAME as a default value (estimated under the assumption that the feedstock for FAME production is 40% rapeseed/30% sunflower/30% palm oil).

**Step 3**: Estimate the fossil part of carbon content of FAME. If country specific information is available about the vegetable oil and animal fat feedstock of FAME, use it to estimate the weighted average fossil fraction of CC. The fossil CC per FAME type could be obtained from Table 2, or any other well documented source. If country specific information is not available, use 5.4% as a default value of fossil carbon content (estimated under the assumption that the feedstock for FAME production is 40% rapeseed/30% sunflower/30% palm oil).

**Step 4**: Calculate both biogenic and fossil CO₂ emissions associated with FAME by applying Eqs. (1) and (2). Calculate biogenic CO₂ emissions associated with HVO by applying Eq. (3).

If the carbon content of HVO is not available, use the carbon content of petro-diesel, as the chemical composition of HVO is similar to that of petro-diesel.

\[
\text{(Fossil origin CO}_2\text{ from FAME in kt)} = (\text{ktFAME}_{\text{step1}}) \times (\text{CCofFAME}_{\text{step2}}) \times (\text{fossil fraction of CC}_{\text{step3}}) \times \frac{44}{12} \tag{1}
\]

\[
\text{(Bio origin CO}_2\text{ from FAME in kt)} = (\text{ktFAME}_{\text{step1}}) \times (\text{CCofFAMET}_{\text{step2}}) \times (100\% - \text{fossil fraction of CC}_{\text{step3}}) \times \frac{44}{12} \times \frac{1}{2} \tag{2}
\]

\[
\text{(Bio origin CO}_2\text{ from HVO in kt)} = (\text{ktHVO}_{\text{step1}}) \times (\text{CCofHVO}_{\text{step2}}) \times \frac{44}{12} \tag{3}
\]

**Net calorific value of biodiesel.** The proposed default CC and Net Calorific Value (NCV) of biodiesel in the 2006 IPCC Guidelines (19.3 kg/TJ and 27 TJ/kt, respectively) are based on “ethanol theoretical number,” although ethanol is not a component of biodiesel. By combining these numbers,
the CC of biodiesel in mass units is calculated as 52.1% (kg/kg). This number deviates by more than 30% from the carbon content calculated in Table 1, which is around 77.0% (kg/kg). In the majority of national GHG inventories, CO₂ emissions, which are associated with the combustion of a fuel, are estimated by multiplying the fuel quantity in mass units (kt) by NCV (in TJ/kt), CC (in tC/TJ) and 44/12 (the ratio of the CO₂ and C molecular weights). This way, the accuracy of the estimation depends on the accuracy of the product NCV*CC (in tC/ktfuel), as well as on the activity data. Therefore, the use of CC and NCV values for biodiesel from the 2006 IPCC Guidelines to estimate CO₂ emissions may lead to an error of more than 30%.

The NCV of biodiesel depends on its type. The NCV of HVO is similar to that of petro-diesel (about 44.0 TJ/kt [19]), while the NCV of FAME is approximately 37.0–38.5 TJ/kt [19–21]. A simple way to calculate the NCV of FAME, depending on the various types of vegetable oil and animal fat, is presented in Table 3. Regarding the CC of biodiesel, both HVO and FAME have a similar CC to petro-diesel, which is 20.2 kg/TJ [6].

**Fossil content of biofuels that replace fossil gasoline**

Biogasoline is used here for the denomination of biofuels replacing fossil gasoline. The following

| Vegetable oil or animal fat | Fatty acid type | % (kg/kg) in oil [17,18] | C | H | O | MW of CH₃ | Molecular weight |
|-----------------------------|----------------|--------------------------|---|---|---|----------|-----------------|
| Sunflower oil               | Palmitic       | 5.0%                     | 16| 32| 2 | 15       | 13.5            |
|                             | Stearic        | 6.0%                     | 18| 36| 2 | 15       | 17.9            |
|                             | Oleic          | 30.0%                    | 18| 34| 2 | 15       | 88.8            |
|                             | Linoleic       | 59.0%                    | 18| 32| 2 | 15       | 173.5           |
| Rapseed (canola)            | Oleic          | 61.0%                    | 18| 34| 2 | 15       | 180.6           |
|                             | Linoleic       | 21.0%                    | 18| 32| 2 | 15       | 61.7            |
|                             | Alpha linoleic | 11.0%                    | 18| 30| 2 | 15       | 32.1            |
|                             | Palmitic       | 4.0%                     | 18| 32| 2 | 15       | 10.8            |
|                             | Stearic        | 2.0%                     | 18| 36| 2 | 15       | 6.0             |
| Palm oil                    | Oleic acid     | 36.6%                    | 18| 34| 2 | 15       | 108.3           |
|                             | Linoleic       | 9.1%                     | 18| 32| 2 | 15       | 26.8            |
|                             | Palmitic       | 43.5%                    | 16| 32| 2 | 15       | 117.5           |
|                             | Stearic        | 4.3%                     | 18| 36| 2 | 15       | 12.8            |
|                             | Myristic       | 1.0%                     | 14| 28| 2 | 15       | 2.4             |
| Cottonseed                  | Palmitic       | 23.0%                    | 16| 32| 2 | 15       | 62.1            |
|                             | Palmitoleic    | 1.0%                     | 16| 30| 2 | 15       | 2.7             |
|                             | Stearic        | 2.5%                     | 18| 36| 2 | 15       | 7.5             |
|                             | Oleic          | 17.0%                    | 18| 34| 2 | 15       | 50.3            |
|                             | Trans oleic    | 0.1%                     | 18| 34| 2 | 15       | 0.3             |
|                             | Linoleic       | 56.0%                    | 18| 32| 2 | 15       | 164.6           |
|                             | Trans linoleic | 0.1%                     | 18| 32| 2 | 15       | 0.3             |
|                             | Linolenic      | 0.3%                     | 18| 30| 2 | 15       | 0.9             |
| Tallow                      | Palmitic       | 26.0%                    | 16| 32| 2 | 15       | 70.2            |
|                             | Stearic        | 14.0%                    | 18| 36| 2 | 15       | 41.7            |
|                             | Myristic       | 3.0%                     | 14| 28| 2 | 15       | 7.3             |
|                             | Oleic          | 47.0%                    | 18| 34| 2 | 15       | 139.1           |
|                             | Linoleic       | 3.0%                     | 18| 32| 2 | 15       | 8.8             |
|                             | Palmitoleic    | 3.0%                     | 16| 30| 2 | 15       | 8.0             |
|                             | Linolenic      | 1.0%                     | 18| 30| 2 | 15       | 2.9             |
| Lard                        | Palmitic       | 26.5%                    | 16| 32| 2 | 15       | 71.6            |
|                             | Stearic        | 13.0%                    | 18| 36| 2 | 15       | 38.7            |
|                             | Myristic       | 5.0%                     | 14| 28| 2 | 15       | 2.4             |
|                             | Oleic          | 45.5%                    | 18| 34| 2 | 15       | 134.7           |
|                             | Linoleic       | 8.0%                     | 18| 32| 2 | 15       | 23.5            |
|                             | Palmitoleic    | 3.0%                     | 16| 30| 2 | 15       | 8.0             |
| Soybean                     | Oleic          | 23.1%                    | 18| 34| 2 | 15       | 68.4            |
|                             | Linoleic       | 53.0%                    | 18| 32| 2 | 15       | 155.8           |
|                             | Palmitic       | 11.0%                    | 18| 32| 2 | 15       | 29.7            |
|                             | Stearic        | 2.4%                     | 18| 36| 2 | 15       | 7.2             |
|                             | Linolenic      | 10.5%                    | 18| 30| 2 | 15       | 30.7            |

| Number of atoms | Carbon content (bio and fossil) in % kgC/kgFAME |
|-----------------|-----------------------------------------------|
|                 |                                               |
|                 |                                               |
|                 |                                               |
|                 |                                               |
|                 |                                               |

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Table 1. Carbon content of biodiesel (FAME) for various types of vegetable oil and animal fat.
Table 2. Fossil carbon part of biodiesel (FAME) for various types of vegetable oil and animal fat.

| Vegetable oil or animal fat | Fatty acid type | % (kg/kg) in oil [17,18] | C atoms in FA (based on formula) | C atoms in R part (fatty part) of FAME | C atoms in CH3- of R part (fatty part) | C atoms in CH3- of CH3- | C fossil part (origin from methanol) |
|-----------------------------|----------------|--------------------------|----------------------------------|----------------------------------------|----------------------------------------|--------------------------|------------------------------------|
| Sunflower                   | Palmitic       | 5.0%                     | 16                               | 0.8                                    |                                        |                          |                                    |
|                             | Stearic        | 6.0%                     | 18                               | 1.1                                    |                                        |                          |                                    |
|                             | Oleic          | 30.0%                    | 18                               | 5.4                                    |                                        |                          |                                    |
|                             | Linoleic       | 59.0%                    | 18                               | 10.6                                   |                                        |                          |                                    |
|                             |                |                          |                                  |                                        |                                        |                          |                                    |
| Rapeseed (canola)           | Oleic          | 61.0%                    | 18                               | 11.0                                   |                                        |                          | 5.3%                              |
|                             | Linoleic       | 21.0%                    | 18                               | 3.8                                    |                                        |                          |                                    |
|                             | Alpha linoleic | 11.0%                    | 18                               | 2.0                                    |                                        |                          |                                    |
|                             | Palmitic       | 4.0%                     | 16                               | 0.6                                    |                                        |                          |                                    |
|                             | Stearic        | 2.0%                     | 18                               | 0.4                                    |                                        |                          |                                    |
| Palm oil                    | Oleic          | 36.6%                    | 18                               | 6.6                                    |                                        |                          |                                    |
|                             | Linoleic       | 9.1%                     | 18                               | 1.6                                    |                                        |                          |                                    |
|                             | Palmitic       | 43.5%                    | 16                               | 7.0                                    |                                        |                          |                                    |
|                             | Stearic        | 4.3%                     | 18                               | 0.8                                    |                                        |                          |                                    |
|                             | Myristic       | 1.0%                     | 14                               | 0.14                                   |                                        |                          |                                    |
| Cottonseed                  | Palmitic       | 23.0%                    | 16                               | 3.7                                    |                                        |                          |                                    |
|                             | Palmitoleic    | 1.0%                     | 16                               | 0.2                                    |                                        |                          |                                    |
|                             | Stearic        | 2.5%                     | 18                               | 0.5                                    |                                        |                          |                                    |
|                             | Oleic          | 17.0%                    | 18                               | 3.1                                    |                                        |                          |                                    |
|                             | Trans oleic    | 0.1%                     | 18                               | 0.0                                    |                                        |                          |                                    |
|                             | Linoleic       | 56.0%                    | 18                               | 10.1                                   |                                        |                          |                                    |
|                             | Trans linoleic | 0.1%                     | 18                               | 0.0                                    |                                        |                          |                                    |
|                             | Linolenic      | 0.3%                     | 18                               | 0.1                                    |                                        |                          |                                    |
|                             |                |                          |                                  |                                        |                                        |                          |                                    |
| Tallow                      | Palmitic       | 26.0%                    | 16                               | 4.2                                    |                                        |                          |                                    |
|                             | Stearic        | 14.0%                    | 18                               | 2.5                                    |                                        |                          |                                    |
|                             | Myristic       | 3.0%                     | 14                               | 0.4                                    |                                        |                          |                                    |
|                             | Oleic          | 47.0%                    | 18                               | 8.5                                    |                                        |                          |                                    |
|                             | Linoleic       | 3.0%                     | 18                               | 0.5                                    |                                        |                          |                                    |
|                             | Palmitoleic    | 3.0%                     | 16                               | 0.5                                    |                                        |                          |                                    |
|                             | Linolenic      | 1.0%                     | 18                               | 0.2                                    |                                        |                          |                                    |
|                             |                |                          |                                  |                                        |                                        |                          |                                    |
| Lard                        | Palmitic       | 26.5%                    | 16                               | 4.2                                    |                                        |                          |                                    |
|                             | Stearic        | 13.0%                    | 18                               | 2.3                                    |                                        |                          |                                    |
|                             | Myristic       | 1.0%                     | 14                               | 0.1                                    |                                        |                          |                                    |
|                             | Oleic          | 45.0%                    | 18                               | 8.2                                    |                                        |                          |                                    |
|                             | Linoleic       | 8.0%                     | 18                               | 1.4                                    |                                        |                          |                                    |
|                             | Palmitoleic    | 3.0%                     | 16                               | 0.5                                    |                                        |                          |                                    |
|                             |                |                          |                                  |                                        |                                        |                          |                                    |
| Soybean                     | Oleic          | 23.1%                    | 18                               | 4.2                                    |                                        |                          |                                    |
|                             | Linoleic       | 53.0%                    | 18                               | 9.5                                    |                                        |                          |                                    |
|                             | Palmitic       | 11.0%                    | 16                               | 1.8                                    |                                        |                          |                                    |
|                             | Stearic        | 2.4%                     | 18                               | 0.4                                    |                                        |                          |                                    |
|                             | Linolenic      | 10.5%                    | 18                               | 1.9                                    |                                        |                          |                                    |

Figure 3. Step-by-step method to estimate fossil CO2 emissions from biodiesel.
biofuels are used to replace or as additives to fossil gasoline:

1. Bio-alcohols (i.e. bio-methanol, bio-ethanol and bio-butanol)
2. Bio-ethers (i.e. bio-MTBE, bio-ETBE, bio-TAEE)

Bio-alcohols (i.e. bio-methanol, bio-ethanol and bio-butanol) are produced by the fermentation of biomass, and their carbon is considered to be 100% of bio origin. Bio-ethers (i.e. bio-MTBE, bio-ETBE, bio-TAEE) are synthesized by mixing bio-alcohols and isobutylene (methylbutene for TAAE), and reacting them with heat over a catalyst. They are commonly used as an oxygenate gasoline additive in the production of gasoline from crude oil. Given that isobutylene is currently derived from fossil sources (either petroleum refining or natural gas), bio-ethers have a fossil part. Table 4 presents the CC of biogasoline and its fossil fraction.

Both bio-ethers and bio-alcohols are used as biogasoline in the EU. Bio-ETBE is preferred in conventional vehicles and distribution systems of fuels, as it requires minimal investment in infrastructure. On the other hand, there are countries, such as Sweden, where biogasoline is almost 100% bio-ethanol, because of the increased share of pure or high blended ethanol vehicles.

Activity data of biogasoline in kt (mass units) can be obtained from national energy balances. Regulation (EC) No 1099/2008 on energy statistics defines reporting obligations and includes reporting of biogasoline and its component bio-ethanol.

Equations (4) and (5) can be used for the calculation of fossil and biogenic CO2 associated with biogasoline consumption.
Table 4. Carbon content and fossil fraction of CC of biogasoline.

| C atoms | MW | Carbon content [fossil + bio] in % kg/kg | Fossil fraction of CC |
|---------|----|--------------------------------------|----------------------|
| Bio-MTBE | 5  | 88.2 | 68.0% | 80.0% |
| Bio-ETBE | 6  | 102.2 | 70.5% | 71.4% |
| Bio-TAEE | 7  | 116.2 | 72.3% | 71.4% |
| Bio-methanol | 1 | 32.0 | 37.5% | 0.0% |
| Bio-ethanol | 2 | 46.1 | 52.1% | 0.0% |
| Isobutylene | 4 | 56.1 | |
| Methyl butene | 5 | 70.1 | |

Chemical reactions
- Bio-methanol + isobutylene → MTBE
- Bio-ethanol + isobutylene → ETBE
- Bio-ethanol + methyl butene → TAAE

(Fossil origin CO₂ in kt) = (kt biogasoline) 
× (CC in kgC/kg biogasoline) × (fossil fraction of CC) × 44/12

(6)

(Bio origin CO₂ in kt) = (kt biogasoline) 
× (CC in kgCs/kg biogasoline) × (100% – fossil fraction of CC) × 44/12

(7)

According to the 2006 IPCC Guidelines, the default CC and NCV for biogasoline are 19.3 kg/TJ and 27 TJ/kt, respectively. By combining these numbers, the CC of biogasoline is calculated in mass units at 52.1% (kg/kg), which is the bio-ethanol CC (see Table 4). Therefore, when a type of biogasoline other than bio-ethanol is used, the default CC and NCV values from the 2006 IPCC Guidelines are not accurate and should be avoided.

Results

The higher tier step-by-step method presented in the previous section, was applied for the estimation of the CO₂ emissions of the fossil part of biofuels consumed within EU-27 in the year 2019. Table 5 summarizes the calculations and results.

The activity data (i.e. biodiesel and biogasoline consumption) were obtained from Eurostat [22]. It is assumed that biodiesel is 100% FAME and biogasoline is 50% bio-ETBE and 50% bio-ethanol. The fossil part of biofuel CO₂ emissions in EU-27 was around 5.2 Mt in the year 2019.

According to the annual EU GHG inventory report [8], the CO₂ emissions of EU-27 from the fossil part of biofuels were reported to be around 2.7 Mt in the year 2019. The difference between this value and the value estimated in this study may be attributed to the fact that a number of EU member states did not estimate the fossil CO₂ emissions (potentially due to the absence of a solid method) or reported the emissions under a different category of the inventory. The application of the method presented in this paper could contribute to a more accurate, consistent and transparent estimation and reporting of CO₂ emissions associated with the combustion of biofuels.

Discussion and conclusions

The transport sector is responsible for a significant part of CO₂ emissions globally. A mitigation policy that is promoted for the reduction of CO₂ emissions from the transport sector is the replacement of fossil fuels with biofuels. Biofuels are considered to be carbon-neutral, regarding the direct CO₂ emissions associated with their combustion, because they do not deliver any additional CO₂ into the environment, taking into account the CO₂ that has been absorbed by the plants through photosynthesis. A part of the carbon of biofuels, however, may have a fossil source and therefore is associated with “non-neutral” CO₂ emissions. This issue was recognized by the IPCC, which is the organization that provides guidance to GHG inventory compilers and practitioners on the estimation of GHG emissions per source category. Although the 2006 IPCC Guidelines and their recent 2019 Refinement provided some examples concerning the fossil part of biofuels, the exact fraction of fossil carbon content per each biofuel type is not explicitly provided in the guidelines or the scientific literature. As a result, there is confusion among GHG inventory compilers and other practitioners about how to estimate the relevant emissions.

The method presented in this paper is a higher tier step-by-step approach for the estimation of CO₂ emissions associated with the fossil part of all types of biofuels nowadays used to replace fossil diesel and gasoline. The method is separated into...
two modules, one for the bio-alternatives of diesel and one for the bio-alternatives of gasoline. The minimum data required are the type of biofuel and its amount. The more information is available about the feedstock used for the production of biofuels, the more accurate can be the estimation of CO₂ emissions provided by the method. In addition, it was concluded that the use of CC and NCV values for biodiesel from the 2006 IPCC Guidelines to estimate CO₂ emissions may lead to an error of more than 30%. Therefore, it is proposed to update the CC and NCV values for biodiesel in the next version of the IPCC Guidelines document, in order to take into consideration the chemical composition of the fuel, as demonstrated in this paper. Furthermore, the reported NCV for biogasoline in the 2006 IPCC Guidelines corresponds to bio-ethanol and it is not representative of other types of biogasoline, such as bio-ethers.

By applying the proposed method, it was possible to estimate, as a case study, the CO₂ emissions associated with the fossil part of biofuels in EU-27. They were estimated to be around 5.2 Mt CO₂ in the year 2019. These CO₂ emissions are of the same level of magnitude as the total national GHG emissions of each of the smallest EU member states, i.e. Malta and Cyprus. In addition, they correspond to about 0.13% of the EU-27 total GHG emissions. The 2021 EU GHG inventory report [8] estimated the uncertainty of emissions of the transport sector at 0.6%. Therefore, it could be concluded that the CO₂ emissions from the fossil fraction of biofuels are rather low and comparable to the level of uncertainty regarding the transport sector’s emissions.

On the other hand, according to the current UNFCCC reporting guidelines on annual national GHG inventories for Parties included in Annex I to the Convention [23], an emission source could be considered insignificant if the likely level of emissions is below 0.05% of the national total GHG emissions. Therefore, for the case of EU-27, the CO₂ emissions from the fossil fraction of biofuels do not fall under that threshold and need to be included in the GHG inventory. The proposed methodology could be useful to either EU Member States or other countries in estimating these emissions both where only limited data are available (e.g. only the activity data of biodiesel and biogasoline) and where more country specific information is available that allows a detailed and more accurate estimation (e.g. types of biodiesel/biogasoline used in the country and raw materials used for the production of biofuel).

The method of this study covers the bio-alternatives mainly used nowadays to replace diesel and gasoline. It does not cover biofuels that are not currently being produced at significant volumes or those whose production technology is at demonstration level and not yet mature.

Acknowledgments

The following GHG experts provided input to and/or peer-reviewed the method presented in this paper: Bernd Gugelé, Graham Anderson, Marc Schuman, Nora Becker, Peter Brown, Jean-Pierre Chang, Ole-Kenneth Nielsen, Veronica Eklund, Edith Brodda, Fernando Diaz-Alonso, Andreas Gumbert.

Data availability statement

The author confirms that the data supporting the findings of this study are available within the article.

Disclosure statement

The author declares no conflict of interest.

Funding

This research was funded by European Commission (Ref. no. 340201/2017/765292/SER/CLIMA.C2).

References

(1). IPCC. 2021: Summary for Policymakers. In: Climate Change 2021: The Physical Science Basis. Contribution of Working Group I to the Sixth Assessment Report of the Intergovernmental Panel on Climate Change (MassonDelmotte V, P Zhai, A Pirani, SL Connors, C Péan, S Berger, N Caud, Y Chen, L Goldfarb, MI Gomis M, Huang K, Leitzell E, Lonnoy JBR, Matthews, T K Maycock, T Waterfield, O Yelekçi, R Yu, and B Zhou (Eds.)). Cambridge University Press. In Press

(2). IPCC. Climate change 2014: impacts. In: Field CB, Barros VR, Dokken DJ, et al., editors. Adaptation, and vulnerability. Part A: global and sectoral aspects. Contribution of working group II to the fifth assessment report of the intergovernmental panel on climate change. Cambridge, UK and New York, NY: Cambridge University Press; 2014. 1132 p.

(3). WMO. 2020: Greenhouse Gas Bulletin (GHG Bulletin) - No.16. The state of greenhouse gases in the atmosphere based on global observations through 2019; 2020 (accessed 1 November 2021). Available online: https://library.wmo.int/index.php?id=21795&lvl=notice_display#.YOa1QugzaF4.

(4). Perugini L, Pellis G, Grassi G, et al. Emerging reporting and verification needs under the paris agreement: how can the research community effectively contribute? Environ Sci Policy. 2021;122:116–126. doi:10.1016/j.envsci.2021.04.012.
(5) Sebos I, Progiou A, Kallinikos L, et al. Mitigation and adaptation policies related to climate change in Greece. In Green energy and technology, edited by P Grammelis, Switzerland: Springer; 2016. p. 35–49. doi: 10.1007/978-3-319-30127-3_4.

(6) IPCC. 2006 IPCC guidelines for national greenhouse gas inventories, prepared by the national greenhouse gas inventories programme. Eggleston HS, Buendia L, Miwa K, et al., editors. Japan: IGES; 2006.

(7) IPCC. 2019. 2019 Refinement to the 2006 IPCC guidelines for national greenhouse gas inventories. Buendia EC, Tanabe K, Kranjc A, et al., editors. Switzerland: IPCC.

(8) EEA (European Environment Agency). Submission under the United Nations framework convention on climate change and the kyoto protocol. EEA Report No 5/2021. Copenhagen, Denmark (accessed 1 November 2021). Available online: https://www.eea.europa.eu/publications/annual-european-union-greenhouse-gas-inventory-2021.

(9) Li M, Lu Y, Huang M. Evolution patterns of bioenergy with carbon capture and storage (BECCS) from a science mapping perspective. Sci Total Environ. 2021; 766:144318. doi:10.1016/j.scitotenv.2020.144318.

(10) Full J, Merseburg S, Miehe R, et al. New perspective for climate change mitigation—introducing carbon negative hydrogen production from biomass with carbon capture and storage (HyBECCS). Sustainability. 2021;13(7):4026. doi:10.3390/su13074026.

(11) Adeniyi OM, Azimov U, Burluka A. Algae biofuel: current status and future applications. Renew Sustain Energy Rev. 2018;90:316–335. doi:10.1016/j.rser.2018.03.067.

(12) Malode SJ, Prabhu KK, Mascarenhas RJ, et al. Recent advances and viability in biofuel production. Energy Convers Manag. 2021;10:100070. doi:10.1016/j.enconman.2020.10.0070.

(13) Sebos I, Progiou A, Kallinikos L. Methodological framework for the quantification of GHG emission reductions from climate change mitigation actions. SPEE. 2020;39:3–4. doi:10.13052/spee1048-4236.391411.

(14) Reddy CM, Demello JA, Carmichael CA, et al. Determination of biodiesel blending percentages using natural abundance radiocarbon analysis: testing the accuracy of retail biodiesel blends. Environ Sci Technol. 2008;42(7):2476–2482. doi:10.1021/es071814j.

(15) Ofgem Great Britain’s independent energy regulator. Renewables Obligation: biodiesel and fossil-derived bioliquids guidance 2015 (accessed 1 November 2021). Available online: https://www.ofgem.gov.uk/publications/renewables-obligation-biodiesel-and-fossil-derived-bioliquids-guidance-2015

(16) Vonortas A, Papayannakos N. Comparative analysis of biodiesel versus green diesel. WIREs Energy Environ. 2014;3(1):3–23. doi:10.1002/wene.78.

(17) Orsavova J, Misurcova L, Ambrozova JM, et al. Fatty acids composition of vegetable oils and its contribution to dietary energy intake and dependence of cardiovascular mortality on dietary intake of fatty acids. Int J Mol Sci. 2015;16(6):12871–12890. doi:10.3390/ijms160612871.

(18) Rohman A, Triyana K, Sisimindari, Erwanto Y. Differentiation of lard and other animal fats based on triacylglycerols composition and principal component analysis. Int. Food Res J. 2012;19:475–479.

(19) Neste renewable diesel handbook. Available online: https://www.neste.com/sites/default/files/attachments/neste_renewable_diesel_handbook.pdf.

(20) Wood BM, Kirwan K, Maggs S, et al. Study of combustion performance of biodiesel for potential application in motorsport. J Clean Prod. 2015;93:167–173. doi:10.1016/j.jclepro.2014.12.091.

(21) Rakopoulos CD, Antonopoulos KA, Rakopoulos DC, et al. Comparative performance and emissions study of a direct injection diesel engine using blends of diesel fuel with vegetable oils or bio-diesels of various origins. Energy Convers Manag. 2006;47(18–19): 3272–3287. doi:10.1016/j.enconman.2006.01.006.

(22) Eurostat Energy Balances (accessed 1 November 2021). Available online: https://ec.europa.eu/eurostat/web/energy/data/energy-balances.

(23) UNFCCC (United Nations Framework Convention on Climate Change). Decision 3/CP.5 guidelines for the preparation of national communications by parties included in annex I to the convention, Part I: UNFCCC Reporting Guidelines on Annual Inventories (FCCC/CP/1999/7); 2000.