

Article

Determining the Unit Values of the Allocation of Greenhouse Gas Emissions for the Production of Biofuels in the Life Cycle

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Abstract: Thanks to the allocation methods, i.e., the division of the total GHG emissions between each of the products generated in the production of biofuels, it is possible to reduce the emissions of these gases by up to 35% in relation to the production and combustion of fuels derived from crude oil. As part of this study, the biodiesel production process was analyzed in terms of greenhouse gas (GHG) emissions. On the basis of the obtained results, the key factors influencing the emissions level of the biodiesel production process were identified. In order to assess the sensitivity of the results of the adopted allocation method, this study included calculations of GHG emissions with an allocation method based on mass, energy, and financial shares. The article reviews recent advances that have the potential to enable a sustainable energy transition, a green economy, and carbon neutrality in the biofuels sector. The paper shows that the technology used for the production of biodiesel is of great importance for sustainable development. The possibility of using renewable raw materials for the production of fuels leads to a reduction in the consumption of fossil fuels and lower emission of pollutants. It showed that during the combustion of biodiesel, the percentages of released gas components, with the exception of nitrogen oxides, which increased by 13%, were significantly lower: CO₂—78%, CO—43%, SO₂—100%, PM₁₀—32%, and volatile hydrocarbons—63%. Moreover, it was found that biodiesel undergoes five times faster biodegradation in the environment than diesel oil.

Keywords: biofuel; greenhouse gas emissions; reduction in GHG emissions



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1. Introduction

The progressive exploitation of non-renewable resources, such as coal, oil, or gas, leads to the excessive use of these raw materials and the exhaustion of stocks. The beginning of the industrial era based on energy-intensive systems has increased the demand for energy. For several years, an increase in interest in the production of fuels from organic sources has been observed in the world [1]. This is a result of the overlapping of several factors: high oil prices, individual countries' striving for energy sovereignty, counteracting global warming, and the limited resources of non-renewable resources. In order to meet the challenges faced by the energy sector and meet environmental protection requirements, the development of renewable energy sources is essential [2–4]. Biofuels are all fuels that are produced from biomass. Biomass is considered to be all biodegradable animal and plant matter, as well as their metabolic products. Biofuels can be in the form of: gaseous, solid, or liquid. The representative of the first group is biogas obtained in the process of anaerobic fermentation [5–8]. Liquid biofuels are mainly: bioethanol (ethyl alcohol produced from plants in fermentation and distillation processes) and biodiesel (chemically processed vegetable oil). Solid biofuels are processed and unprocessed biomass, as well as a biodegradable fraction of municipal waste. All the mentioned biofuels are used in heating and power engineering [9–11].

Many researchers have reported that different blends of biodiesel and diesel can be effective in reducing CO, HC, and PM emissions such as cooking oil waste biodiesel [12], jatropha oil biodiesel [13], caranja biodiesel [14], biodiesel from rapeseed oil [15], soybean

oil biodiesel [16], and palm oil biodiesel [17]. Many researchers have also studied the effect of biofuels on the performance of internal combustion and diesel engines [18–27]. Few studies have been carried out on the calculation of GHG emissions with the use of the allocation method based on mass, energy, and financial contributions of biodiesel. Therefore, this article fills this research gap, and the applied methods have a potential application value for further analysis of the physicochemical properties of, for example, PM particles emitted from diesel engines in the future.

Poland, like other EU Member States, is obliged to implement the provisions of EU directives, including Directive 2009/28/EC [1] promoting renewable energy sources (RED Directive). It is a comprehensive document with a lot of attention to the assessment of biofuels and bioliquids and the need to demonstrate that they meet the sustainability criteria. Confirmation of this fact is to be obtained by the supplier of an appropriate certificate under the selected certification system. One of the elements of the audit is the assessment of the determination of the value of greenhouse gas emissions over the life cycle. The correctness of the determination of this value is therefore extremely important, and it is influenced by many factors, including the method of allocating GHG emissions, as well as the calculation tools used.

The new directive on renewable energy, introduced in 2021, provides for a reduction in greenhouse gas emissions by 40% by 2030, compared to the result from 1990. In addition, the standard provides for a 32% energy share renewable in final energy consumption [28]. One of the most important changes envisaged by the RED II directive is the fact that not only the rules relating to the biofuel production chain will be implemented in the EU-wide sustainable development, but also for biomass fuels that are used in the electricity sector, as well as in the heating and cooling sector. In the context of biofuels themselves, the new regulations put more emphasis on reducing greenhouse gas emissions. In this regard, it sets new criteria to reduce gas emissions by 65–70% for installations that will start operating after 1 January 2021, and 80% for installations that will start operating after 1 January 2026 [29]. First generation fuels, produced on the basis of agricultural raw materials, will be additionally burdened with indirect land-user risk indicators. The assumptions of the latest regulations prioritize the development of advanced biofuels because they assume an increase in the share of these fuels from 0.5%, which took place in 2020, to the forecasted 3.5% in 2030. As part of advanced biofuels, the production of biodiesel from used cooking oils will continue to play a significant role [30,31]. In connection with the above activities, greater supervision and monitoring of entities dealing with their greenhouse gas emissions for the production of biofuels in the life cycle is expected.

2. Materials and Methods

The issues of the allocation method and other factors influencing the GHG emissions result for biodiesel are presented in this paper. In addition, all the components of GHG emissions generated during the cultivation of the raw material used to produce the final biocomponent were determined and their legitimacy was determined. This article analyzes rapeseed–agricultural raw materials most often used in Poland for the production of vegetable oil, from which methyl esters of fatty acids are produced at a later stage. The calculations made in this study were based on real data obtained from various entities. The obtained data was averaged and served as input data for the calculations of greenhouse gas emissions.

Due to the fact that for the purposes of meeting the requirements of Directive 2009/28/EC [1], the GHG emissions for the cultivation stage is given in g CO₂eq per 1 MJ of the obtained biofuel, the obtained emissions for one ton of agricultural raw material should be recalculated taking into account all successive conversion processes. In the case of oilseed rape, these are the most common processes leading to the production of fatty acid methyl esters (FAME). For this purpose, calculations are made with the use of conversion factors for a given treatment process and emission allocation factors are applied taking into account the type of obtained products: main and by-products. As a result, the final

result may be influenced by the selection of conversion factors used in the calculations for oil pressing and FAME production, as well as allocation factors depending on the mass share of individual process products and their calorific value.

2.1. Overall Mass Balance for the Entire Process

In order to analyze GHG emissions on the basis of various allocation methods, the overall mass balance of the entire production process was calculated according to individual stages (Figure 1):

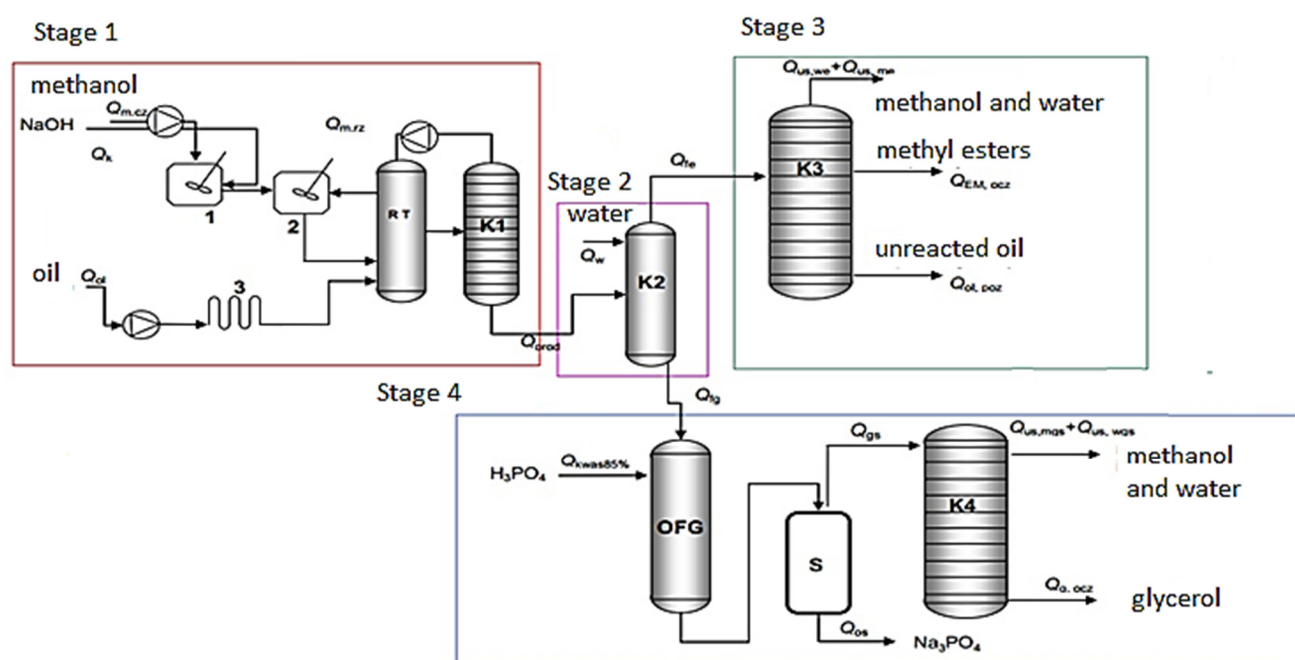


Figure 1. Diagram of biodiesel production by transesterification with the use of a basic catalyst in a flow system. Source: own study.

Figure 1 shows a technological scheme for the production of biodiesel from rapeseed oil by transesterification with the use of a basic catalyst (NaOH), including 4 stages:

- (1) Transesterification and recovery of methanol;
- (2) Separation of methyl esters and glycerin fractions;
- (3) Purification of methyl esters;
- (4) Purification of the glycerin fraction.

The production of biodiesel as part of the research consisted in directing the stream of crude rapeseed oil, after increasing the pressure and heating (temperature 60 °C and pressure 4 bar) for transesterification. Fresh methanol and catalyst (NaOH) are then routed to the mixer, to which also the methanol recovered from transesterification is recirculated. The resulting sodium methoxide is successively directed to the column where the transesterification is carried out, after which the mixture is sent to the distillation column. Methanol is recovered at the temperature of 150 °C, and then, after cooling down to the temperature of 60 °C, it is returned to the process. The remaining components, after cooling in a heat exchanger, are directed to the separation, where the ester phase is separated from the glycerin phase and impurities. Then, the esters are routed to purification. Initially, in the countercurrent reactor they are rinsed with water at 25 °C to remove soaps. From the countercurrent column, they are directed to a centrifuge, where they separate from impurities, and then pass them to vacuum distillation to dry them. In this way, products with a purity of 99.8% are obtained. Subsequently, the glycerin phase is directed to the tank where H_3PO_4 is introduced in order to neutralize the basic catalyst. After centrifugation in the centrifuge, the Na_3PO_4 sediment formed is treated as waste. Then,

after the distillation of crude glycerin, technical glycerin is obtained. The advantages of the process include: complexity of the system, high efficiency, and high quality of esters.

Process description:

Stage 1

- Combination of sodium base (Q_k) with methanol ($Q_{m, cz}$) in the mixer (1);
- Feeding the obtained mixture and recirculated methanol ($Q_{m, rz}$) to the mixer (2);
- Supplying oil (Q_{ol}) and methanol with the catalyst to the RT reactor for transesterification;
- Feeding the transesterified mixture to the distillation column (K1) to recover the methanol;
- Recirculation of the recovered condensed methanol ($Q_{m, rz}$) to the mixer (2).

Stage 2

- Feeding the transesterification products: esters, glycerin, unreacted oil, catalyst, and water as a washing substance to the washing column (K2);
- Separation of the ester phase (Q_{fe}) from the glycerin phase (Q_{fg}) in the K2 column.

Stage 3

- Directing impure esters (Q_{fe}) to column K3 in order to remove from them methanol ($Q_{us, me}$), water ($Q_{us, we}$) and unreacted oil ($Q_{ol, poz}$);
- Collection of purified methyl esters ($Q_{EM, eyes}$) in the tank.

Stage 4

- Directing the contaminated glycerin phase (Q_{fg}) to a neutralization reactor (OFG) to remove the catalyst, methanol, and water;
- Feeding phosphoric acid to the reactor;
- Directing the products resulting from the neutralization to the separator (S) in order to remove the sediment (Q_{osad});
- Crude glycerin (Q_{gs}) is directed to the distillation column (K4) to remove water ($Q_{us, wg}$) and methanol ($Q_{us, mg}$);
- Purified glycerin ($Q_{g, ocz}$) is formed in the K4 column.

2.2. GHG Emissions Allocation

In the production of biofuels, in addition to the main product, there are also by-products and waste. In line with the methodology set out in the RED directive, the GHG emissions generated during production are allocated to the main product and by-products. Emissions are not allocated to waste if it is used for other purposes (e.g., energy). Then the emissions amount for the generation step is assumed to be zero. The way in which the resulting GHG emissions are “split” between the produced biofuel and by-products will have an impact on the final result of the biofuel’s ability to reduce greenhouse gas emissions. Emissions allocation should be carried out at the production stage, which produces the biofuel, bioliquid, or by-product suitable for storage and sale. The allocation of GHG emissions can be carried out at individual stages of the production of the final product and by-products, after which these products are still processed in subsequent stages. If the subsequent stages of production (products and by-products) are related to the previous ones (material or energy factors), the allocation should be made at the moment when these stages become separate processes, not related in any way to the previous ones.

The total GHG emissions and allocation to the main product and by-product were calculated on the basis of the following formulas [32,33]:

$$C_t = C_f + C_m + C_e \quad (1)$$

where

C_t —total emissions related to all inputs, CO₂eq,

C_f —emissions contributed with the raw material, CO₂eq,

C_m —emissions brought in with other materials, CO₂eq,

C_e —emissions related to energy consumption, CO₂eq.

The allocation of GHG emissions to biofuels/bioliquids and to the by-product was calculated from the following formulas:

$$C_1 = C_t \cdot Q_1 \cdot \frac{LHV_1}{Q_1 \cdot LHV_1 + Q_2 \cdot LHV_2}$$

$$C_2 = C_t \cdot Q_2 \cdot \frac{LHV_1}{Q_1 \cdot LHV_1 + Q_2 \cdot LHV_2} \quad (2)$$

where

C_t —total emissions related to all inputs, CO₂eq,

C_1 —GHG emissions allocation to biofuel/bioliquid, CO₂eq,

C_2 —allocation of GHG emissions to the by-product, CO₂eq,

$Q_{1/2}$ —the quantity of the product 1/2, expressed in mass units,

$LHV_{1/2}$ —calorific value of product 1/2, expressed as a unit of energy per unit mass.

As part of the research, the allocation was carried out:

- On the basis of physical quantities (mass, energy content).

This method is based on assigning GHG emissions to each of the resulting products and by-products in direct proportion to their obtaining (based on the mass or energy balance) [34]. If the allocation method is adopted based on the mass balance, the mass of the main products, and by-products was initially calculated. Then, based on their percentages of the total mass of production (sum of the masses of the main product and the by-product), they were assigned an emissions percentage.

- On the basis of economic figures.

Allocation based on economic quantities gives the least stable and less comparable results. The allocation can be made based on the market prices of raw materials and finished products, production costs, storage, transportation of the final product and by-products. Analyzes carried out in different regions of the world may differ from each other, because the prices of raw materials and by-products, as well as production costs, can vary significantly depending on the economic policy of a country and on the location of the region.

- Based on an extensive system.

The allocation made by the extended system method is used especially by scientists from the USA. According to the concept of this method, the system boundaries are extended to include additional alternative products. The activities not related to the life cycle of a given product are also included in the calculations. First, you need to define the amount of biofuel produced and the by-products and products that are on the market that can be replaced by biofuel by-products. Next, the ratio to which the products in question can be replaced by by-products of the biofuel production process is calculated and the environmental impact of the products to be replaced is determined. It may turn out that you replace existing products on the market with products byproducts of the biofuel production process will reduce the negative environmental impact of the biofuel life cycle.

2.3. GHG Emissions Calculation Method

According to the RED Directive, greenhouse gas emissions from the production and use of transport fuels, biofuels and bioliquids are calculated from the formula [32,33]:

$$E = e_{ec} + e_l + e_p + e_{td} + e_u - e_{sca} - e_{ccs} - e_{ccr} - e_{ee} \quad (3)$$

where

E —total emissions caused by the use of fuel,

e_{ec} —emissions caused by the extraction or cultivation of raw materials,

e_l —annual emissions caused by changes in the amount of the carbon element in connection with the change in land use,
 e_p —emissions caused by technological processes,
 e_{td} —emissions from transport and distribution,
 e_u —emissions caused by the fuel used,
 e_{sca} —emissions saving value due to carbon accumulation in the soil thanks to better farming,
 e_{ccs} —reduction in emissions due to carbon capture and storage in deep geological structures,
 e_{ccr} —emissions reduction due to carbon capture and replacement,
 e_{ee} —emissions reduction due to increased electricity production from cogeneration.

3. Results and Discussion

3.1. Overall Mass Balance for the Entire Process

Technological calculations for the four stages of biodiesel production.

Stage 1. The alcohol transesterification and recovery process include the calculation of methanol and catalyst charge and calculations related to methanol recovery and recirculation (Table 1).

Table 1. Technological assumptions for methanol transesterification and recovery.

Parameter	Symbol	Unit	Assumed Value
oil flow rate	Q_{ol}	kg/h	1050
methanol concentration	$\eta_{m,e}$	% weight of raw material	11
catalyst concentration	η_k	% weight of raw material	1.0
alcohol density	ρ_m	g/cm ³	0.797
oil density	ρ_{ol}	g/cm ³	0.899
content of triacylglycerols	η_{Ac}	%	~100
transesterification temperature	T_e	°C	60
transesterification pressure	P_e	kPa (atm)	400 (4.07)
yield of transesterification	η_e	%	95
alcohol distillation temperature	T_{dest}	°C	150
alcohol distillation pressure	P_{dest}	kPa (atm)	30 (3.06)
alcohol recovery efficiency	η_{dest}	%	94

Source: own study based on [32,33].

- Supply of raw materials

The calculations concern the required amounts of methanol and catalyst to carry out the transesterification [33,35]:

Amount of methanol needed for transesterification $Q_{m,t}$ (kg/h):

$$Q_{m,t} = Q_{ol} \cdot \frac{\eta_{m,e}}{100} = 1050 \cdot \frac{11}{100} = 115.5 \left[\frac{\text{kg}}{\text{h}} \right] \quad (4)$$

The amount of methanol supplied to the reactor Q_m (kg/h), with its twofold excess:

$$Q_m = 2 \cdot Q_{m,t} = 2 \cdot 115.5 = 231 \left[\frac{\text{kg}}{\text{h}} \right] \quad (5)$$

Required amount of catalyst Q_k (kg/h):

$$Q_k = Q_{ol} \cdot \frac{\eta_k}{100} = 1050 \cdot \frac{1.0}{100} = 10.5 \left[\frac{\text{kg}}{\text{h}} \right] \quad (6)$$

- Recovery of methanol

The calculations concern the possibility of methanol recovery and its reuse in the transesterification process and the amount of pure methanol supplied to the process.

Amount of methanol theoretically recoverable $Q_{m,teor}$ (kg/h):

$$Q_{m,teor} = Q_m - \left(Q_{m,t} \cdot \frac{\eta_e}{100} \right) = 231 - \left(115.5 \cdot \frac{95}{100} \right) = 121.275 \left[\frac{\text{kg}}{\text{h}} \right] \quad (7)$$

Actual amount of methanol recovered $Q_{m,rz}$ (kg/h):

$$Q_{m,rz} = Q_{m,teor} \cdot \frac{\eta_{dest}}{100} = 121.275 \cdot \frac{94}{100} = 113.9985 \left[\frac{\text{kg}}{\text{h}} \right] \quad (8)$$

Amount of pure methanol to be fed to the reactor, taking into account its recirculation, $Q_{m,cz}$ (kg/h):

$$Q_{m,cz} = Q_m - Q_{m,rz} = 231 - 113.9985 = 117.0015 \left[\frac{\text{kg}}{\text{h}} \right] \quad (9)$$

Amount of methanol remaining after distillation in the stream of transesterification products $Q_{m,poz}$ (kg/h):

$$Q_{m,poz} = Q_{m,teor} - Q_{m,rz} = 121.275 - 113.9985 = 7.2762 \left[\frac{\text{kg}}{\text{h}} \right] \quad (10)$$

- Transesterification products

Based on the transesterification equation, when reacting with 100 kg of oil, 100.45 kg of biodiesel and 10.55 kg of glycerol can be obtained (assuming the molar weight of the oil is 871.67 g/mol, and the methyl esters are 875.6 g/mol). The material balance of raw materials, products and by-products after the alcohol transesterification and recovery stage is presented in Table 2.

Amount of Q_{ME} methyl esters (kg/h):

$$Q_{ME} = \frac{100.45 \cdot Q_{ol}}{100} \cdot \frac{\eta_e}{100} = \frac{100.45 \cdot 1050}{100} \cdot \frac{95}{100} = 1001.9888 \left[\frac{\text{kg}}{\text{h}} \right] \quad (11)$$

Amount of unreacted rapeseed oil $Q_{ol,poz}$ (kg/h):

$$Q_{ol,poz} = Q_{ol} \cdot \left(1 - \frac{\eta_e}{100} \right) = 1050 \cdot \left(1 - \frac{95}{100} \right) = 52.5 \left[\frac{\text{kg}}{\text{h}} \right] \quad (12)$$

Amount of glycerol $Q_{glycerol}$ (kg/h):

$$Q_{glycerol} = \frac{10.4 \cdot Q_{ol}}{100} \cdot \frac{\eta_e}{100} = \frac{10.4 \cdot 1050}{100} \cdot \frac{95}{100} = 103.74 \left[\frac{\text{kg}}{\text{h}} \right] \quad (13)$$

Stage 2. Separation of methyl esters and glycerin fraction. At the stage of separation of methyl esters and glycerin fractions, the water charge needed for ester washing, methanol and catalyst loads, and water drained from the esters and glycerin phase should be calculated on the basis of the shares of individual components. The technological assumptions for the separation of methyl esters and the glycerol fraction are presented in Table 3.

Table 2. Material balance of raw materials, products, and by-products after the stage of alcohol transesterification and recovery.

Raw Materials			Products		
Type	Symbol	Load (kg/h)	Type	Symbol	Load (kg/h)
canola oil	Q_{ol}	1050	methyl esters	Q_{ME}	1001.9888
			unreacted oil glycerol	$Q_{ol,poz}$	52.5
			unreacted oil glycerol	$Q_{glycerol}$	103.7400
catalyst (NaOH)	Q_k	10.5	catalyst (NaOH)	Q_k	10.5
fresh methanol	$Q_{m,cz}$	117.0015	unreacted methanol	$Q_{m,poz}$	7.2765
Sum				Q_{prod}	1176.0150

Source: own study based on [32,33].

Table 3. Technological assumptions for the separation of methyl esters and glycerin fraction.

Parameter	Symbol	Unit	Value
amount of water for rinsing the methyl esters	η_w	% wag. Q_{prod}	1.0
water fraction (ester fraction/glycerin fraction)	$\eta_{w,e}/\eta_{w,g}$	%	10/90
methanol fraction (ester fraction/glycerol fraction)	$\eta_{m,e}/\eta_{m,g}$	%	60/40
catalyst fraction (NaOH) (ester fraction/glycerol fraction)	$\eta_{k,e}/\eta_{k,g}$	%	0/100
unreacted oil fraction (ester fraction/glycerin fraction)	$\eta_{ol,e}/\eta_{ol,g}$	%	100/0
temperature (separator inlet/outlet)	T_s	°C	50/60
pressure (separator inlet/outlet)	p_s	kPa (atm.)	110/120
			1.12/1.22

Source: own study based on [32,33].

Amount of water needed for rinsing methyl esters Q_w (kg/h):

$$Q_w = Q_{prod} \cdot \frac{\eta_w}{100} = 1176.015 \cdot \frac{1.0}{100} = 11.7602 \left[\frac{kg}{h} \right] \quad (14)$$

Amount of water discharged with the ester fraction $Q_{w,e}$ (kg/h):

$$Q_{w,e} = Q_w \cdot \frac{\eta_{w,e}}{100} = 11.7602 \cdot \frac{10}{100} = 1.176 \left[\frac{kg}{h} \right] \quad (15)$$

Amount of methanol discharged with the ester fraction $Q_{m,e}$ (kg/h):

$$Q_{m,e} = Q_{m,poz} \cdot \frac{\eta_{m,e}}{100} = 7.2765 \cdot \frac{60}{100} = 4.3657 \left[\frac{kg}{h} \right] \quad (16)$$

Amount of catalyst (NaOH) discharged with the ester fraction $Q_{k,e}$ (kg/h):

$$Q_{k,e} = Q_k \cdot \frac{\eta_{k,e}}{100} = 10.5 \cdot 0 = 0 \left[\frac{kg}{h} \right] \quad (17)$$

Amount of unreacted oil discharged with the ester fraction $Q_{ol,e}$ (kg/h):

$$Q_{ol,e} = Q_{ol,poz} \cdot \frac{\eta_{ol,e}}{100} = 52.5 \cdot \frac{100}{100} = 52.5 \left[\frac{kg}{h} \right] \quad (18)$$

Amounts of water, methanol, catalyst, and unreacted oil discharged with the glycerin fraction, analogous to the ester fraction:

$$Q_{w,g} = Q_w \cdot \frac{\eta_{w,g}}{100} = 11.7602 \cdot \frac{90}{100} = 10.5842 \left[\frac{kg}{h} \right]$$

$$\begin{aligned}
 Q_{m,g} &= Q_{m,poz} \cdot \frac{\eta_{m,g}}{100} = 7.2765 \cdot \frac{40}{100} = 2.9106 \left[\frac{\text{kg}}{\text{h}} \right] \\
 Q_{k,g} &= Q_k \cdot \frac{\eta_{k,g}}{100} = 10.5 \cdot \frac{100}{100} = 10.5 \left[\frac{\text{kg}}{\text{h}} \right] \\
 Q_{ol,g} &= Q_{ol,poz} \cdot \frac{\eta_{ol,g}}{100} = 52.5 \cdot 0 = 0 \left[\frac{\text{kg}}{\text{h}} \right]
 \end{aligned} \quad (19)$$

The ester and glycerol fractions discharged from the separator are presented Table 4.

Table 4. Ester and glycerol fractions discharged from the separator.

Parameter	Unit	Value	
		Ester Phase	Glycerin Phase
load of methyl esters/glycerol	kg/h	Q_{ME} 1001.9888	$Q_{glycerol}$ 103.74
water load	kg/h	$Q_{w,e}$ 1.176	$Q_{w,g}$ 10.5842
methanol charge	kg/h	$Q_{m,e}$ 4.3657	$Q_{m,g}$ 2.9106
catalyst load (NaOH)	kg/h	$Q_{k,e}$ 0	$Q_{k,g}$ 10.5
unreacted oil load	kg/h	$Q_{ol,e}$ 52.5	$Q_{ol,g}$ 0
Charge of the ester phase/glycerol phase	kg/h	Q_{fe} 1060.0305	Q_{fg} 127.7348

Source: own study based on [32,33].

Stage 3. Purification of methyl esters. The purification of methyl esters consists in removing water, methanol, and unreacted oils from them based on the degree of removal of individual components from the main product. The technological assumptions for the purification of methyl esters are presented in Table 5.

Table 5. Technological assumptions for the purification of methyl esters.

Parameter	Symbol	Unit	Value
degree of water removal	$\eta_{us w,e}$	%	99.6
methanol removal rate	$\eta_{us m,e}$	%	99.6
degree of removal of unreacted oil	$\eta_{us ol,e}$	%	100
temperature in the distillation column	$T_{dest,c}$	°C	193.7
pressure in the distillation column	$P_{dest,e}$	kPa (atm.)	10 (0.102)

Source: own study based on [32,33].

Removed amount of water $Q_{us w,e}$ (kg/h):

$$Q_{us w,e} = Q_{w,e} \cdot \frac{\eta_{us w,e}}{100} = 1.176 \cdot \frac{99.6}{100} = 1.1713 \left[\frac{\text{kg}}{\text{h}} \right] \quad (20)$$

Removed amount of methanol $Q_{us m,e}$ (kg/h):

$$Q_{us m,e} = Q_{m,e} \cdot \frac{\eta_{us m,e}}{100} = 4.3657 \cdot \frac{99.6}{100} = 4.3482 \left[\frac{\text{kg}}{\text{h}} \right] \quad (21)$$

The amount of unreacted oil removed $Q_{us ol,e}$ (kg/h):

$$Q_{us ol,e} = Q_{ol,e} \cdot \frac{\eta_{us ol,e}}{100} = 52.5 \cdot \frac{100}{100} = 52.5 \left[\frac{\text{kg}}{\text{h}} \right] \quad (22)$$

Amount of purified methyl esters $Q_{EM,ocz}$ (kg/h):

$$Q_{EM,ocz} = Q_{fe} - Q_{us w,e} - Q_{us m,e} - Q_{us ol,e} = 1060.0305 - 1.1713 - 4.3482 - 52.5 = 1002.0011 \left[\frac{\text{kg}}{\text{h}} \right] \quad (23)$$

The material balance of raw materials, products and by-products after the purification stage of methyl esters is presented in Table 6.

Table 6. Material balance of raw materials, products, and by-products after the methyl ester purification step.

Raw Materials		Products		Side Products	
Type	Load (kg/h)	Type	Load (kg/h)	Type	Load (kg/h)
ester fraction	Q_{fe} 1060.0305	purified methyl esters	$Q_{EM,ocz}$ 1002.0011	water removed	$Q_{us\ w,e}$ 1.1713
				methanol removed	$Q_{us\ m,e}$ 4.3482
				unreacted oil removed	$Q_{us\ ol,e}$ 52.5
Sum					58.0195

Source: own study based on [32,33].

Stage 4. Purification of the glycerin fraction. The purification of the glycerol fraction consists in removing the catalyst.

- Catalyst removal (NaOH)

To neutralize 1 kg of NaOH, use 0.81667 kg of pure phosphoric acid. The reaction produces 1.3667 kg of sodium triphosphate and 0.450 kg of water.

Amount of pure phosphoric acid to neutralize the sodium hydroxide $Q_{kwas,100}$ (kg/h):

$$Q_{kwas,100} = 0.81667 \cdot Q_{k,g} = 0.81667 \cdot 10.5 = 8.575 \left[\frac{kg}{h} \right] \quad (24)$$

The amount of phosphoric acid at 85% concentration to neutralize the sodium hydroxide $Q_{kwas,85}$ (kg/h):

$$Q_{kwas,85} = \frac{100}{85} \cdot Q_{kwas,100} = \frac{100}{80} \cdot 8.575 = 10.7188 \left[\frac{kg}{h} \right] \quad (25)$$

Amount of water introduced with 85% phosphoric acid $Q_{w\ kwas,85}$ (kg/h):

$$Q_{w\ kwas,85} = \left(\frac{100 - 85}{85} \right) \cdot Q_{kwas,85} = \left(\frac{100 - 85}{85} \right) \cdot 10.7188 = 1.8916 \left[\frac{kg}{h} \right] \quad (26)$$

Amount of tri-sodium phosphate formed Q_{osad} (kg/h):

$$Q_{osad} = 1.3667 \cdot Q_{k,g} = 1.3667 \cdot 10.5 = 14.35 \left[\frac{kg}{h} \right] \quad (27)$$

Amount of water formed by the neutralization reaction of sodium hydroxide $Q_{w,z}$ (kg/h):

$$Q_{w,z} = 0.450 \cdot Q_{k,g} = 0.450 \cdot 10.5 = 4.725 \left[\frac{kg}{h} \right] \quad (28)$$

Amount of glycerin fraction after catalyst removal (crude glycerin) $Q_{fg,n}$ (kg/h):

$$Q_{fg,n} = Q_{fg} - Q_{k,g} = 127.7348 - 10.5 = 117.2348 \left[\frac{kg}{h} \right] \quad (29)$$

The material balance of raw materials, products and by-products after the catalyst removal stage from the glycerin fraction is presented in Table 7.

Table 7. Material balance of raw materials, products, and by-products after the catalyst removal step from the glycerin fraction.

Raw Materials		Products		Side Products	
Type	Load (kg/h)	Type	Load (kg/h)	Type	Load (kg/h)
glycerin fraction	Q_{fg} 127.7348	glycerin fraction after catalyst removal	$Q_{fg,n}$ 117.2348	tri-sodium phosphate (precipitate)	Q_{osad} 14.35
pure phosphoric acid	$Q_{kwas,100}$ 8.575	water formed by the neutralization reaction	$Q_{w,z}$ 4.725		
water introduced from acid. phosphorus 85%	$Q_{kwas,85}$ 1.8916	water introduced from phosphoric acid 85%	$Q_{w,kwas,85}$ 1.8916		
Sum		$Q_{gs} = 123.8514$			

Source: own study based on [32,33].

- Purification of crude glycerin

The purification of crude glycerin is based on the removal of water and methanol based on the degree of removal of these components. Technological assumptions for the purification of raw glycerin is presented in Table 8.

Table 8. Technological assumptions for the purification of raw glycerin.

Parameter	Symbol	Unit	Value
degree of water removal	$\eta_{us w,gs}$	%	33.7
methanol removal rate	$\eta_{us m,gs}$	%	100

Source: own study based on [32,33].

Removed amount of water $Q_{us w,gs}$ (kg/h):

$$Q_{us w,gs} = Q_{gs} - Q_{fg,n} \cdot \frac{\eta_{us w,gs}}{100} = 123.8514 - 117.2348 \cdot \frac{33.7}{100} = 84.3433 \left[\frac{\text{kg}}{\text{h}} \right] \quad (30)$$

Removed amount of methanol $Q_{us m,gs}$ (kg/h):

$$Q_{us m,gs} = Q_{m,g} \cdot \frac{\eta_{us m,gs}}{100} = 2.9106 \cdot \frac{100}{100} = 2.9106 \left[\frac{\text{kg}}{\text{h}} \right] \quad (31)$$

Amount of purified glycerin $Q_{g,ocz}$ (kg/h):

$$Q_{g,ocz} = Q_{gs} - Q_{us w,gs} - Q_{us m,gs} = 123.8514 - 84.3433 - 2.9106 = 36.5975 \left[\frac{\text{kg}}{\text{h}} \right] \quad (32)$$

Material balance of raw materials, products, and by-products after the crude glycerin purification step is presented in Table 9.

Table 9. Material balance of raw materials, products, and by-products after the crude glycerin purification step.

Raw Materials		Products		Side Products	
Type	Load (kg/h)	Type	Load (kg/h)	Type	Load (kg/h)
raw glycerin	Q_{gs} 123.8514	purified glycerin	$Q_{g,ocz}$ 36.5975	water removed	$Q_{us w,gs}$ 84.3433
				methanol removed	$Q_{us m,gs}$ 2.9106
Suma					84.1049

Source: own study based on [32,33].

Overall mass balance. On the basis of mass balances prepared for each stage of biodiesel production, a general balance was prepared for an hour of the entire technological process. Material balance of raw materials, products, and by-products after taking into account all four stages of the technological process is presented in Table 10.

Table 10. Material balance of raw materials, products, and by-products after taking into account all four stages of the technological process.

Raw Materials		Products		Side Products	
Type	Load (kg/h)	Type	Load (kg/h)	Type	Load (kg/h)
canola oil	1050	methyl esters purified	1002.0011	unreacted oil	52.5
catalyst	10.5			purified glycerin	36.5975
methanol	117.0015			methanol	4.3482
water	11.7602			water	1.1713
phosphoric acid	8.575			tri-sodium phosphate	14.35
Sum	1197.837		1002.0011		108.867

Source: own study based on [32,33].

Table 11 presents the annual mass balance of the transesterification process. It was assumed that the process installation works 8000 h a year, and to facilitate the calculations, a ton was taken as the basic unit. The annual material balance of raw materials, products, and by-products of the transesterification process is presented in Table 11.

Table 11. The annual material balance of raw materials, products, and by-products of the transesterification process.

Raw Materials		Products		Side Products	
Type	Load (t/Number of Hours a Year (8000 h))	Type	Load (t/Number of Hours a Year (8000 h))	Type	Load (t/Number of Hours a Year (8000 h))
canola oil	8400	methyl esters purified	8016	unreacted oil	420
catalyst	84			purified glycerin	292.8
methanol	936			methanol	346.4
water	94.08			water	9.6
phosphoric acid	688			tri-sodium phosphate	115.2
Sum	10,202.08		8016		1184

Source: own study based on [32,33].

3.2. GHG Emissions Allocation

To assess the impact of emissions allocation in biodiesel production, it was assumed that the emissions would be split between the main product—biodiesel (purified methyl esters) and the by-product—glycerin. Three different ways of allocating emissions were carried out on the basis of mass balance, financial, and calorific values. Allocation based on the mass balance is presented in Table 12.

Table 12. Allocation based on the mass balance.

Product	Annual Production (t)	Total Weight of Products	% of Assigned Emissions
biodiesel	8016	8308.8	96.5
glycerin	292.8		3.5

Source: own study based on [32,33].

- Allocation based on the mass balance of the installation

The allocation on the basis of a mass balance showed that 96.5% of the emissions are attributed to biodiesel and the remaining 3.5% to glycerin. Allocation of emissions taking into account the market value of the resulting products is presented in Table 13.

Table 13. Allocation of emissions taking into account the market value of the resulting products.

Product	Annual Production (t)	Value (EUR/ton)	Product Value (EUR)	The Total Value of EUR	% of Assigned Emissions
biodiesel	8016	800	6,273,391.31	6507146.67	98.50%
glycerin	292.8	322.23	94,346.67		1.50%

Source: own study based on [32,33].

- Financial allocation

The financial allocation of the issue takes into account the market values of the products. The prices of biodiesel and glycerin were taken from internet sources. In this case, the attributed emissions for biodiesel is 98.6%, while for glycerin only 1.5% (this is due to the high price of biodiesel in relation to glycerin and higher annual biofuel production). Allocation of emissions based on the calorific value of products is presented in Table 14.

Table 14. Allocation of emissions based on the calorific value of products.

Product	Annual Production (t)	Calorific Value (GJ/t)	Energy Contained in Product (GJ)	Total Energy (GJ)	% of Assigned Emissions
biodiesel	8016.0	37.5	300,600	306,543.84	98
glycerin	292.8	20.3	5943.84		2

Source: own study based on [32,33].

- Allocation based on the calorific value of the products

Taking into account the calorific values of the products, the emissions assigned to biodiesel is 98% and to glycerin 2%. This is due to almost twice the calorific value of biofuel as glycerin. As can be seen from the above calculations, the allocation method is important in estimating GHG emissions for the main product (i.e., *biodiesel*). The attributed GHG emissions to the biofuel ranges from 96.5% (allocation based on a mass balance) to 98.5% (financial allocation).

3.3. GHG Emissions in the Life Cycle of Biodiesel with Different Allocation Factors for the Transesterification Stage

The final result of GHG emissions is also influenced by the values of emitted pollutants obtained in the entire process (cultivation, storage, and transport). An analysis was performed to assess the impact of the adopted method of GHG emissions allocation at the production stage on the final value. It was based on the GHG emissions values (converted into GJ of energy contained in the biofuel) presented in the Biograce calculator. According to Biograce, the emissions allocation factor for biodiesel is 95.7% and is close to the calculated results. The calculations assume that the land-use change emissions and the brownfield rehabilitation bonus are zero and are not taken into account in the analysis. GHG emissions in the biofuel life cycle based on mass share is presented in Table 15.

For the allocation factor of 96.50%, the GHG emissions result is 51.92 g CO₂ eq/MJ for the transesterification process. GHG emissions in the biofuel life cycle based on financial allocation is presented in Table 16.

For the allocation factor of 98.50%, the GHG emissions result is 52.27 g CO₂ eq/MJ for the transesterification process. GHG emissions in the life cycle of a biofuel based on the energy content is presented in Table 17.

Table 15. GHG emissions in the biofuel life cycle based on mass share.

Stage	Issue without Taking into Account the Allocation (g CO ₂ eq/MJ)	Allocation Factor	Issue after Taking into Account the Allocation (g CO ₂ eq/MJ)	Share of Emissions GHG
stage _{ec}				
Cultivation	48.35	58.60%	28.33	54.57%
Storage	0.72	58.60%	0.42	0.81%
stage _p				
Oil extraction	6.5	58.60%	3.81	7.34%
Refining	1.06	95.70%	1.01	1.95%
Transesterification	17.51	96.50%	16.90	32.54%
stage _{td}				
Rapeseed transport	0.3	58.60%	0.18	0.34%
Rapeseed oil transport	0	95.70%	0.00	0.00%
Transport of biodiesel to the warehouse	0.47	100.00%	0.47	0.91%
Transport to petrol stations	0.8	100.00%	0.80	1.54%
Sum	75.71		51.92	100.00%

Source: own study based on [32,33].

Table 16. GHG emissions in the biofuel life cycle based on financial allocation.

Stage	Issue without Taking into Account the Allocation (g CO ₂ eq/MJ)	Allocation Factor	Issue after Taking into Account the Allocation (g CO ₂ eq/MJ)	Share of Emissions GHG
stage _{ec}				
Cultivation	48.35	58.60%	28.33	54.20%
Storage	0.72	58.60%	0.42	0.81%
stage _p				
Oil extraction	6.50	58.60%	3.81	7.29%
Refining	1.06	95.70%	1.01	1.94%
Transesterification	17.51	98.50%	17.25	33.00%
stage _{td}				
Rapeseed transport	0.30	58.60%	0.18	0.34%
Rapeseed oil transport	0.00	95.70%	0.00	0.00%
Transport of biodiesel to the warehouse	0.47	100.00%	0.47	0.90%
Transport to petrol stations	0.80	100.00%	0.80	1.53%
Sum	75.71		52.27	100.00%

Source: own study based on [32,33].

For an allocation factor of 98%, the GHG emissions result is 52.18 g CO₂ eq/MJ for the transesterification process. The GHG emissions result for the esterification process ranges between 52.27 and 51.92 g CO₂ eq/MJ. In the case of financial allocation, 52.27 g CO₂ eq/MJ was obtained, which is the highest of all GHG emission results. The allocation based on mass shares resulted in a lower emissions result—51.92 g CO₂ eq/MJ. Fluctuations in the final result, depending on the method adopted, amount to a maximum of 0.35 g CO₂ eq/MJ. The lowest GHG emissions result was observed when using the allocation based on mass share and it is lower by 0.26 g CO₂ eq/MJ than the emissions result obtained according to the allocation based on energy content (52.18 g CO₂ eq/MJ). The result based on the financial allocation is 0.09 g CO₂ eq/MJ higher than the allocation based on energy content. The presented calculations show the influence of the adopted allocation method on the final result of the greenhouse gas emissions reduction capacity. The analysis of the obtained GHG emission results shows that for one stage of the biofuel production

process (in this case transesterification) the use of different allocation methods does not significantly affect the total GHG emissions result (the maximum difference is 0.35 g CO₂ eq/MJ). It should be remembered that the analysis was carried out only for one production stage, which is the transesterification of rapeseed oil.

Table 17. GHG emissions in the life cycle of a biofuel based on the energy content.

Stage	Issue without Taking into Account the Allocation (g CO ₂ eq/MJ)	Allocation Factor	Issue after Taking into Account the Allocation (g CO ₂ eq/MJ)	Share of Emissions GHG
stage _p				
Cultivation	48.35	58.60%	28.33	54.29%
Storage	0.72	58.60%	0.42	0.81%
stage _p				
Oil extraction	6.5	58.60%	3.81	7.30%
Refining	1.06	95.70%	1.01	1.94%
Transesterification	17.51	98%	17.16	32.88%
stage _{td}				
Rapeseed transport	0.3	58.60%	0.18	0.34%
Rapeseed oil transport	0	95.70%	0.00	0.00%
Transport of biodiesel to the warehouse	0.47	100.00%	0.47	0.90%
Transport to petrol stations	0.8	100.00%	0.80	1.53%
Sum	75.71		52.18	100.00%

Source: own study based on [32,33].

4. Conclusions

Based on the research, the following conclusions were drawn:

1. The use of biofuels has a better environmental impact than the use of petroleum products, as their combustion emits an average of 35% less greenhouse gases compared to the combustion of diesel fuel.
2. By allocating pollutants, total GHG emissions can be reduced over the life cycle of the main product (biodiesel) by about 31% as emissions are split between it and the by-product (glycerin).
3. The least favorable method of allocating GHG emissions is financial allocation, because its result depends on the prices of raw materials used for production and the prices of final products and by-products, which may differ in individual countries of the world. The high price of biodiesel in relation to the price of glycerin makes the total GHG emissions for the main product the highest.
4. The allocation of pollutants on the basis of mass contributions is the most advantageous method of allocating emissions GHG, as its percentage attribution is calculated on the basis of the quantities actually produced of the main product and the by-product during the year. The total amount of greenhouse gas emissions attributed to the main product is the smallest.
5. Carrying out the allocation of GHG emissions for one stage of the biofuel life cycle—transesterification does not significantly affect the total value of greenhouse gases produced, because this cycle not only consists of the production process, but also the cultivation and storage of raw materials, transport of raw materials to the plant, and transport final products to recipients.

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Abbreviations

GHG	greenhouse gases
FAME	higher fatty acid methyl esters
RME	rapeseed oil methyl esters
WKT	free fatty acids
ppm	parts per million
$\eta_{m,e}$	methanol concentration
η_k	catalyst concentration
η_e	transesterification efficiency
η_{des}	alcohol recovery efficiency
Q_{ol}	rapeseed oil flow rate
$Q_{m,t}$	amount of methanol needed for transesterification
Q_m	the amount of methanol fed to the reactor, with its double excess
Q_k	required amount of catalyst
$Q_{m,teor}$	the amount of methanol theoretically possible to recover
$Q_{m,rz}$	actual amount of recovered methanol
$Q_{m,cz}$	the amount of pure methanol to be fed to the reactor, taking into account its recirculation
$Q_{m,poz}$	the amount of methanol remaining in the stream of transesterification products after distillation
Q_{ME}	amount of methyl esters
$Q_{ol,poz}$	quantity of unreacted rapeseed oil
$Q_{glycerol}$	amount of glycerol
Q_{prod}	the amount of esters, glycerin, unreacted oil and catalyst going to the separation of methyl esters and glycerin fraction
Q_w	the amount of water needed to rinse the methyl esters
η_w	the amount of rinsing water methyl esters
$Q_{w,e}$	the amount of water discharged with the ester fraction
$\eta_{w,e}$	water share in the ester fraction
$Q_{m,e}$	amount of methanol discharged with the ester fraction
$\eta_{m,e}$	share of methanol in the ester fraction
$Q_{k,e}$	amount of catalyst discharged with the ester fraction
$\eta_{k,e}$	catalyst share in the ester fraction
$Q_{ol,e}$	the amount of unreacted oil discharged with the ester fraction
$\eta_{ol,e}$	share of unreacted oil in the ester fraction
$Q_{w,g}$	the amount of water discharged with the glycerin fraction
$\eta_{w,g}$	water share in the glycerin fraction
$Q_{m,g}$	amount of methanol discharged with the glycerin fraction
$\eta_{m,g}$	share of methanol in the glycerin fraction
$Q_{k,g}$	the amount of catalyst discharged with the glycerin fraction
$\eta_{k,g}$	catalyst share in the glycerin fraction
$Q_{ol,g}$	the amount of unreacted oil discharged with the glycerin fraction
$\eta_{ol,g}$	share of unreacted oil in the glycerin fraction
Q_{fe}	charge of the ester fraction discharged from the separator
Q_{fg}	charge of glycerin fraction discharged from the separator
$Q_{us w,e}$	the amount of water removed from the methyl esters
$\eta_{us w,e}$	degree of water removal from esters methyl
$Q_{us m,e}$	removed amount of methanol from methyl esters
$\eta_{us m,e}$	the degree of methanol removal from methyl esters
$Q_{us ol,e}$	the amount of unreacted oil removed from methyl esters
$\eta_{us ol,e}$	the degree of removal of unreacted oil from methyl esters
$Q_{ME,ocz}$	amount of purified methyl esters
$Q_{kwas,100}$	the amount of pure phosphoric acid to neutralize the catalyst
$Q_{kwas,85}$	85% phosphoric acid to neutralize the catalyst
$Q_{w kwas,85}$	amount of water discharged with 85% phosphoric acid
Q_{osad}	amount of tri-sodium phosphate precipitate
$Q_{w,z}$	the amount of water formed in the catalyst neutralization reaction

$Q_{fg,n}$	the amount of glycerin fraction after catalyst removal
Q_{gs}	the amount of crude glycerin after the catalyst removal step
$Q_{us\ w,gs}$	the amount of water removed from the glycerin fraction
$\eta_{us\ w,gs}$	the degree of water removal from the glycerin fraction
$Q_{us\ m,gs}$	the amount of methanol removed from the glycerin fraction
$\eta_{us\ m,gs}$	the degree of methanol removal from the glycerin fraction
$Q_{g,ocz}$	the amount of purified glycerin

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