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Effect of Fertilization with Meat and Bone Meal on the Production of Biofuel Obtained from Corn Grain

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Abstract: The large volumes of meat and bone meal (MBM) being produced are leading to an increased demand for research into innovative methods of utilizing MBM and obtaining further benefits. The object of this study is to analyze the efficiency of bioethanol and biodiesel production obtained from corn grain fertilized with meat and bone meal produced from animal waste. For the realization of this study, a four-year field experiment was carried out with grain corn fertilized with different doses of meat and bone meal in comparison to fertilization with mineral fertilizers and no fertilization. Fertilization with meat and bone meal should be considered not only for its direct effect but also for the after-effect. The effect of meat and bone meals on obtaining a grain yield higher than that obtained on objects without fertilization and those fertilized with mineral fertilizers was noticeable after applying higher doses from the third year of the study. Fertilization with meat and bone meals did not significantly affect the average fat content of grain, and it only slightly affected the starch content. The positive effect of meat and bone meals on the yield of bioethanol from grain extracted from one hectare was responsible for their yield-forming effect. The differences obtained between years and between fertilizer variants in the yields of ethyl biodiesel and methyl biodiesel per one hectare were mainly related to grain yields, rather than the obtained volume per 1 kg from grain.

Keywords: corn; meat and bone meal; bioethanol; ethyl biodiesel; methyl biodiesel

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1. Introduction

The term animal byproducts means whole, dead animals or their parts, products of animal origin or other products derived from animals, not intended for human consumption [1]. On the territory of the European Union, more than 20 million tons of animal byproducts are generated annually, including about 2 million tons in Poland [2]. Illegal management of animal byproducts can have a negative impact on sanitary and veterinary safety through the possibility of spreading animal diseases (e.g., BSE) or chemical contaminants (e.g., dioxins). Animal byproducts can be hazardous to human and animal health if not disposed of properly. EU regulations [3] regulate their movement, processing and disposal. Animal byproducts are classified on the basis of risk analysis as Category 1 (special risk), Category 2 (high risk) or Category 3 (low risk) materials. The procedure for handling them depends on the product category. Category 1 of animal byproducts can mainly be incinerated, while categories 2 and 3 can be used as soil improvers but also as feed for fur-bearing animals or to feed pets, or to make pet food, or for composting and conversion to biogas. The secondary use of nutrients from the processing of organic wastes for growing crops is important from an energy, economic [4] and environmental [5] aspect, as it allows the replacement of mineral fertilizer components in crop production without burdening the environment. Animal wastes from the meat processing industry represent a large reservoir of material [6–11] that can be recovered using various technologies. The simplest technology for disposing of these wastes is incineration in furnaces [12,13]. However, some of the minerals are irretrievably lost. Another method is to process the waste by physical and chemical treatment into meat and bone meal [6]. Meat and bone meal (MBM), due to its very high nitrogen and phosphorus content, can be used as an organic fertilizer. Meat and bone meal (MBM) is considered an excellent potential organic fertilizer due to its balanced nutrient availability [14–16]. MBMs are rich in organic matter (50–80%,); total nitrogen (8%); phosphorus (5%); calcium (10%); and much less in potassium (<0.01%); magnesium (<0.001%); and valuable micronutrients, such as copper, iron, manganese and zinc. The nutrients in meat and bone meal are in biological form. Mineralization occurs gradually, so the effect of these fertilizers is long lasting, making them beneficial for plants with a long growing season, such as corn [14,17]. The production and use of biofuels has grown tremendously over the past few years. Two products, bioethanol and biodiesel, are mainly produced. While biodiesel is obtained from oilseeds through extraction and esterification, bioethanol can be produced from any material containing carbohydrates or cellulose through fermentation [18,19]. Bioethanol is the most widely used biofuel in the world [20]. The production of bioethanol from biomass is a way to reduce oil consumption and environmental pollution [21,22].

The main raw materials for bioethanol production in Europe are cereals, corn and wheat [23]. High starch content has made cereals a viable feedstock for ethanol production [24,25]. An important issue regarding bioethanol production is whether the process is economically and socially viable [26,27]. However, the extraction of bioethanol from grain crops is less common due to environmental [27] and social aspects [28]. Biodiesel is derived from vegetable oils and animal fats [29] and is an important tool in the fight against the use of non-renewable energy sources and environmental pollution [28]. Bioethanol production technology makes it possible to obtain crude corn post-fermentation oil, which is a by-product. To date, crude post-fermentation oil is not used for food purposes, but only as a feedstock for biodiesel production and as a feed additive [30]. There is also the possibility of using the glycerin produced after biodiesel production as a feed substitute in other areas of agro-food production [31]. The utilization of MBM, which is a waste from the agri-food industry in fertilizing corn, will allow, on the one hand, getting rid of the potential waste. At the same time, allocating MBM for biofuels gives profit in the form of energy, and there is no fear of potential contamination caused by toxic decomposition products of meat and bone meal [32].

A number of works have investigated the use of MBM waste as a source of nutrients for fertilizing crops [6–11] and the possibility of burning it in furnaces [12,13]. There is a lack of research on evaluating the possibility of post-tenant use of MBM in the production of crops from which plant biofuels can be extracted. Such research will allow the creation of an alternative use for a byproduct such as MBM.

The purpose of this study is to analyze the efficiency of bioethanol and biodiesel production obtained from corn grain fertilized with meat and bone meal produced from animal waste.

2. Materials and Methods

2.1. Field Experiment

Research on the applicability of MBM in continuous corn cultivation was conducted at the Didactic and Experimental Station in Tomaszkowo (53°71′ N, 20° 43′ E), Poland. The study was conducted in 2014–2017 using a strict static field trial established in a randomized block design, in 4 replicates. Meat and bone meal and mineral fertilizers were applied annually under corn grown in experimental plots of 15.0 m^2. During harvesting, the outside area was omitted and the area to be harvested was 11.25 m^2. Agronomic treatments were in accordance with the recommendations for growing corn (Table 1).

Table 1. Description of agrotechnology and the most important development phases of maize.

Agrotechnical Treatment	Specification
Pre-cropping and preparation for sowing corn (2013)	Harvest of pre-crop winter triticale 15.08.2013, tillage: plowing (10 cm), harrowing with a tine harrow (5 cm), pre-winter plowing (25 cm).
Tillage (2014–2017)	Pre-sowing spring tillage (April): cultivation covering mineral fertilizers and MBM (10 cm), harrowing (5 cm). Post-harvest tillage (October): disking (15 cm), harrowing (5 cm), pre-winter plowing (25 cm).
Cultivar description	Cultivar MAS 15P, FAO 200, (early), breeder—Maisadour Semences, two-line hybrid variety, grain type, grain yield 102% of the standard.
Sowing description	Sowing plot size: 3 m × 5 m = 15 m^{-2} (4 rows every 0.75 m), density: 8 plants × m^{-2}.
Fertilization	On mineral fertilized sites (Mineral fertilization:) Nitrogen: 133 kg N ha^{-1} (before sowing, as urea, 46% N), Phosphorus: 79.6 kg N ha^{-1} (triple superphosphate, 20.1% P), Potassium: 83.1 N ha^{-1} (potassium salt, 49.8% K). MBM: applied pre-sowing, doses as shown in Table 2. Supplemented with pre-sowing mineral K fertilization in the form of potassium salt, 49.8% K (doses as in Table 2).
Protection against weeds (monocotyledonous and dicotyledonous)	Spraying Lumax 537.5 SE 4.0 L ha^{-1} (mesotrione 37.5 g L^{-1}, s-metolachlor 312.5 g L^{-1}, terbuthylazine 187.5 g L^{-1}).
Protection against diseases	Mesurol 537.5 SE seed treatment at 1 L per 100 kg of grain (537.5 SE (methiocarb 500 g L^{-1}).
Protection against pests	Not applied
Harvesting	Harvest plot size: 2.25 m × 5 m = 11.25 m^2 (3 rows every 0.75 m)
The most important agrotechnical dates and physiological phases	Sowing date (BBCH * 00 Dry seed) 25.04.2014, 04.05.2015, 04.05.2016, 09.05.2017. Germination (BBCH 09): 16.05.2014, 04.05.2015, 20.05.2016, 31.05.2017. Inflorescence emergence, heading, (BBCH 55–59) 07.07.2014, 10.07.2015, 15.07.2016, 20.07.2017. Flowering, anthesis, female: tip of ear emerging from leaf sheath (BBCH 61): 16.07.2014, 22.07.2015, 20.07.2016, 28.07.2017. Ripening, early dough (BBCH 83): 04.08.2014, 11.08.2015, 15.08.2016, 31.08.2017. Harvest date: 01.10.2014, 05.10.2015, 03.10.2016, 04.10.2017.

* BBCH—Biologische Bundesanstalt, Bundessortenamt and Chemical industry.

Table 2. Design of the field experiment. The amount of macronutrients introduced to soil with fertilizers (mean of 2014–2017, kg ha^{-1}).

Treatments	$C_{org.}$	N	P	K	
				MBM *	K_{min} **
Without fertilization	0.0	-	-	-	-
Mineral fertilization	0.0	133.0	79.6	-	83.1
Meat and Bone Meal (MBM) 1.0 tha^{-1}	666.9	61.0	31.1	4.0	79.1
Meat and Bone Meal (MBM) 2.0 t ha^{-1}	1333.8	122.0	62.2	8.0	75.1
Meat and Bone Meal (MBM) 3.0 t ha^{-1}	2000.7	183.0	93.3	12.0	71.1

* MBM = meat and bone meal, ** $K_{min.}$ = mineral K.

The soil on which the experiment was conducted was described as Haplic Luvi-sol Loamic soil [14]. It was characterized by the following fraction contents: sand fraction—60%; fine silt—15%; fine clay—9%; coarse clay—6%; colloidal clay—6%; coarse silt—4%; and skeletal part—4%. The organic matter content of the soil was 10.1 g kg^{-1}; N_{total}—0.55 l g kg^{-1}; P—0.33 g kg^{-1}; K −1.33 g kg^{-1}. The tested soil was acidic (pH in KCl—4.89). Organic carbon content was determined by determining the excess of dichromate by spectrophotometry at 546 nm. Total nitrogen content was determined by digesting the sample in sulfuric acid (VI) with copper, followed by distillation of the sample with 40% sodium base and boric acid as a binding reagent. The tested values were obtained by titration of the distilled ammonia with 0.1 M hydrochloric acid. The ammonium part of nitrogen was determined spectrophotometrically at 440 nm using Nessler's reagent. The nitrate (V) content was determined calorimetrically with phenylsulfophenoic acid at 410 nm. Spectrophotometric determinations were made on an Ultraspec 2 spectrophotometer (LKB, Biochrom, Markham, ON, Canada). The amount of potassium and available phosphorus was determined using the Egner Rhiem method by acidifying the sodium lactate extract to pH 3.6 with hydrochloric acid. The pH was determined using pH-meter HI 991,000 (Hanna, Germany) in 1 M KCl solution.

2.2. Weather Conditions

Average air temperatures during the corn growing season (April–September), differed slightly between years. Temperature in the latter two years of the experiment are similar in relation to the 1981–2010 average temperature (Figure 1). The higher temperature in April–September 2014 resulted in faster warming of the soil before sowing. Compared to other years of the study and the multi-year period, a slightly warmer May and June in 2016 resulted in better thermal conditions for corn development and optimal conditions for the decomposition of organic matter in the soil. A 2–3 °C warmer July of 2014 and August of 2015 than in other years and multi-year periods favored photosynthesis of corn plants. Temperatures in September were similar in the evaluated years and the multi-year period. In the years of the study, the average amount of precipitation during the growing season, as well as its distribution in individual months, differed from the 1981–2010 growing season. A large amount of precipitation occurred in 2017, and this was the result of the occurrence of 2–3 times more precipitation in July and September than in the 1981–2010 comparable period. This may have influenced faster mineralization of organic matter and increased the availability of nutrients. In 2014 and 2015, the amount of precipitation was 30% lower than in the comparable decade. There was especially little precipitation in these years during the months of intensive growth. The shortage of water during the period of corn growth and development may have had a lasting effect on the formation of grain quality and grain yield.

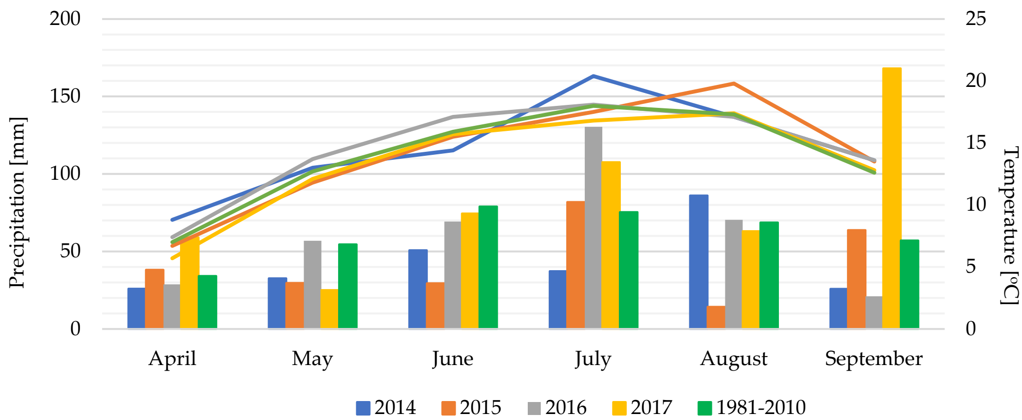

Figure 1. Meteorological conditions during 2014–2017 period. Meteorological data against the years 1981–2010 (Data obtained from the Meteorological Station at Tomaszkowo (53°71′ N, 20°30′ E), Poland.

2.3. Design of Experiment

The meat and bone meal came from a utilization plant of byproducts from the production food of animal origin SARIA Poland Ltd. (Branch Sarval Plant, Długi Borek, NE Poland). The chemical composition of MBM dry matter, which accounted for 90%, was as follows: 66.9 g kg^{-1} C; 6.10 g kg^{-1} N; 3.10 g kg^{-1} P; 0.40 g kg^{-1} K; 8.85 g kg^{-1} Ca; 0.30 g kg^{-1} Mg; 8.0 mg g^{-1} Cu, 1189 mg g^{-1} Fe; 86.5 mg g^{-1} Zn; and 29.0 mg g^{-1} Mn. In the pre-sowing experiment, MBM was applied at doses of: 1.0, 2.0 and 3.0 t ha^{-1}. The scheme of the experiment and the content of nutrients contributed with MBM doses are shown in Table 2. Field sites without fertilization and with mineral fertilizers (NPK) were established in the experiment as control sites. In order to compensate for the 83.1 kg ha^{-1} of potassium applied to the objects fertilized with mineral fertilizers, potassium fertilization (denoted "$K_{min.}$" in Table 2) was applied along with MBM.

2.4. Bioethanol Synthesis Process

The corn grain was ground and weighed. The resulting flour was dried at 105 °C to a constant weight. The ground and dried samples were hydrolyzed using a two-step process carried out in the presence of α–amylase (Pol–aura, 92%) and glucoamylase (Pol–aura, 95%). The resulting hydrolysates were fermented in the presence of Saccharomyces cerevisiae yeast (Safale s-04, Fermentis, Lille, France). During hydrolysis and fermentation, the amount of reducing sugars was measured by spectrophotometric method at 570 nm wavelength using 3.5-dinitrosalicylic acid as a dye (Ultraspec 2, LKB, Biochrom, Markham, ON, Canada). Alcohol content was measured by density method and converted to the amount of 96% alcohol solution obtained from one kilogram of dry matter. An immersion method was used to measure density. Measurements were made on an AS110/C2 analytical balance with Kit 128 (Radwag, Radom, Poland).

2.5. Biodiesel Synthesis Process

Corn oil was obtained by extraction from the crushed feedstock with hexane. The obtained oil samples were used for transesterification with ethanol and methanol. The reaction was carried out with heating the oil to 60 °C and in the presence of KOH as a catalyst. The conversion rate of the oil to biodiesel was 99 ± 0.1 percent. Distillation of methanol and ethanol was carried out and glycerol was separated by liquid–liquid extraction. The quantities of biodiesel obtained were measured, and their density and viscosity were measured in accordance with ISO 3104 [33] and ISO 12185 [34]. Each test was carried out three times for each sample. The results of the biodiesel density tests ranged from 860 to 880 kg m^{-3}, and the viscosity ranged from 4.62 to 4.70 mm^2 s^{-1}. The obtained values are within the performance parameters for biofuels according to EN 14214 [35]. Density was measured using a density measurement kit on a Radwag AS110/C2 analytical balance (Radwag, Radom, Poland). Viscosity was measured with a thermostable (25 °C) Ubbelohd viscometer with a constant k = 0.01 mm^2 s^{-2}.

2.6. Yield of Grain and Determination of Starch and Fat Content

When harvesting corn cobs by hand, the two outer rows of sown plants were discarded. The collected grain was used to determine the yield from one hectare and for further analyses. Corn grain yield was measured using a WTC 2000 scale (Radwag, Radom, Poland). After harvest, grain moisture was measured using a GMS v2 moisture meter (Dramiński, Gietrzwałd, Poland), and the yields were converted to a uniform moisture content of 15%. The fat and starch contents of the 1.0 kg grain samples were determined using an NIR System Infratec 1241 Analyzer (Foss, Hillerod, Denmark).

2.7. Statistical Analysis

The results obtained from the experiment were subjected to statistical analysis using Statistica v.13.1 program. The first stage of statistical analysis of the data consisted of determining the characteristics of the studied variables with the indication of the arithmetic mean, extreme values (minimum, maximum), standard deviation and variance, as well as the values of skewness and kurtosis. Statistical inference consisted of comparing the studied variables to detect statistically significant differences (Pearson's correlation) thanks to which the strength and direction of the relationship between the analyzed fertilizer objects and yield were identified. In assessing the significance of the effects, a significance level of 0.05 was adopted. The next stage of statistical analysis consisted of demonstrating significant differences in fertilizer variants using one-way analysis of variance (ANOVA). The significance of differences in fertilizer variants was determined using one-way analysis of variance (ANOVA). Homogeneous groups were determined using the Tukey test. Calculations were performed at a significance level of $\alpha = 0.05$. Pearson's correlation coefficient (r) was calculated, and a linear regression equation was determined. The correlations between the two characteristics are shown in scatter plots.

3. Results

3.1. Preliminary Statistical Analysis of the Data

The determined measures of dispersion indicate that the highest variability and dispersion are calculated for the amounts of bioethanol, methyl biodiesel and ethyl biodiesel obtained from grain extracted from one hectare (Table 3). The values of the obtained grain yield are also characterized by high variability.

Table 3. Values of statistical parameters for analyzed variables.

Variable	Mean	Minimum	Maximum	Variance	Standard Deviation	Skewness	Kurtosis
Yield of grain [t ha^{-1}]	3.85	1.67	8.12	1.80	1.36	1.06	1.26
Content of fat [%]	4.71	4.00	5.30	0.11	0.35	−0.39	−0.88
Content of starch [%]	70.15	67.8	72.2	1.22	1.12	0.06	−0.70
Bioethanol [L kg^{-1} grain]	0.49	0.41	0.53	0.07	0.02	−0.90	1.78
Bioethanol [L kg^{-1} grain ha^{-1}]	1881.17	833.86	4240.88	511,043.8	714.87	1.27	1.75
Ethyl biodiesel [L kg^{-1} grain	0.08	0.06	0.1	0.02	0.01	0.12	−0.36
Ethyl biodiesel [L kg^{-1} grain ha^{-1}]	291.99	127.79	621.51	12,040.83	109.73	1.06	1.2
Methyl biodiesel [L kg^{-1} grain]	0.07	0.04	0.1	0.05	0.01	−0.04	−0.87
Methyl biodiesel [L kg^{-1} grain ha^{-1}]	266.97	110.17	630.33	13,073.17	114.34	1.43	2.07

The kurtosis and skewness values for the variables indicate that the variables have a distribution that deviates from the normal distribution. A distribution close to the normal distribution was found for the starch content of grain (skewness = 0.058) and the obtained methyl biodiesel from 1 kg of grain (skewness = –0.042). Among the analyzed variables, right-skewed distributions were observed for the variables: yield of grain, content of fat, ethyl biodiesel obtained from 1 kg of grain and bioethanol, ethyl and methyl biodiesel obtained from grain obtained from plots per one hectare. The distribution of the variables: content of starch, bioethanol and methyl biodiesel obtained from 1 kg of grain is left-skewed.

The values of kurtosis for yield of grain, bioethanol, ethyl and methyl biodiesel obtained from plots per 1 hectare and bioethanol obtained from 1 kg of grain indicate a significant concentration of results around the mean (kurtosis takes a value above 0). The values of the other test results are more likely to show extreme values (further from the average).

Correlation analysis between variables showed that no significant correlation was observed between nutrient content (fat and starch) and the amount of biofuel obtained, both in terms of grain weight and yield (Table 4). In the case of bioethanol, a reciprocal correlation ($p < 0.001$; $p < 0.01$; $p < 0.05$) was observed between the quantities obtained from grain weight as from one hectare of field. In addition, both quantities show a high positive correlation (r = 0.99) with respect to grain yield. The quantities of both fatty acid esters show a weaker correlation between the quantities obtained from the weight of 1 kg of grain and from grain yield per hectare (ethyl biodiesel, r = 0.29, methyl biodiesel, r = 0.48). Only the amounts of esters obtained from grain yield per one hectare show a relationship with yield (ethyl biodiesel, r = 0.96, methyl biodiesel, r = 0.88).

Table 4. Correlation analysis of results for bioethanol.

Variable	Yield of Grain [t ha^{-1}]	Content of Fat [%]	Ethyl Biodiesel [L kg^{-1} grain]	Ethyl Biodiesel [L kg^{-1} Grain ha^{-1}]	Methyl Biodiesel [L kg^{-1} Grain]	Methyl Biodiesel [L kg^{-1} Grain ha^{-1}]
Yield of grain [t ha^{-1}]	1	−0.0052	0.0408	0.9633	0.0309	0.8825
Content of fat [%]	−0.0052	1	−0.1494	−0.0484	−0.0369	−0.0135
Ethyl biodiesel [L kg^{-1} grain	0.0408	−0.1494	1	0.2934		
Ethyl biodiesel [L kg^{-1} grain ha^{-1}]	0.9633	−0.0484	0.2934	1	–	–
Methyl biodiesel [L kg^{-1} grain]	0.0309	−0.0369	–	–	1	0.4780
Methyl biodiesel [L kg^{-1} grain ha^{-1}]	0.8825	−0.0135	–	–	0.4780	1
Variable	**Yield of Grain [t ha^{-1}]**	**Content of Starch [%]**	**Bioethanol [L kg^{-1} Grain]**		**Bioethanol [L kg^{-1} Grain ha^{-1}]**	
Yield of grain [t ha^{-1}]	1	−0.1694	0.3634		0.9929	
Content of starch [%]	−0.1694	1	0.1178		−0.1489	
Bioethanol [L kg^{-1} grain]	0.3634	0.1178	1		0.4668	
Bioethanol [L kg^{-1} grain ha^{-1}]	0.9929	−0.1489	0.4668		1	

3.2. Grain Yield

On average, the highest grain yield was obtained in the fourth year of the study (2017) (Figure 2). This was the result of the occurrence of optimal weather conditions for plant vegetation and the subsequent effect of meat and bone meal applied at higher rates (2.0 and 3.0 t ha^{-1}). In the second year of the study (2015), on average, the lowest grain yields were obtained (3.22 t ha^{-1}). The reason for this was the occurrence of unfavorable amounts and distribution of precipitation for corn vegetation and for the release of nutrients from meat and bone meal.

(**a**) (**b**)

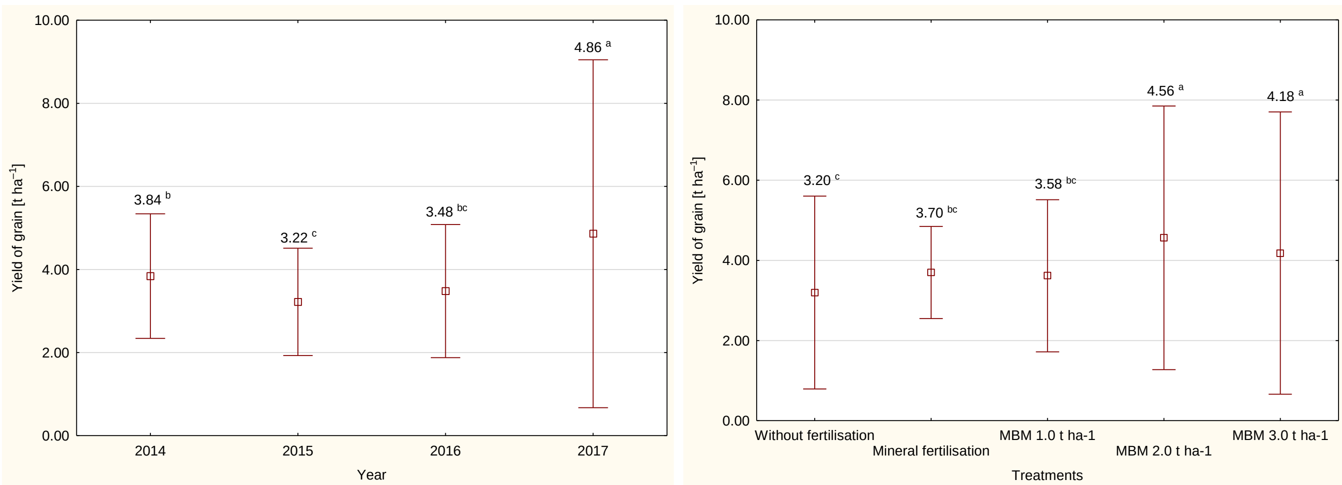

Figure 2. The corn grain yield (mean value and standard deviation), (**a**) average for the years, (**b**) average for the treatment. MBM—Meat and Bone Meal. [a,b,c]—Values followed by the same letters do not differ significantly in Tukey's (HSD) test ($p < 0.05$).

Regardless of the years of the study, the highest grain yields were obtained after the application of MBM at 2.0, and 3.0 t ha^{-1}, and lower and comparable between each other on objects without fertilization, fertilized with mineral fertilizers and MBM at a rate of 1.0 t ha^{-1}.

Grain yield from objects without fertilization was highest in the first year of harvesting and decreased as the experiment progressed (Table 5). Grain yield from mineral fertilized fields showed complete stagnation during the years of the study. Fertilization with MBM at 1.0 t ha^{-1} resulted in lower yields in the 2nd and 3rd years of the experiment, and a 17% increase in the 4th year compared to the 1st year of the study. After an initial decrease in yield (after the application of 2.0 t ha^{-1}) or a noted lack of response (3.0 t ha^{-1}) compared to the first year of the study, the positive effects of the direct and subsequent effects of the applied MBM at 2.0 t ha^{-1} and 3.0 t ha^{-1} were found in the 3rd and 4th year. The largest increases in grain yields compared to 2014 were found in 2017. After application: 2.0 t ha^{-1} increase of 86%, and 3.0 t ha^{-1} increase of 151%.

Table 5. The corn grain yield, interaction between the years and treatments (mean value and standard deviation), t ha^{-1}.

Year	Without Fertilization	Mineral Fertilization	MBM * 1.0 t ha^{-1}	MBM 2.0 t ha^{-1}	MBM 3.0 t ha^{-1}
2014	4.60 ± 0.41 ^{b}	4.06 ± 0.46 $^{b–e}$	3.98 ± 0.23 $^{b–e}$	3.82 ± 0.46 $^{b–e}$	2.74 ± 0.67 $^{e–g}$
2015	3.96 ± 0.43 $^{b–e}$	3.41 ± 0.83 ^{b}	2.80 ± 0.44 $^{e–g}$	3.03 ± 0.25 $^{c–g}$	2.91 ± 0.58 $^{d–g}$
2016	2.42 ± 0.32 ^{fg}	3.45 ± 0.27 $^{b–g}$	3.04 ± 0.68 $^{c–g}$	4.28 ± 0.071 ^{bc}	4.21 ± 0.31 $^{b–d}$
2017	1.81 ± 0.11 ^{g}	3.87 ± 0.53 $^{b–e}$	4.64 ± 0.95 ^{b}	7.12 ± 0.78 ^{a}	6.87 ± 0.29 ^{a}

* MBM—Meat and Bone Meal. ^{a,b,c,d,e,f,g}—Values followed by the same letters do not differ significantly in Tukey's (HSD) test ($p < 0.05$).

3.3. Fat and Starch Content

Fat content was found to be lowest in 2016 and higher and similar between the other years of the study (Figure 3). Grain fat content obtained from fertilizer facilities did not differ significantly from each other, ranging from 4.64% to 4.76%. The interaction of study years and fertilizer variants showed a certain tendency for the fat content to decrease as a result of fertilizer application (mineral and 2.0 and 3.0 t ha^{-1} MBM) by the 3rd year of application (2016) (Table 6). Indeed, the highest fat content (5.23%) was shown in 2017 in grain obtained from unfertilized plots.

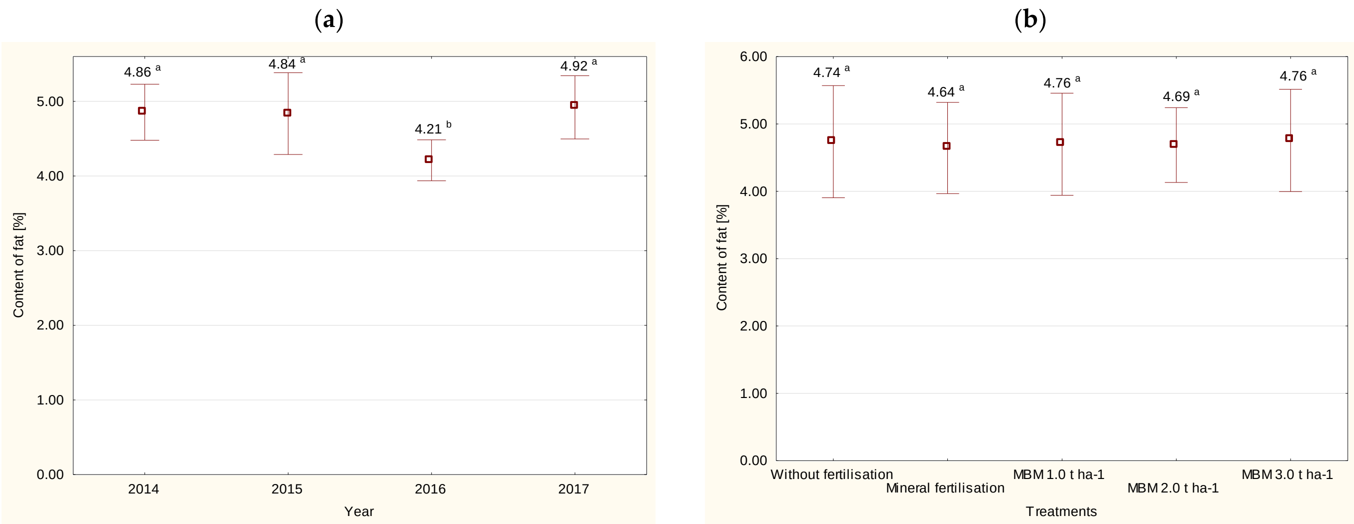

Figure 3. Fat content in corn grains (mean value and standard deviation), (**a**) average for the years, (**b**) average for the treatment. MBM—Meat and Bone Meal. ^{a,b}—Values followed by the same letters do not differ significantly in Tukey's (HSD) test ($p < 0.05$).

Table 6. The fat content in corn grains (mean value and standard deviation), interaction between the years and treatments %.

Year	Without Fertilization	Mineral Fertilization	MBM * 1.0 t ha^{-1}	MBM 2.0 t ha^{-1}	MBM 3.0 t ha^{-1}
2014	4.75 ± 0.19 ^{bc}	4.95 ± 0.13 ^{ab}	4.65 ± 0.06 $^{b–d}$	4.88 ± 0.13 ^{ab}	5.05 ± 0.13 ^{ab}
2015	4.83 ± 0.15 ^{ab}	4.73 ± 0.24 ^{bc}	5.05 ± 0.19 ^{ab}	4.70 ± 0.33 ^{bc}	4.88 ± 0.39 ^{ab}
2016	4.15 ± 0.13 ^{e}	4.15 ± 0.13 ^{e}	4.18 ± 0.10 ^{e}	4.35 ± 0.13 $^{c–e}$	4.23 ± 0.15 ^{de}
2017	5.23 ± 0.05 ^{a}	4.75 ± 0.10 ^{bc}	4.93 ± 0.26 ^{ab}	4.83 ± 0.15 ^{ab}	4.88 ± 0.05 ^{ab}

* MBM—Meat and Bone Meal. ^{a,b,c,d,e}—Values followed by the same letters do not differ significantly in Tukey's (HSD) test ($p < 0.05$).

Unlike in the case of fat, 2016 showed a slightly higher starch value than in the other years of the study (Figure 4), which was confirmed by all fertilizer variants (Table 7). On average, the applied fertilizer variants only slightly differentiated the starch content. Grain harvested from fields fertilized with the highest (3.0 t ha^{-1}) dose of MBM had the lowest starch content at 69.5%. Grain harvested from the other fertilizer facilities had similar carbohydrate contents between them, with average values ranging from 70.0% to 70.5%.

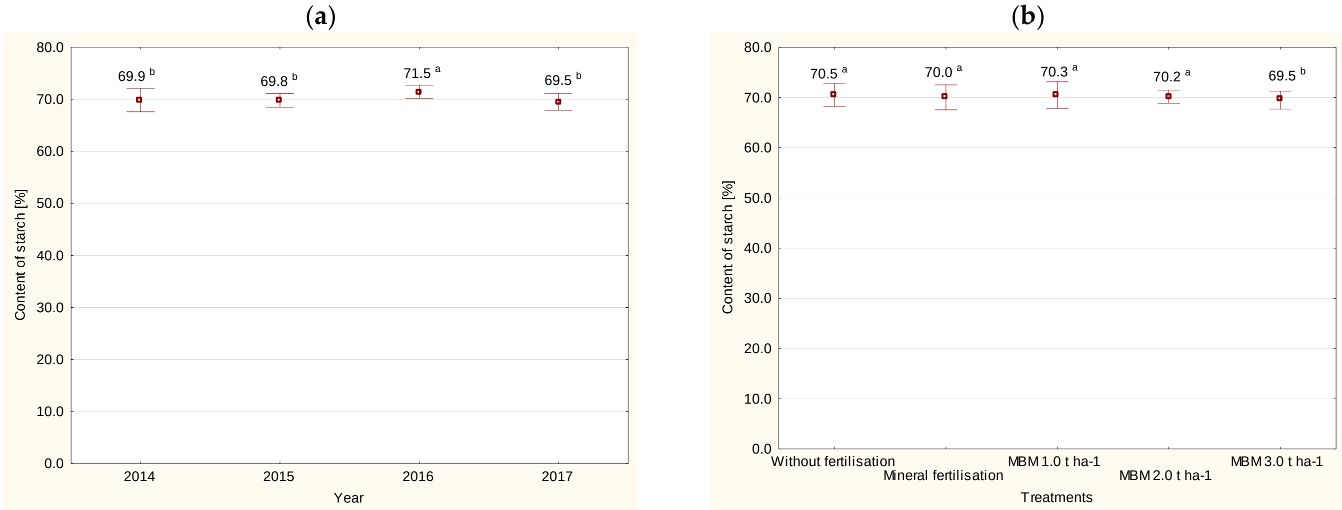

Figure 4. Starch content in corn grains (mean value and standard deviation), (**a**) average for the years, (**b**) average for the treatment. MBM—Meat and Bone Meal. ^{a,b}—Values followed by the same letters do not differ significantly in Tukey's (HSD) test ($p < 0.05$).

Table 7. Starch content in corn grains (mean value and standard deviation), interaction between the years and treatments, %.

Year	Without Fertilization	Mineral Fertilization	MBM * 1.0 t ha^{-1}	MBM 2.0 t ha^{-1}	MBM 3.0 t ha^{-1}
2014	70.7 ± 0.88 $^{a–c}$	68.7 ± 0.62 ^{d}	71.0 ± 0.060 $^{a–c}$	70.2 ± 0.64 $^{b–d}$	68.8 ± 0.40 ^{d}
2015	69.9 ± 0.81 $^{b–d}$	70.1 ± 0.39 $^{b–d}$	70.0 ± 0.62 $^{b–d}$	69.9 ± 0.44 ^{cd}	69.0 ± 0.62 ^{d}
2016	72.1 ± 0.13 ^{a}	71.5 ± 0.34 ^{ab}	72.1 ± 0.13 ^{a}	70.8 ± 0.22 $^{a–c}$	70.8 ± 0.54 $^{a–c}$
2017	69.5 ± 0.47 ^{cd}	69.9 ± 1.28 ^{cd}	69.0 ± 0.97 ^{d}	69.9 ± 0.81 ^{cd}	69.4 ± 0.19 ^{cd}

* MBM—Meat and Bone Meal. ^{a,b,c,d}—Values followed by the same letters do not differ significantly in Tukey's (HSD) test ($p < 0.05$).

3.4. Yield of Bioethanol and Biodiesel

The differences obtained between years in bioethanol yield per 1 hectare (Figures 5 and 6, Table 8) were related to grain yield, not the amount of bioethanol per 1 kg of grain (Figure 7). The highest yield of bioethanol obtained from 1 hectare of grain was found, as in the case of grain yield, in 2017 (2399 L ha^{-1}), and the lowest in 2015 (35% lower). Regardless of the years, the highest bioethanol yields per 1 kg of grain and per 1 hectare were obtained using MBM fertilization at 2.0 and 3.0 t ha^{-1} (Figure 6). Application of MBM at these rates resulted in more than 500 L ha^{-1} more bioethanol compared to the other variants (without fertilization; mineral fertilization, 1.0 t ha^{-1} MBM). The bioethanol yields of the fertilization variants did not change significantly during the study years (Table 8). However, it was found that the highest bioethanol volume per kg of grain and yield per hectare were obtained (as well as grain yield) on sites fertilized with MBM at 2.0 and 3.0 t ha^{-1} in 2017 (3588 L ha^{-1} on average). The lowest volume of bioethanol per 1 kg of grain was found in 2017 as a result of MBM fertilization at 1.0 t ha^{-1} (0.454 L kg^{-1}), and the lowest yield from bioethanol in L per 1 ha^{-1} in the same year, on a facility without fertilization (868 L ha^{-1}).

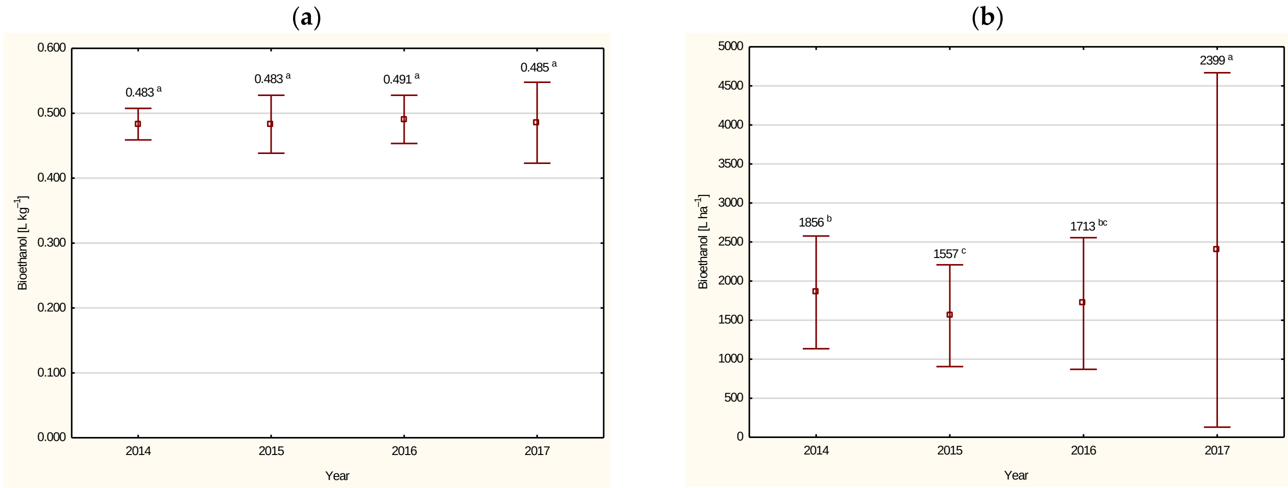

Figure 5. Volume of bioethanol (mean value and standard deviation) obtained from corn grain (**a**), and bioethanol yield from a hectare (**b**), considering year of experiment. MBM–Meat and Bone Meal. [a,b,c]—Values followed by the same letters do not differ significantly in Tukey's (HSD) test ($p < 0.05$).

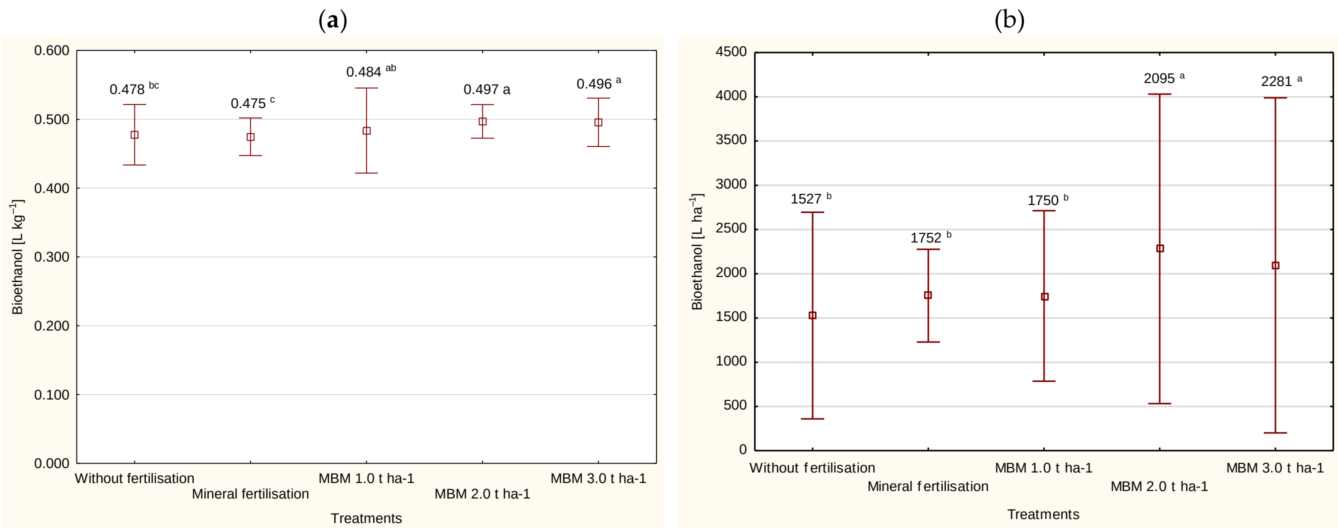

Figure 6. Volume of bioethanol (mean value and standard deviation) obtained from corn grain (**a**), and bioethanol yield from a hectare (**b**), considering fertilization treatment. MBM—Meat and Bone Meal. [a,b,c]—Values followed by the same letters do not differ significantly in Tukey's (HSD) test ($p < 0.05$).

Table 8. Interaction between the years and treatments for volume of bioethanol obtained from corn grain, and yield of bioethanol from a hectare, (mean value and standard deviation).

Year	Without Fertilization	Mineral Fertilization	MBM * 1.0 t ha^{-1}	MBM 2.0 t ha^{-1}	MBM 3.0 t ha^{-1}
		Volume of bioethanol obtained from corn grain, L kg^{-1}			
2014	0.484 ± 0.004 $^{a–c}$	0.468 ± 0.013 ^{bc}	0.492 ± 0.013 $^{a–c}$	0.490 ± 0.008 $^{a–c}$	0.483 ±0.007 $^{a–c}$
2015	0.465 ± 0.039 ^{bc}	0.489 ± 0.006 $^{a–c}$	0.486 ± 0.030 $^{a–c}$	0.487 ± 0.010 $^{a–c}$	0.489 ± 0.386 $^{a–c}$
2016	0.483 ± 0.014 $^{a–c}$	0.472 ± 0.015 $^{a–c}$	0.503 ± 0.013 ^{ab}	0.502 ± 0.006 ^{ab}	0.495 ± 0.024 $^{a–c}$
2017	0.479 ± 0.020 $^{a–c}$	0.469 ± 0.009 $^{a–c}$	0.454 ± 0.042 ^{c}	0.510 ± 0.010 ^{a}	0.516 ± 0.006 ^{a}
		Yield of bioethanol from a hectare, L ha^{-1}			
2014	2226 ± 197 ^{b}	1899 ± 206 $^{b–f}$	1957 ± 96 $^{b–e}$	1873 ± 217 $^{b–f}$	1327 ± 339 $^{e–g}$
2015	1846 ± 308 $^{b–f}$	1675 ± 428 $^{b–f}$	1370 ± 305 $^{d–g}$	1474 ± 110 $^{b–g}$	1420 ± 281 $^{c–g}$
2016	1169 ± 174 ^{fg}	1622 ± 79 $^{b–f}$	1536 ± 378 $^{b–g}$	2148 ± 54 ^{bc}	2089 ± 237 $^{b–d}$
2017	868 ± 43 ^{g}	1814 ± 218 $^{b-f}$	2136 ± 637 ^{bc}	3631 ± 463 ^{a}	3545 ±185 ^{a}

* MBM—Meat and Bone Meal. ^{a,b,c,d,e,f,g}—Values followed by the same letters do not differ significantly in Tukey's (HSD) test ($p < 0.05$).

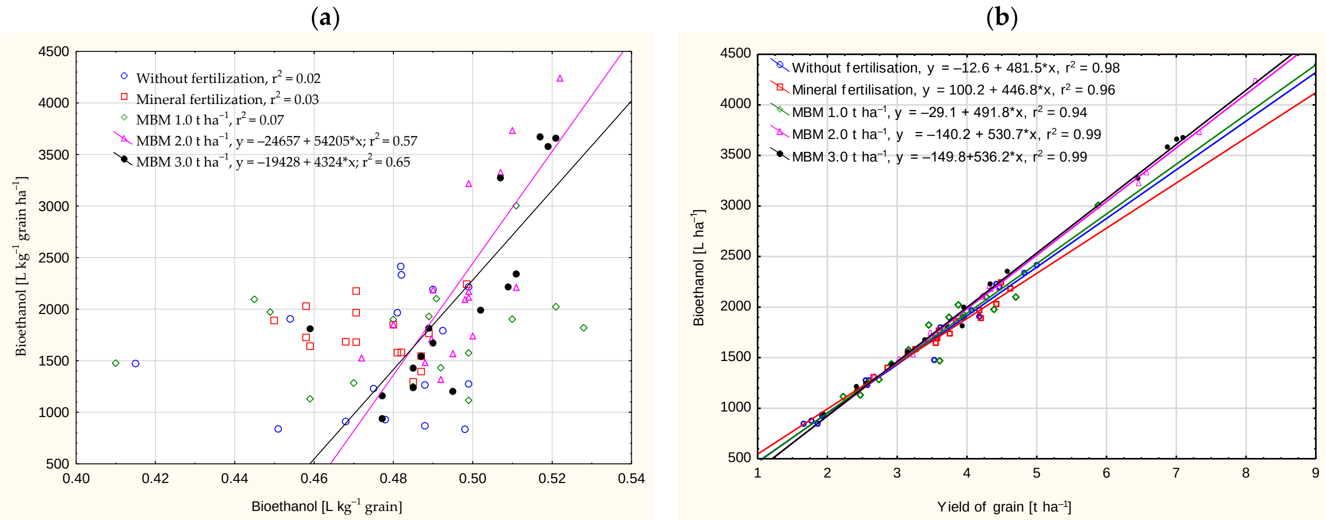

Figure 7. Dependence of bioethanol yield on volume obtained from 1.0 kg^{-1} of grain (**a**) and grain harvest from 1.0 ha^{-1} (**b**) (calculated at significance α = 0.05). MBM—Meat and Bone Meal.

The rectilinear regression indicates that the higher the grain yield per one hectare, the higher the bioethanol yield per one hectare increases (Figure 7). The calculated coefficient of determination (r^2) indicates that, in all fertilizer variants, bioethanol yield per 1 hectare was determined in 94 to 99% by grain yield. In the variant fertilized with MBM at 2.0 and 3.0 t ha^{-1}, the yield of bioethanol per grain harvested from 1 hectare was in 57–65% determined by the yield of bioethanol per 1 kg of grain.

There were no significant differences in the volumes of ethyl biodiesel obtained from 1 kg of grain between the study years (Figure 8). The determinant of the volume of ethyl biodiesel obtained in the study years was the grain yield per one hectare (Figure 9). Thus, similarly, as the most grain was obtained in 2017, such was the amount of ethyl biodiesel obtained (374 L ha^{-1}) (Figure 8).

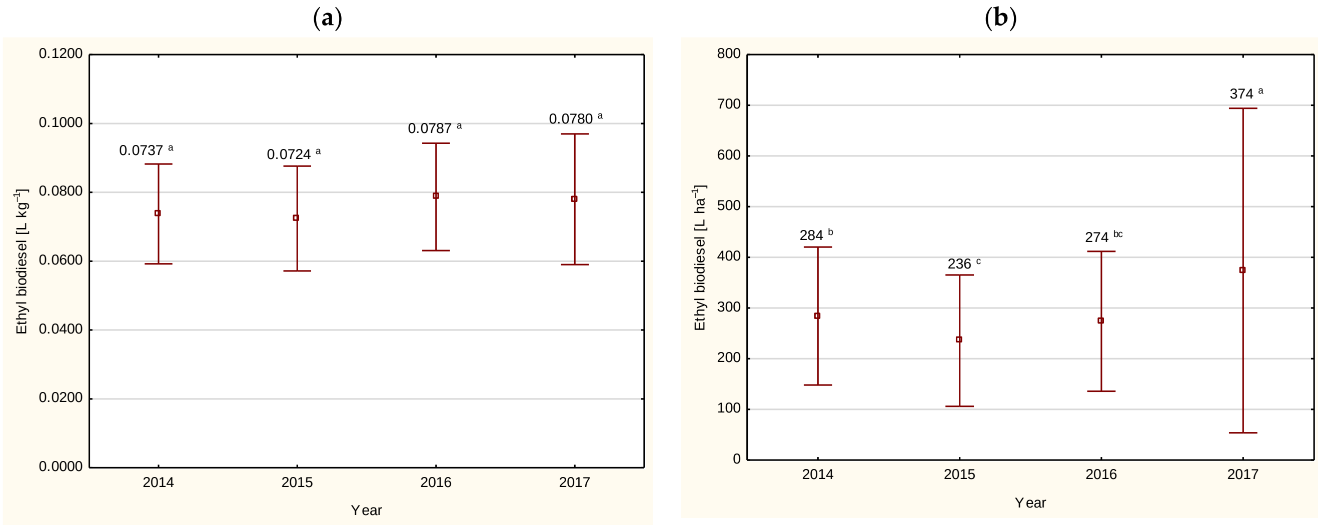

Figure 8. Volume of ethyl biodiesel (mean value and standard deviation), obtained from corn grain (**a**) and ethyl biodiesel yield from a hectare (**b**), considering year of experiment. [a,b,c]—Values followed by the same letters do not differ significantly in Tukey's (HSD) test ($p < 0.05$).

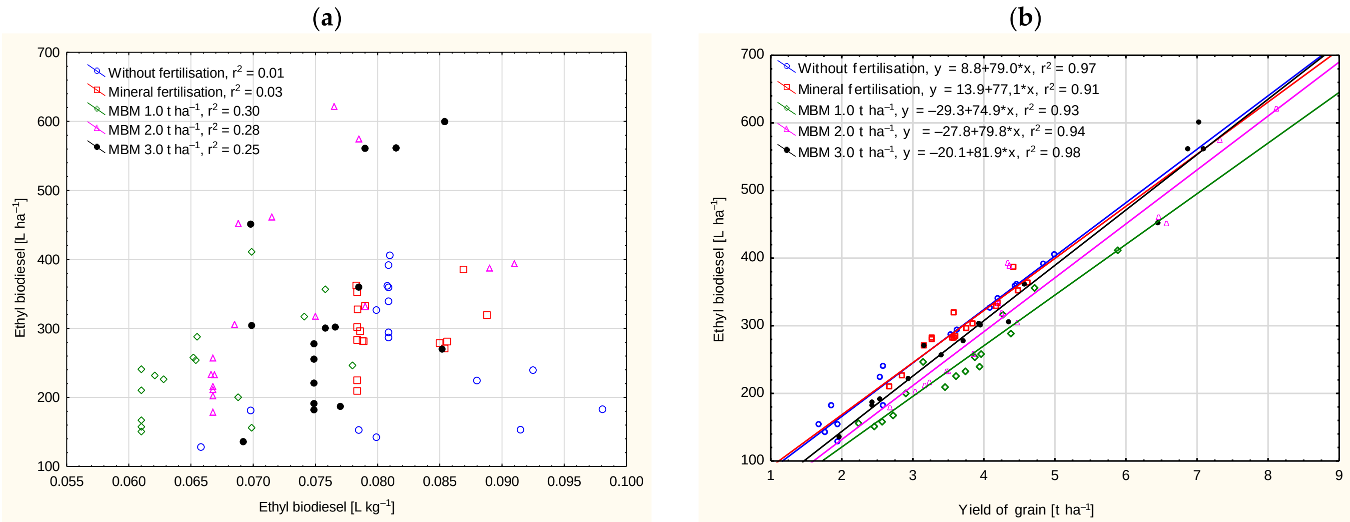

Figure 9. Dependence of ethyl biodiesel yield on volume obtained from 1.0 kg^{-1} of grain (**a**) and grain harvest from 1.0 ha^{-1} (**b**) (calculated at significance $\alpha = 0.05$). MBM—Meat and Bone Meal.

The highest volumes of ethyl biodiesel were found in grain obtained from facilities without fertilization (0.0819 L kg^{-1}) and those fertilized with mineral fertilizers (0.0810 L kg^{-1}) (Figure 10). This did not translate into yields of ethyl biodiesel extracted from grain per hectare of corn crop. The highest amounts of ethyl biodiesel per 1 ha were obtained after applying 2.0 and 3.0 t ha of MBM (336 and 322 L ha^{-1}, respectively), which correlated with the highest yields on these sites.

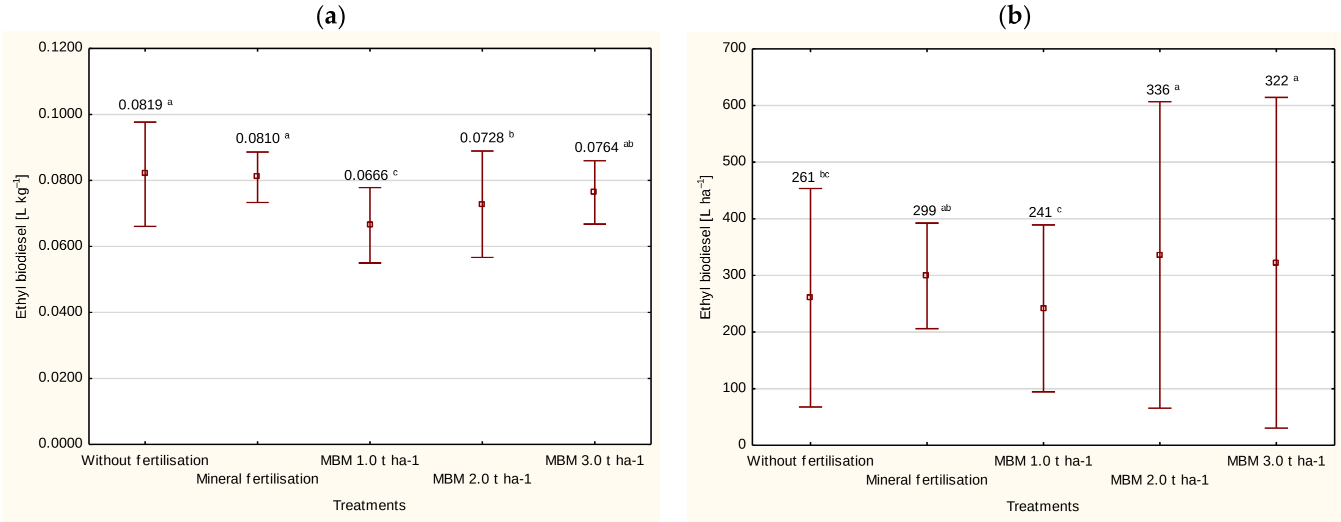

Figure 10. Volume of ethyl biodiesel obtained from corn grain (mean value and standard deviation), (**a**) and bioethanol yield from a hectare, (**b**) considering fertilization treatment. MBM—Meat and Bone Meal. a,b,c—Values followed by the same letters do not differ significantly in Tukey's (HSD) test ($p < 0.05$).

In the first two years of the study (2014 and 2015), higher ethyl biodiesel yields per hectare were found on sites without fertilization and those fertilized with mineral fertilizers (Table 9). In subsequent years, higher yields of ethyl biodiesel per 1 ha were found as a result of direct application of the two highest doses of MBM (2.0 and 3.0 t ha^{-1}) and accumulation of components supplied in previous years.

Table 9. Interaction between the years and treatments for volume of ethyl biodiesel obtained from corn grain, and yield of ethyl biodiesel from a hectare, (mean value and standard deviation).

Year	Without Fertilization	Mineral Fertilization	MBM * 1.0 t ha^{-1}	MBM 2.0 t ha^{-1}	MBM 3.0 t ha^{-1}
Volume of ethyl biodiesel obtained from corn grain, L kg^{-1}					
2014	0.0807 ± 0.001$^{a–c}$	0.0786 ± 0.001 $^{a–d}$	0.0656 ± 0.006 ^{de}	0.0672 ± 0.001 $^{c–e}$	0.0766 ± 0.007 $^{a–d}$
2015	0.0809 ± 0.001 $^{a–c}$	0.0784 ± 0.001 $^{a–d}$	0.0610 ± 0.001 ^{e}	0.0668 ± 0.001 $^{c–e}$	0.0749 ±0.001 $^{a–e}$
2016	0.0822 ± 0.010 ^{ab}	0.0820 ± 0.004 ^{ab}	0.0705 ± 0.005 $^{a–e}$	0.0835 ± 0.006 ^{a}	0.0752 ± 0.004 $^{a–e}$
2017	0.0838 ± 0.014 ^{a}	0.0849 ± 0.003 ^{a}	0.0685 ± 0.006 $^{b–e}$	0.0738 ± 0.004 $^{a–e}$	0.0789 ± 0.007 $^{a–d}$
Yield of ethyl biodiesel from a hectare, L ha^{-1}					
2014	371 ± 35.2 ^{b}	319 ± 35.3 $^{b–d}$	262 ± 38.3 $^{b–f}$	257 ± 34.3 $^{b–f}$	212 ± 62.2 $^{c–f}$
2015	320 ± 35.1 $^{b–d}$	267 ± 64.9 $^{b–f}$	171 ± 26.9 ^{ef}	202 ± 16.5 $^{d–f}$	218 ± 43.3 $^{c–f}$
2016	199 ± 39.7 $^{d–f}$	282 ± 10.5 $^{b–e}$	214 ± 45.4 $^{c–f}$	358 ± 38.4 ^{b}	317 ± 28.7 $^{b–d}$
2017	151 ± 23.2 ^{f}	328 ± 43.1 ^{bc}	320 ± 80.6 $^{b–d}$	527 ± 84.1 ^{a}	543 ± 64.3 ^{a}

* MBM—Meat and Bone Meal. a,b,c,d,e,f—Values followed by the same letters do not differ significantly in Tukey's (HSD) test ($p < 0.05$).

The coefficient of determination (r^2) indicates that ethyl biodiesel yield was influenced in all fertilizer variants by grain yield (r^2 = 91—98%) (Figure 9).

The yields of methyl biodiesel from 1 kg of grain and from harvested plots per hectare were slightly different than the yields of ethyl biodiesel. The lowest yields of methyl biodiesel from 1 kg of grain were obtained in the first year of the study and calculated from harvested grain per hectare in the first three years of the study (Figure 11). In 2017, the yields of methyl biodiesel from 1 kg of grain and in terms of grain yields harvested from 1 ha were, respectively: 0.0737 L kg^{-1}, 359 L ha^{-1}.

(**a**) (**b**)

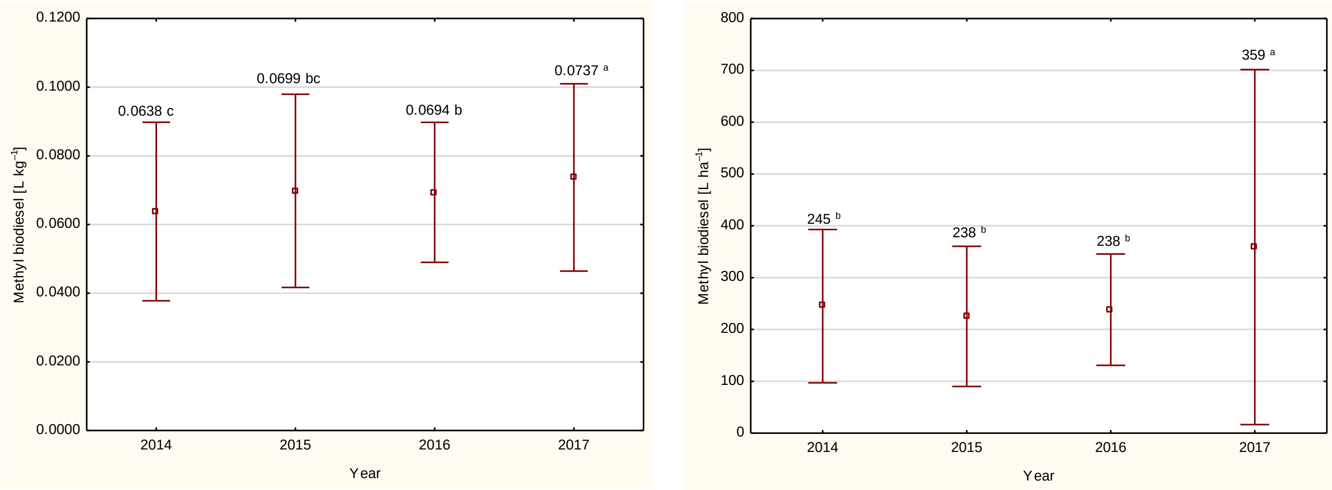

Figure 11. Volume of methyl biodiesel (mean value and standard deviation) obtained from corn grain (**a**) and bioethanol yield from a hectare (**b**), considering year of experiment. [a,b,c]—Values followed by the same letters do not differ significantly in Tukey's (HSD) test ($p < 0.05$).

Among the fertilizer variants, the highest yield of methyl biodiesel as a component of their content in grain and grain yield was found as a result of fertilization with 3.0 ha^{-1} MBM (338 L ha^{-1}), and the lowest after the application of 1.0 t ha^{-1} MBM (204 L ha^{-1}) (Figure 12). The application of 2.0 t ha MBM in the initial 3 years of the study resulted in lower methyl biodiesel yields per kg of grain than on the other sites (Table 10). This translated into an average of fairly low methyl biodiesel yields per one hectare from this facility after four years of testing (Figure 11). The highest methyl biodiesel yields per 1 hectare were found in 2017 after the application of 3.0 t ha^{-1} MBM (Table 10). This is the result of supplying nutrients with 3.0 t ha^{-1} MBM directly in that year and cumulation of nutrients supplied in previous years of the study. After application in 2017, MBM at 3.0 t ha^{-1} yields of methyl biodiesel per hectare were nearly 5 times higher than on the control (no fertilization) site. The high yield of methyl biodiesel per 1 kg of grain and the high grain yield obtained from this facility were responsible for this.

(**a**) (b)

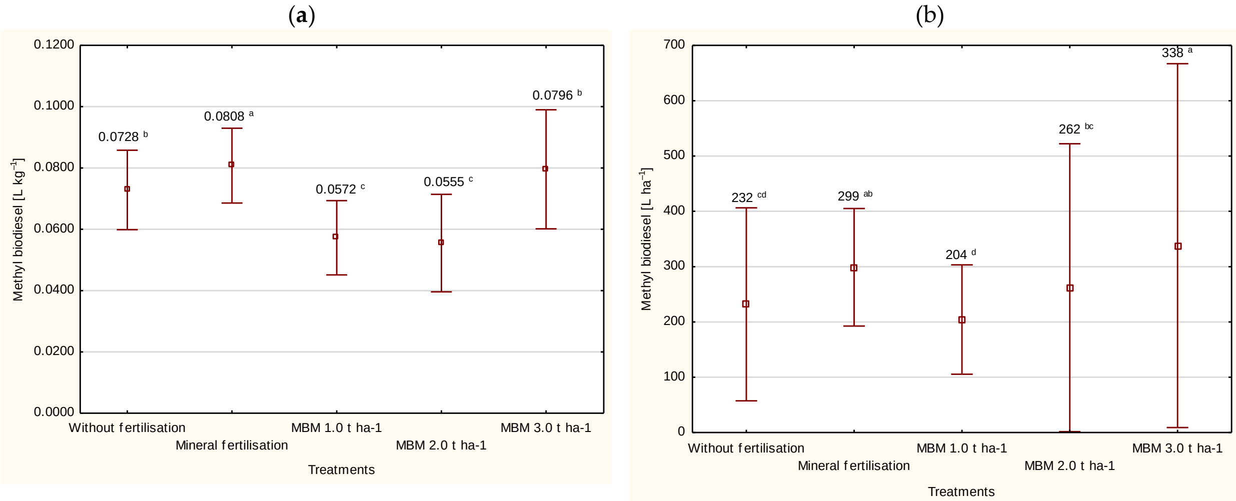

Figure 12. Volume of methyl biodiesel (mean value and standard deviation) obtained from corn grain (**a**) and bioethanol yield from a hectare (**b**), considering fertilization treatment. MBM—Meat and Bone Meal. [a,b,c,d]—Values followed by the same letters do not differ significantly in Tukey's (HSD) test ($p < 0.05$).

Table 10. Interaction between the years and treatments for volume of methyl biodiesel obtained from corn grain and yield of methyl biodiesel from a hectare (mean value and standard deviation).

Year	Without Fertilization	Mineral Fertilization	MBM * 1.0 t ha^{-1}	MBM 2.0 t ha^{-1}	MBM 3.0 t ha^{-1}
Volume of methyl biodiesel obtained from corn grain, L kg^{-1}					
2014	0.0751 ± 0.001 $^{b–e}$	0.0750 ± 0.001 $^{b–e}$	0.0515 ± 0.001 ^{hi}	0.0457 ± 0.001 ^{i}	0.0718 ± 0.002 $^{c–f}$
2015	0.0677 ± 0.002 $^{c–g}$	0.0810 ± 0.005 $^{a–c}$	0.0591 ± 0.010 $^{f–i}$	0.0539 ± 0.003 ^{hi}	0.0874 ±0.007 ^{ab}
2016	0.0766 ± 0.009 $^{a–d}$	0.0784 ± 0.004 $^{a–c}$	0.0619 ± 0.002 $^{e–g}$	0.0578 ± 0.001 $^{g–i}$	0.0723 ± 0.010 $^{c–f}$
2017	0.0719 ± 0.008 $^{c–f}$	0.0888 ± 0.003 ^{a}	0.0565 ± 0.002 $^{g–i}$	0.0647 ± 0.007 $^{d–h}$	0.0868 ± 0.004 ^{ab}
Yield of methyl biodiesel from a hectare, L ha^{-1}					
2014	345 ± 27.8 ^{c}	304 ± 29.3 ^{cd}	205 ± 10.6 $^{d–g}$	175 ± 21.6 $^{e–g}$	197 ± 50.9 $^{d–g}$
2015	268 ± 32.7 $^{c–f}$	277 ± 72.8 $^{c–e}$	162 ± 5.3 ^{fg}	164 ± 20.3 ^{fg}	256 ± 68.0 $^{c–f}$
2016	184 ± 16.3 $^{e–g}$	271 ± 34.1 $^{c–f}$	188 ± 38.7 $^{e–g}$	247 ± 9.4 $^{c–f}$	302 ± 28.4 ^{cd}
2017	130 ± 15.4 ^{g}	344 ± 48.6 ^{c}	263 ± 57.3 $^{c–f}$	462 ± 83.9 ^{b}	596 ± 37.3 ^{a}

* MBM—Meat and Bone Meal. [a,b,c,d,e,f,g,h,i]—Values followed by the same letters do not differ significantly in Tukey's (HSD) test ($p < 0.05$).

The coefficient of determination (r^2) indicates that methyl biodiesel yield was 80% to 96% dependent on grain yield in all fertilizer variants (Figure 13). In the variant fertilized with MBM at 2.0 t ha^{-1}, 70% of the methyl biodiesel yield per grain obtained from 1 ha was determined by the methyl biodiesel yield per kg of grain.

(**a**) (**b**)

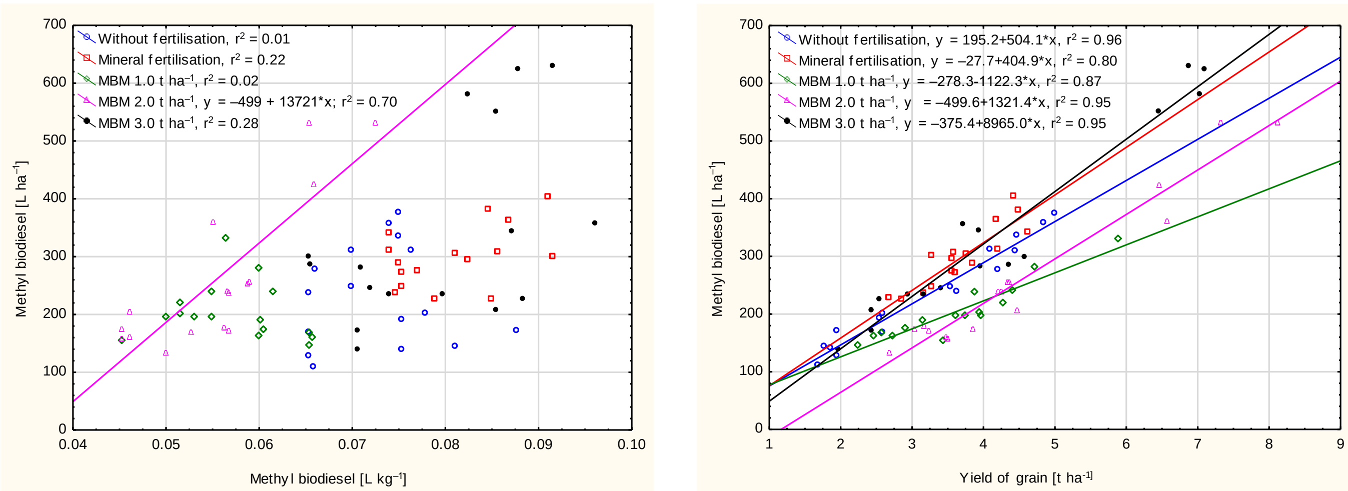

Figure 13. Dependence of methyl biodiesel yield on volume obtained from 1.0 kg^{-1} of grain (**a**) and grain harvest from 1.0 ha^{-1} (**b**) (calculated at significance α = 0.05). MBM—Meat and Bone Meal.

4. Discussion

The effect of meat and bone meals on obtaining a grain yield higher than that obtained on unfertilized and mineral fertilized objects was noticeable after the application of higher doses (2.0 and 3.0 t ha^{-1}) from the 3rd year of the study. This was the result of the direct effect of the nutrients contained in MBM and the aftereffects of the previous years. This shows that the fertilization with meat and bone meal should be considered not only as a direct effect but through a follow-up effect [14,36,37]. This thesis is confirmed by Kivalä et al. [38], further demonstrating in their study that the supply of nitrogen from MBM is not sufficient to achieve the same yields as when mineral fertilizers are applied. According to a study by Cheema et al. [39], the determinant of corn grain yields is the availability of mineral nitrogen to the plants. The nutrients contained in MBM are in biological form and are available to the plant only after mineralization, which takes place in optimal soil moisture [36,40] and with the participation of soil microorganisms [41]. In proprietary studies, optimal weather conditions for the decomposition of supplied organic matter in the form of MBM were demonstrated in 2017, which translated into high yields from these sites.

Corn grain, relative to other cereals, has a high nutritional value, as it contains about 61–78% starch, 6−12 protein and 3.1–5.7% oil [42]. Out of all nutrients contained in plants, starch and fat content are of greatest importance for biofuel production [43]. When developing a fertilization strategy, an intermediate option should be chosen, as too much applied nitrogen in corn crops can promote protein synthesis while reducing oil and starch biosynthesis [43–48]. In our own research, the oil content in corn grain ranged from 4.35% to 5.23% and did not differ significantly from those obtained by other authors [48,49]. In a study by Holou et al. [50], variability in oil content was found between years, which was also demonstrated in our own study. In the studies of Ali et al. [51] and Kaplan et al. [52], it was shown that the oil content depends on the availability of water during the vegetation period of the plants, and in regions with a shortage of water, it can be increased by irrigation. In our study, both organic fertilization in the form of MBM and fertilization with mineral fertilizers (control) did not significantly affect the average oil content of grains. Similarly, in a study by Holou et al. [50], nitrogen fertilization did not affect the fat content of corn grain but did affect final fat yield. In their study, as N fertilization increased, fat yield also increased until it reached a maximum value of 134 N kg ha^{-1}. In the work of Simion et al. [45] and Syomina et al. [46], it was found that increasing nitrogen fertilization led to a decrease in fat content in grain. Ibrahim and Kindil [53] found an increase in oil content with an increase in N and P. In the study of Simion et al. [45], there was no effect of organic fertilizer application on fat content. They explain this lack of response in fat content to fertilization with organic fertilizers by the feature of maintaining a constant relationship between the growth of the endosperm and the embryo (the organ in which fat accumulates). Such conditions ensure the most favorable kinetics of physiological processes taking place in the plant after the application of this form of fertilizer.

An important role for the quality of corn whose grain is destined for starch is the course of the weather [25]. In our study, only in one year (2016) did the starch content differ from that obtained in the other years of the study. Ali et al. [51] and Liu et al. [54] found that the carbohydrates content of grains decreased as drought progressed, which can be offset by the positive effect of irrigation on grain starch content [53]. Agrotechnical factors, such as experimental stand and fertilization treatment, are primarily yield forming and do not fundamentally affect the quality of grain for starch production [25]. In our study, the fertilizer variants used did not significantly affect the variation of starch content in corn grain. The work of Illés et al. [48], Miao et al. [44], Simion et al. [45], Syomina et al. [46], Shynkaruk and Lykhochvor [47] showed that increasing nitrogen fertilization led to a decrease in carbohydrate content in grain. Similarly, Holou et al. [50] showed that, as the N rate increased, the starch content of grain decreased, while starch yields increased, reaching a maximum at a rate of 179.0 kg N ha^{-1}. In studies by Simion et al. [45] and Nelson et al. [49], the starch content of corn grain decreased under the influence of applied organic fertilizers relative to grain obtained from fields fertilized with mineral fertilizers. The differences obtained between years and between fertilizer variants in bioethanol yields and ethyl biodiesel and methyl biodiesel yields per one hectare were mainly related to grain yields, rather than the obtained volume per kg from grain.

In a study by Palamarchuk et al. [55], bioethanol yields from corn crops between 2746 L ha^{-1} and 4691 L ha^{-1} were achieved. In their study, similar bioethanol yields were obtained only for corn from fields fertilized with the two highest doses of meat and bone meal. According to Mohanty and Swain [56], in the European Union, bioethanol yields should be around 7000 L ha^{-1} in order to achieve economic viability. Therefore, there is a need for further modification of crop production technology and improvement of bioethanol extraction methods to increase its yield per hectare. Studies by Rátonyi et al. [57] confirm that increasing the complex fertilization with mineral fertilizers, while not increasing the starch content of the grain, does increase the starch yield and the final yield of bioethanol per one hectare. In our own experiment, an average yield of ethyl biodiesel of 323 L ha^{-1} and methyl biodiesel of 338 L ha^{-1} was obtained. According to a study by Dhugg [58], corn is not suitable for biodiesel production due to its low yield reaching 570 L ha^{-1} under the conditions of the North American continent. However, according to Long et al. [59] and Jia et al. [60], recovering corn oil generated after bioethanol production and using it for biodiesel production is a valuable form of supplementing the biofuel market.

5. Conclusions

The effect of meat and bone meal on obtaining grain yields higher than those obtained on unfertilized and mineral fertilized objects was noticeable after applying higher doses (2.0 and 3.0 t ha^{-1}) from the 3rd year of the study. This shows that fertilization with meat and bone meal should be considered not only as a direct effect but also through a follow-up effect. Fertilization with meat and bone meals did not significantly affect the average fat content of grain, and starch content was only slightly affected. The positive effect of meat and bone meals on the yield of bioethanol from grain extracted from one hectare was responsible for their yield-forming effect. The differences obtained between years and between fertilizer variants in the yields of ethyl biodiesel and methyl biodiesel per one hectare were mainly related to grain yields, rather than the obtained volume per 1 kg from grain.

Applying the highest doses of MBM (2.0 and 3.0 t ha^{-1}) to corn for 4 years resulted in higher grain and biofuel yields than from fertilizing with mineral fertilizers. However, since meat and bone meal itself can already be used as a source of energy, an economic analysis must be carried out for a full evaluation in order to recommend the practice of using it in fertilizing corn from which we want to produce biofuel.

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Conflicts of Interest: The authors declare no conflict of interest.

References

1. Liu, D.C. *Metter Utilization of by-Products from the Meat Industry*; Food and Fertiliser Technology Center: Taipei, Taiwan, 2002; Available online: https://www.fftc.org.tw/htmlarea_file/library/20110706135001/eb515.pdf (accessed on 15 December 2022).
2. Jędrejek, D.; Levic, J.; Wallace, J.; Oleszek, W. Animal by-products for feed: Characteristics, European regulatory framework, and potential impacts on human and animal health and the environment. *J. Anim. Feed Sci.* **2016**, *26*, 189–202. [CrossRef]
3. Regulation (EC) No 1774/2002 of the European Parliament and of the Council of 3 October 2002 Laying Down Health Rules. Available online: https://op.europa.eu/en/publication-detail/-/publication/28ab554e-8e93-4976-89a9-8b6c9d17dfb4/language-en (accessed on 15 December 2022).
4. Concerning Animal by–Products Not Intended for Human Consumption. Available online: https://eur-lex.europa.eu/legalcontent/EN/TXT/?uri=CELEX:32002R1774 (accessed on 28 October 2022).
5. Jankowski, K.J.; Nogalska, A. Meat and Bone Meal and the Energy Balance of Winter Oilseed Rape—A Case Study in North-Eastern Poland. *Energies* **2022**, *15*, 3853. [CrossRef]

6. Odlare, M.; Arthurson, V.; Pell, M.; Svensson, K.; Nehrenheim, E.; Abubaker, J. Land application of organic waste—Effects on the soil ecosystem. *Appl. Energy* **2011**, *88*, 2210–2218. [CrossRef]
7. Cascarosa, E.; Ortiz de Zarate, M.C.; Sánchez, J.L.; Gea, G.; Arauzo, J. Sulphur removal using char and ash from meat and bone meal pyrolysis. *Biomass Bioenergy* **2012**, *40*, 190–193. [CrossRef]
8. Möller, K.; Oberson, A.; Bünemann, E.K.; Cooper, J.; Friedel, J.K.; Glaesner, N.; Hörtenhuber, S.; Løes, A.K.; Möder, P.; Meyer, G.; et al. Improved phosphorus recycling in organic farming: Navigating between constraints. *Adv. Agron.* **2018**, *147*, 159–237. [CrossRef]
9. Staroń, P.; Kowalski, Z.; Staroń, A.; Banach, M. Thermal conversion of granules from feathers, meat and bone meal and poultry litter to ash with fertilising properties. *Agric. Food Sci.* **2017**, *26*, 173–180. [CrossRef]
10. Darch, T.; Dunn, R.M.; Guy, A.; Hawkins, J.M.B.; Ash, M.; Frimpong, K.A.; Blackwell, M.S.A. Fertiliser produced from abattoir waste can contribute to phosphorus sustainability, and biofortify crops with minerals. *PLoS ONE* **2019**, *14*, e0221647. [CrossRef]
11. Chojnacka, K.; Moustakas, K.; Witek-Krowiak, A. Bio-based fertilisers: A practical approach towards circular economy. *Bioresour. Technolol.* **2020**, *295*, 122223. [CrossRef]
12. Kowalski, Z.; Banach, M.; Makara, A. Optimisation of the co-combustion of meat–bone meal and sewage sludge in terms of the quality produced ashes used as substitute of phosphorite. *Environ. Sci. Pollut. Res.* **2021**, *28*, 8205–8214. [CrossRef]
13. Krupa-Żuczek, K.; Szynkowska, M.I.; Wzorek, Z.; Sobczak-Kupiec, A. Physicochemical properties of meat-bone meal and ashes after its thermal treatment. *Archit. Civil Eng. Environ.* **2012**, *4*, 95.
14. Kantorek, M.; Jesionek, K.; Polesek-Karczewska, S.; Ziółkowski, P.; Stajnke, M.; Badur, J. Thermal utilization of meat-and-bone meal using the rotary kiln pyrolyzer and the fluidized bed boiler—The performance of pilot-scale installation. *Renew. Energy* **2021**, *164*, 1447–1456. [CrossRef]
15. Stępień, A.; Wojtkowiak, K.; Kolankowska, E. Use of meat industry waste in the form of meat-and-bone meal in fertilising maize (*Zea mays* L.) for grain. *Sustainability* **2021**, *13*, 2857. [CrossRef]
16. Załuszniewska, A.; Nogalska, A. The effect of meat and bone meal (MBM) on the seed yield and quality of winter oilseed rape. *Agronomy* **2020**, *10*, 1952. [CrossRef]
17. Nogalska, A.; Zaluszniewska, A. The effect of meat and bone meal applied without or with mineral nitrogen on macronutrient content and uptake by winter oilseed rape. *J. Elem.* **2020**, *25*, 905–915. [CrossRef]
18. Nogalska, A.; Czapla, J.; Nogalski, Z.; Skwierawska, M.; Kaszuba, M. The effect of increasing doses of meat and bone meal (MBM) on maize (*Zea mays* L.) grown for grain. *Agric. Food Sci.* **2012**, *21*, 325–331. [CrossRef]
19. Pohl, F.; Senn, T. A rapid and sensitive method for the evaluation of cereal grains in bioethanol production using near infrared reflectance spectroscopy. *Bioresour. Technol.* **2011**, *102*, 2834–2841. [CrossRef]
20. Kumar, S.P.J.; Kumar, N.S.; Chintagunta, A.D. Bioethanol production from cereal crops and lignocelluloses rich agroresidues: Prospects and challenges. *SN Appl. Sci.* **2020**, *2*, 1673. [CrossRef]
21. Mata, T.M.; Rodrigues, S.; Caetano, N.S.; Martins, A.A. Life cycle assessment of bioethanol from corn stover from soil phytoremediation. *Energy Rep.* **2022**, *8*, 468–474. [CrossRef]
22. Börjesson, P. Good or bad bioethanol from a greenhouse gas perspective—What determines this? *Appl. Energy* **2009**, *86*, 589–594. [CrossRef]
23. Jarosz, Z.; Księżak, J.; Faber, A. Assessment of greenhouse gas emissions in systems used in cropping maize for bioethanol production. *Rocz. Nauk. Stowarzyszenia Ekon. Rol. Agrobiz* **2017**, *19*, 60–65. (In Polish) [CrossRef]
24. Erdei, B.; Barta, Z.; Sipos, B.; Réczey, K.; Galbe, M.; Zacchi, G. Research Ethanol production from mixtures of wheat straw and wheat meal. *Biotechnol. Biofuels* **2010**, *3*, 16. [CrossRef] [PubMed]
25. Niedziółka, I.; Szymanek, M. Utilization of maize grain for industrial and energetistics purposes. *Motrol. Motoryz. Energetyka Rol.* **2003**, *285*, 115–121. (In Polish) Available online: http://old-panol.ipan.lublin.pl/wydawnictwa/Motrol5/Niedziolka.pdf (accessed on 15 December 2022).
26. Saini, J.K.; Saini, R.; Tewari, L. Lignocellulosic agriculture wastes as biomass feedstocks for second-generation bioethanol production: Concepts and recent developments. *Biotech* **2015**, *5*, 337–353. [CrossRef] [PubMed]
27. Prasad, S.; Singh, A.; Joshi, H.C. Ethanol as an alternative fuel from agricultural, industrial and urban residues. *Resour. Conserv. Recycl.* **2007**, *50*, 1–39. [CrossRef]
28. Skendi, A.; Zinoviadou, K.G.; Papageorgiou, M.; Rocha, J.M. Advances on the Valorisation and Functionalization of By-Products and Wastes from Cereal-Based Processing Industry. *Foods* **2020**, *9*, 1243. [CrossRef]
29. Maceiras, R.; Cancela, A.; Rodríguez, M.; Sánchez, A.; Urréjola, S. An Innovative Biodiesel Production. *Chem. Eng. Trans.* **2010**, *19*, 97–102. [CrossRef]
30. Marchetti, J.M.; Miguel, V.U.; Errazu, A.F. Possible methods for biodiesel production. *Renew. Sustain. Energy Rev.* **2007**, *11*, 1300–1311. [CrossRef]
31. Susik, J. Corn oil production methods determining its chemical properties. *ŻYWNOŚĆ. Nauka. Technol. Jakość* **2021**, *4*, 47–56. (In Polish) [CrossRef]

32. Manchester, S.J. Fire and explosion hazards of meat & bone meal: Storage, transport and processing. *Symp. Ser.* **2003**, *149*, 289–302.
33. *33. ISO 3104:2020*; Petroleum Products—Transparentand Opaque Liquids—Determination of Kinematic Viscosity and Calculation of Dynamic Viscosity. ISO: Geneva, Switzerland, 2020.
34. *EN ISO 12185:1996*; Crude Petroleum and Petroleum Products. Determination of Density-Oscillating U-Tube Method. ISO: Geneva, Switzerland, 1996.
35. *EN 14214:2012*; Liquid Petroleum Products—Fatty Acid Methyl Esters (FAME) for Use in Diesel Engines and Heatingap Plications—Requirements and Test Methods. ISO: Geneva, Switzerland, 2012.
36. Jeng, A.S.; Vagstad, N. Potential nitrogen and phosphorus leaching from soils fertilised with meat and bone meal. *Acta Agric. Scand. Sect. B–Soil Plant Sci.* **2009**, *59*, 238–245. [CrossRef]
37. Chaves, C.; Canet, R.; Albiach, R.; Marin, J.; Pomares, F. Meat and bone meal: Fertilising value and rates of nitrogen mineralization. *Nutr. Carbon Cycl. Sustain. Plant Soil Syst.* **2005**, *1*, 177–180. Available online: http://ramiran.uvlf.sk/doc04/Proceedings%2004/Chaves.pdf (accessed on 15 December 2022).
38. Kivelä, J.; Chen, L.; Muurinen, S.; Kivijärvi, P.; Hintikainen, V.; Helenius, J. Effects of meat bone meal as fertiliser on yield and quality of sugar beet and carrot. *Agric. Food Sci.* **2015**, *24*, 68–83. [CrossRef]
39. Cheema, M.A.; Farhad, W.; Saleem, M.F.; Khan, H.Z.; Munir, A.; Wahid, M.A.; Rasul, F.; Hammad, H.M. Nitrogen management strategies for sustainable maize production. *Crop. Environ.* **2010**, *1*, 49–52.
40. Mondini, C.; Cayuela, M.L.; Sinicco, T.; Sánchez-Monedero, M.A.; Bertolone, E.; Bardi, L. Soil application of meat and bone meal. Short-term effects on mineralization dynamics and soil biochemical and microbiological properties. *Soil Biol. Biochem.* **2008**, *40*, 462–474. [CrossRef]
41. Pérez-Piqueres, A.; Edel-Hermann, V.; Alabouvette, C.; Steinberg, C. Response of soil microbial communities to compost amendments. *Soil Biol. Biochem.* **2006**, *38*, 460–470. [CrossRef]
42. Revilla, P.; Alves, M.L.; Andelković, V.; Balconi, C.; Dinis, I.; Mendes-Moreira, P.; Redaelli, R.; de Galarreta, J.I.R.; Patto, M.C.V.; Žilić, S.; et al. Traditional foods from maize (*Zea mays* L.) in Europe. *Front. Nutr.* **2021**, *8*, 683399. [CrossRef]
43. Yang, C.; Du, W.; Zhang, L.; Dong, Z. Effects of sheep manure combined with chemical fertilisers on maize yield and quality and spatial and temporal distribution of soil inorganic nitrogen. *Complexity* **2021**, *2021*, 4330666. [CrossRef]
44. Miao, Y.; Mulla, D.J.; Robert, P.C.; Hernandez, J.A. Within-field variation in corn yield and grain quality responses to nitrogen fertilisation and hybrid selection. *Agron. J.* **2006**, *98*, 129–140. [CrossRef]
45. Simion, E.; Simion, D.; Miron, L.; Enache, G. The Influence Of Organic Fertilisers On The Quality Of The Main Harvest Concerning the Ecologically Cropped Corn. *Lucrări Ştiinţifice* **2010**, *5*, 412–415. Available online: http://www.uaiasi.ro/revagrois/PDF/2010_2_414.pdf (accessed on 15 December 2022).
46. Syomina, S.A.; Paliychuk, A.S.; Gavryushina, I.V.; Lysenko, I.A. Fertilisers, plant density and nutritional properties of corn grain. *Earth Environ. Sci.* **2021**, *843*, 012036. [CrossRef]
47. Shynkaruk, L.; Lykhochvor, V. Influence of fertilisation and foliar feeding on maize grain qualitative indicators. *Ukr. J. Ecol.* **2021**, *11*, 113–116. [CrossRef]
48. Illés, Á.; Mousavi, S.M.; Bojtor, C.; Nagy, J. The plant nutrition impact on the quality **and** quantity parameters of maize hybrids grain yield based on different statistical methods. *Cereal Res. Commun.* **2020**, *48*, 565–573. [CrossRef]
49. Nelson, K.A.; Motavalli, P.P.; Smoot, R.L. Utility of dried distillers grain as a fertiliser source for corn. *J. Agric. Sci.* **2009**, *1*, 3–12. [CrossRef]
50. Holou, R.A.Y.; Kindomihou, V. Impact of Nitrogen Fertilisation on the Oil, Protein, Starch, and Ethanol Yield of Corn (*Zea mays* L.). Grown for Biofuel Production. *J. Life Sci.* **2011**, *5*, 1013–1021. [CrossRef]
51. Ali, A.S.; Elozeiri, A.A. Metabolic Processes During Seed Germination. In *Advances in Seed Biology*; Jimenez-Lopez, J.C., Ed.; IntechOpen: London, UK, 2017. [CrossRef]
52. Kaplan, M.; Kalea, H.; Karaman, K.; Unlukara, A. Influence of different irrigation and nitrogen levels on crude oil and fatty acid composition of maize (*Zea mays* L.). *Grasas Aceites* **2017**, *68*, e207. [CrossRef]
53. Ibrahim, S.A.; Kandil, H. Growth, yield and chemical constituents of corn (*Zea Maize* L.) as affected by nitrogen and phosphors fertilisation under different irrigation intervals. *J. Appl. Sci. Res.* **2007**, *3*, 1112–1120.
54. Liu, L.; Klocke, N.; Yan, S.; Rogers, D.; Schlegel, A.; Lamm, F.; Chang, S.I.; Wang, D. Impact of deficit irrigation on maize physical and chemical properties and ethanol yield. *Cereal Chem.* **2013**, *90*, 453–462. [CrossRef]
55. Palamarchuk, V.; Honcharuk, I.; Honcharuk, T.; Telekalo, N. Effect of the elements of corn cultivation technology on bioethanol production under conditions of the right-bank forest-steppe of Ukraine. *Ukr. J. Ecol.* **2018**, *8*, 42–50. Available online: https://cyberleninka.ru/article/n/effect-of-the-elements-of-corn-cultivation-technology-on-bioethanol-production-under-conditions-of-the-right-bank-forest-steppe-of (accessed on 28 October 2022).
56. Mohanty, S.K.; Swain, M.R. Bioethanol production from corn and wheat: Food, fuel, and future. In *Bioethanol Production from Food Crops*; Academic Press: Cambridge, MA, USA, 2019; pp. 45–59. [CrossRef]
57. Rátonyi, T.; Nagy, O.; Bakó, K.; Fejér, P.; Harsányi, E. Effects of fertilisation on grain quality and bio-ethanol production of maize. In Proceedings of the 13th Alps-Adria Scientific Workshop, Villach, Austria, 28 April–3 May 2014; Volume 63, pp. 31–34. [CrossRef]

58. Dhugga, K.S. Maize biomass yield and composition for biofuels. *Crop. Sci.* **2007**, *47*, 2211–2227. [CrossRef]
59. Long, S.P.; Karp, A.; Buckeridge, M.S.; Davis, S.C.; Jaiswal, S.; Moore, P.H.; Moose, S.P.; Murphy, D.J.; Onwona-Agyeman, S.; Vonsha, A. Feedstocks for Biofuels and Bioenergy. In *Bioenergy & Sustainability: Bridging the Gaps*; Souza, G.M., Victoria, R.L., Joly, C.A., Verdade, L.M., Eds.; Sao Paulo, Brasil, 2015; pp. 302–346. Available online: https://bioenfapesp.org/scopebioenergy/images/chapters/bioenergy_sustainability_scope.pdf (accessed on 15 December 2022).
60. Jia, Y.; Kumar, D.; Winkler-Moser, J.K.; Dien, B.; Singh, V. Recoveries of oil and hydrolyzed sugars from corn germ meal by hydrothermal pretreatment: A model feedstock for lipid-producing energy crops. *Energies* **2020**, *13*, 6022. [CrossRef]