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Review

The Use of Waste to Produce Liquid Fertilizers in Terms of Sustainable Development and Energy Consumption in the Fertilizer Industry—A Case Study from Poland

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Abstract: The topical challenge for the Polish, European, and global fertilizer industry is to produce sufficient nutrients for growing plants using more energy-efficient and environmentally friendly methods. The appropriate course of action, in terms of the challenges posed, could be the production of liquid fertilizers, made from waste materials that exhibit fertilizer properties. This solution makes it possible not only to reduce the exploitation of natural resources but above all, to implement elements of a circular economy and reduce the energy intensity of the fertilizer industry. This study shows that both in Poland and the European Union, there are current regulations aimed at elements of a circular economy and indicating the need to obtain fertilizers containing valuable plant nutrients from organic waste or recycled materials. The recognition carried out for the Polish market clearly indicates that to produce liquid organic fertilizers and soil conditioners, the most used is the digestate from the fermentation process. The preparation of liquid organic–mineral fertilizers is mainly based on algae extracts. Mine minerals are used in the production of mineral–liquid fertilizers. An analysis of data has shown that the above-mentioned waste materials, used as substrates to produce fertilizers, contain chemical substances and elements important for, among other things, stimulation of proper plant development, growth of aboveground and underground parts of plants, increased resistance to diseases and pests, and regulation of plant water management. Referring to the above information, the production of liquid fertilizers from waste materials seems reasonable and is an alternative to mineral–solid fertilizers, whose production process is energy-intensive and produces air emissions. Detailed identification of the properties of the various components made it possible to demonstrate their usefulness in terms of fertilizing plants and soils, but also to emphasize the importance of this line of research and the need to look for other groups of waste for reuse within the framework of a circular economy.

Keywords: liquid fertilizers; waste materials; sustainable energy policy; digestate; algae; mine materials

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1. Introduction

Food production requires a lot of energy. Energy demand in the "farm to fork" cycle accounts for about 26% of total energy consumption in the European Union [1]. Energy inputs in plant production can be classified as direct and indirect energy inputs. Direct energy is most easily recognized as fuel and electricity, whereas indirect energy recourses include fertilizers, water for irrigation, plant protection chemicals, technical systems, and human labor [2]. Efficient use of energy is one of the basic requirements of sustainable agriculture. The growing production of mineral fertilizers is a response to the growth of the world's population and the increasing food needs of mankind [2–4].

The latest studies show that in the coming years, we will face the development of the mineral fertilizer market, both single and multi-component fertilizers [5]. They are used in modern agriculture to maximize yields. Therefore, the level and dynamics of fertilizer use is decisively determined by the state of the economic development of a given country [6]. Some adverse effects are greenhouse gas emissions, surface water eutrophication, and excessive fast plant nutrition [7–10]. Currently, the leaders in the production of mineral fertilizers are the United States, China, India, and European Union countries [11]. Nitrogen fertilizers (about 60% of all fertilizers), followed by phosphorus (about 20%), and potassium (about 20%) fertilizers have by far the largest share of the production in the world. Nitrogen fertilizers were produced in most of the countries where mineral fertilizers were produced. However, not all countries also produced phosphorus or potassium fertilizers, or they were produced only in small amounts, because of this, it is necessary to import raw materials—phosphate rock and potassium salt. One-component fertilizers dominate the production structure of nitrogen fertilizers. Urea is by far the most important fertilizer in this group, followed by ammonium nitrate, ammonium sulphate, calcium ammonium nitrate, and urea ammonium nitrate solution.

Currently, most fertilizers containing phosphorus and potassium are multi-component fertilizers. The dominant phosphorus fertilizers are 40% enriched superphosphate and simple superphosphates. Potassium fertilizers are mainly potassium salt and potassium sulphate [12]. Additionally, an increase in the demand for fertilizers for agriculture is inevitable, and their consumption varies greatly between countries. In most Central and Eastern European countries, the consumption of nutrients such as nitrogen, potassium, and phosphorus is increasing, while in Western Europe, and especially in Germany, the consumption of these nutrients is expected to decrease, mainly due to the tightening of national regulations on the use of mineral fertilizers.

A significant barrier to the development of the global fertilizer market is very strong competition in this industry. For European Union countries, including Poland, the main market barrier is the cost of acquiring strategic raw materials, such as phosphorus, potassium and, above all, natural gas, and high consumption of electricity. Natural gas cost is a major variable cost in the production of nitrogen fertilizer [13]. For example, 72–85% of natural gas prices determine the prices of ammonia, which is used to produce nitrogen fertilizers [14]. In 2022, European countries are struggling with rapidly rising natural gas and electricity prices amid the energy crisis caused in part by the Russia–Ukraine war. The increase in gas prices is profoundly affecting energy-intensive sectors in Europe, particularly the fertilizer industry. As natural gas is used in large quantities to make fertilizers, many manufacturers in Europe have been pushed to change business practices, with some producers forced to either reduce or suspend production in fertilizer plants. In September 2022, soaring prices of gas have already curtailed a quarter of Europe's nitrogen fertilizer capacity [15–17]. Therefore, in the time of the energy crisis, it becomes advisable to use waste materials to produce fertilizers to reduce the consumption of gas and, above all, electricity.

Recently, many studies have demonstrated the possibility of producing organic fertilizers from organic waste, such as the organic fraction of municipal waste, municipal solid waste compost, and agricultural waste [18–25]. Agricultural biomass can be also a source of raw material for fertilizer production [26]. These fertilizer products should not be applied directly on soils due to the possible presence of pathogens and potentially toxic elements [8,10]. It is worth noting that as part of a circular economy, it is possible to use the products of animal biomass combustion for fertilizer purposes, as they are rich in plant nutrients [27]. Also, ashes from plant biomass are characterized by their content of macronutrients such as Ca, K, P, and S, and at the same time low content of toxic elements (As, Pb), which allows them to be considered a valuable component of products used for agricultural purposes [28,29]. Naturally, the diversity of plant biomass as well as animal biomass determines the different properties of the obtained ashes. An innovative method in recent years has become the use of sewage sludge to produce fertilizer in solid form

[30–33], and recent studies show that it is also produced in liquid form [34,35]. The advantage of using sewage sludge is certainly its rich formulation, containing nitrogen, phosphorus, and potassium compounds; however, the impact of limitations that apply to sewage sludge cannot be overlooked. The main limitations in terms of agricultural use are the potential content of heavy metals and toxic compounds that pose a threat to the environment [36]. According to scientific data, the pyrolysis process allows such thermal treatment of sewage sludge, where a solid product free of pathogens and at the same time rich in carbon and nutrients is obtained [33]. The liquid form of sludge-based fertilizers, on the other hand, can be obtained, for example, by using alkaline thermal hydrolysis (ATH) with a $Ca(OH)_2$ [34] or by properly treating the sludge (dehydrating, drying, and grinding) and leaching out the micro and macro elements valuable to plants [35]. To compete with inorganic fertilizers, organic fertilizer production from waste must be feasible from a technical, economic, and environmental perspective. Organic fertilizers must comply with the current European regulations regarding organic carbon, nutrients, and heavy metals [37], and their use must comply with the principles of the circular bioeconomy [38,39]. Adequate investment costs and payback time are necessary to assure the economic feasibility of the production process. Moreover, water and energy consumption must be reduced, while the contamination of water bodies through eutrophication should be avoided [10]. One of the current challenges that the European fertilizer industry is facing in the long term is to find an answer to the question of how to produce enough plant nutrients, constantly needed by a growing population, using more energy-saving and environmentally friendly methods, and at the same time, to do it in a less energy-intensive way and with better use of existing natural resources, as well as to use waste for the production of fertilizers. Due to the highly energy-intensive nature of the production of food and fertilizers, especially nitrogen fertilizers, the fertilizer industry is vital to any discussion of energy.

The paper presents issues related to the feasibility of reusing waste materials to produce full-value liquid fertilizers as part of a circular economy and to improve the energy intensity of fertilizer production. It should be noted that the survey included liquid fertilizers available on the Polish market, the production of which is carried out with the exclusion of zoonotic substrates. In addition, the criterion for including a fertilizer in the list was the relevant decision of the Minister of Agriculture.

2. Energy Consumption of the Fertilizer Industry

Fertilizer production alone accounts for roughly 1.2% of global energy consumption and 1% of all greenhouse gases annually [9,12,40,41]. This represents nearly 500 trillion BTUs [42]. Both the production and use of mineral fertilizers contribute to changes in the global-warming potential. Production of mineral fertilizers increases greenhouse gas emissions, mainly CO_2 from fossil fuels used in ammonia production, and to a lesser degree CO_2 in the reaction of phosphorites with sulfuric acid or during extraction of phosphorus- or potassium-rich materials, and N_2O, mainly during production of nitric acid [43]. Energy consumption in this sector depends on the type of mineral fertilizer produced and the technology used to obtain the raw material. While phosphate and potassium are mined as elements of important mineral fertilizers, nitrogen fertilizers are made by combining the hydrogen molecules in natural gas with nitrogen from the air, thus creating ammonia, the basic element of all fertilizers. Consequently, nitrogen fertilizers are an extremely energy-intensive product. Figure 1 presents the general scheme of the production of mineral fertilizers to understand the energy consumption of their production.

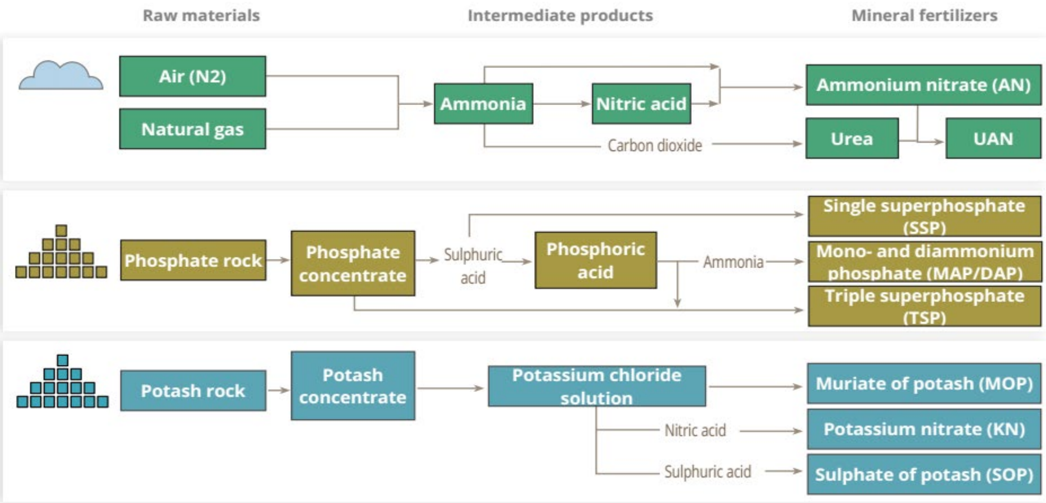

Figure 1. Production of main fertilizer [12].

Ammonia manufacturing makes up approximately 90% of this energy use [12]. This is mainly due to the production of ammonia from hydrogen and atmospheric nitrogen in the Haber-Bosch process, which is a highly energy-intenisve process. The Haber-Bosch process is the main industrial procedure for ammonia production, which involves combining nitrogen in the air with hydrogen under extremely high pressure and temperature. The process requires a large amount of natural gas [44]. Given the availability and price of natural gas, many countries have limited opportunities to engage in such extensive production. Energy efficiency in the ammonium sector has been significantly improved since manufacturing began in the early 20th century. Around 70% of ammonia is used to make fertilizers. Modern ammonia production technology now allows for a theoretical minimum of energy consumption through best-available techniques (BAT's). Best-in-class ammonia plants consume about 28–30 GJ per 1 Mg NH_3. However the conversion of ammonia to solid urea consumes about 3.1 MMBtu/ton urea (3.3 GJ/tonne urea) [12]. Theoretically, the global energy consumption of the fertilizer industry can be reduced by almost 40%, for example, with new technologies. The unit energy consumption of the Western European fertilizer industry is about 15% lower than the world average [45]. In Table 1, energy use in different types of urea installations in fertilizer plants is shown. The ammonia consumption per tonne urea can be also a measure of efficiency of fertilizer production. Nowadays, it is about 0.574 kg NH_3/kg urea [46].

Table 1. The overall energy use for urea production in fertilizer plants [47].

Process (Remarks)	Energy Use (GJ/Mg Urea)-LHV *	Energy Use (MMBtu/Mg urea)-HHV *
Conventional total recycle process		
Conventional total recycle process (Toyo) (excl. electricity use for CO_2 compression)	2.7	2.6
Existing installations (crystallization, natural draft prilling, compression with steam turbine)	5.5	5.2
NH_3 stripping		
Snamprogetti NH_3 stripping (excl. electricity use for CO_2 compression)	1.7	1.6
NH_3 stripping (prilling, CO_2 compression with steam turbine, prilling)	2.9	2.7
NH_3 stripping (prilling, CO_2 compression with steam turbine, granulation)	3.1	2.9
NH_3 stripping (prilling, CO_2 compression with electromotor, prilling)	2.0	1.9

NH_3 stripping (prilling, CO_2 compression with electromotor, granulation)	1.9	1.8
CO_2 stripping		
Stamicarbon CO_2 stripping, (excl. electricity use for CO_2 compression)	1.9	1.8
Stamicarbon CO_2 stripping, (steam and electricity)	2.7	2.6
ACES stripping (spout fluid bed granulation, CO_2/NH_3/carbamate pumps driven by steam turbine)	3.0	2.8
ACES stripping (spout fluid bed granulation, only the CO_2 pump driven by steam turbine)	2.7	2.6

* Total energy use takes into account steam and electricity imports and exports.

During production, fertilizers go through many processes to become the final, useful form. The consistency or form of the fertilizer product is an energy driver. The main consistency forms are granulated, powdered, liquid, and low-release fertilizers (various forms including fertilizer spiker, tabs, etc.). Granulation is part of the value chain, and a process that increases particle size, reduces waste, and guarantees greater precision in fertilizer field applications. However, the granulation of fertilizers significantly affects energy consumption. Electricity (with 92%) was the highest energy input for the NPK fertilizer granulation process [48]. The pelletizing process increases the unit cost of energy by 30.3% compared to the unit cost for the production of powdered fertilizer [49] The drying process is also highly energy-consuming. For example, the energy consumption for drying manure is about 100 kWh/Mg of product [50,51]. Energy consumption for producing, packing, and delivering the main types of mineral fertilizers can be substantial (e.g., up to 50 MJ per N kg for the urea in an average European plant [43,52].

Tables 2 and 3 show energy intensity indicators for the production of fertilizers manufactured in Poland, respectively, in the category of nitrogen and phosphorus fertilizers and multi-component fertilizers.

Table 2. Energy consumption of selected fertilizers [53].

Typ of Fertilizer	Unit Consumption			
	Total Energy	Incl.		
		Hydrocarbon Fuels	Heat	Electricity
	MJ/Mg	MJ/Mg	MJ/Mg	kWh/Mg
Urea $(NH_2)_2CO$	3497.2–4985.7	-	4016.0–5256.1	109.0–134.8
Calcium Ammonium Nitrate (CAN)	545.5–1118.1	7.0–9.3	430.5–870.3	25.0–41.0
Ammonium Nitrate (AN) NH_4NO_3	561.6–598.7	0.1	482.8–520.5	19.5–24.0
Granular single superphosphate (SSP)	688.4–962.0	610.5–850.8	-	16.4–30.9
Triple superphosphate (TSP)	1600.5–2011.9	1130.2–1352.9	203.8–482.7	50.5–83.8

Table 3. Energy consumption of selected compound fertilizers [53].

Typ of Fertilizer	Unit Consumption			
	Total Energy	Incl.		
		Hydrocarbon Fuels	Heat	Electricity
	MJ/Mg	MJ/Mg	MJ/Mg	kWh/Mg
NP Fertilizer	895.8–1725.8	366.3–1024.1	341.0–499.8	30.6–56.1
NPK Fertilizer	990.5–1245.4	681.6–926.6	153.9–182.4	33.5–39.0

The production of nitrogen fertilizers shows the highest energy consumption in the group of mineral fertilizers. Urea production, which is the most concentrated nitrogen fertilizer, is characterized by its relatively high energy consumption. Depending on the type of installation, the total energy consumption for the fertilizer production may be as high as 598.7, 1118.1, and 4985.7 MJ/Mg for AN, CAN, and urea, respectively. Nand and Goswami [46] showed that the latest generation fertilizer plant energy consumption is 5.0 GCal/Mg urea. In other studies, Fiamelda et al. [54] estimated the electricity consumption of urea production at the level of 145.9–200.3 kWh/Mg urea.

In contrast to the energy input for nitrogen fertilizer, the data for phosphorus vary widely. For example, Salami et al. [55] estimated equivalent energy for producing SSP fertilizer was 2.07 MJ/kg. Gellings and Parmenter [56] illustrated the equivalent energy of phosphate fertilizer as 7.7 MJ/kg and 2.6 MJ/kg in the production and packaging process, respectively, that are equal to 10.3 MJ/kg. According to Table 2, the total energy consumption used for the phosphorus fertilizer production may be as high as 962.0 and 2011.9 MJ/Mg for SSP and TSP.

Raw material and semi-finished products in the field of compound fertilizers (natural gas, phosphates, potassium salt, and other products produced by the sulfur processing sub-sector) are of particular importance in shaping the energy consumption indicators to produce these fertilizers. According to Farahani et al. [48], NPK-15:8:15 fertilizer production consumes a total energy of 1.66 MJ/kg, which is mainly due to electricity. Whereas Skowrońska and Filipek [43] showed the energy consumption of the NPK-15:15:15 fertilizer to be on average of 9.81 MJ/kg. It is also worth presenting the energy consumption per pure fertilizer component. Depending on the type of fertilizer and the nature of its production, energy consumption varies greatly (Table 4). Kobayashi and Sago [57] demonstrated that energy consumption in the production of urea, ammonium sulfate, diammonium phosphate (DAP), compound fertilizer, and coating fertilizer were found to be 22.3 MJ/1kg (48.6 MJ/kg N), 4.3 MJ/kg (20.5 MJ/kg N), 13.2 MJ/kg (28.6 MJ/kg P), 2.0 MJ/kg, and 1.9 MJ/kg, respectively.

Table 4. Energy consumption for producing, packing, and delivering the main types of fertilizers [43].

Fertilizer Product	Primary Energy Consumption	Unit
Ammonium nitrate (AN)	40 */29.8	MJ/kg N
Urea	51.6 */44.1 **	
Calcium ammonium nitrate (CAN)	42.6 */31.4 **	
Ammonium sulphate (AS)	42	
Triple superphosphate (TSP)	30.25	MJ/kg P
Single superphosphate (SSP)	13	
Muriate of potash (MOP)	10.06	MJ/kg K
Limestone	2.3	MJ/kg Ca

* production (European average) at plant gate. ** production (BAT) at plant gate.

A review of the scientific literature on energy consumption during the production of mineral fertilizers indicates the need to search for new technological solutions or to produce fertilizers from waste materials. Utilization of waste from industry to fertilizer production is an option for reducing the use of mineral fertilizers in agriculture and improvement of the energy consumption rates of their production. Most considerable alternatives are biomass sources generated in great amounts and with a high nutrient content [58,59]. Utilization of waste from industry to fertilizer production is an option for reducing the use of mineral fertilizers in agriculture and improvement of the energy consumption rates of their production. The nutrient concentration of recycled fertilizers can be considerably lower than in mineral fertilizers, and therefore, the amount of fertilizer applied per unit area needs to be multiplied, resulting in higher environmental impacts from the transport, storage, and application of the fertilizers. Recycled fertilizers have the advantage that the raw materials for their production are locally sourced, and the fertilizers are used locally. However, enhancing nutrient recycling can reduce the environmental impact of agriculture and save non-renewable resources and energy in fertilizer production [59–63].

However, the knowledge of the impacts of different recycled fertilizers on energy use is lacking [59]. There is very little information in the scientific literature on this subject. For example, the energy consumption for converting biogas digestate into recycled fertilizer is only 0.23 MJ/kg [64]. Fadare et al. [49] presented production of organic fertilizer from market refuse and abbatoir waste by the aerobic composting and drying process The authors estimated energy consumption of fertilizer production as 0.28 and 0.35 MJ/kg for powder and pellet form, respectively. The most energy-intensive operation was identified as the pulverizing unit with an energy intensity of 0.09 MJ/kg [49]. Tampio et al. [65] showed the possibility of concentrating the liquid fraction from the digestate with a significant share of energy. The energy consumption of the digestate liquid treatment per recovered nitrogen in the concentrated fertilizer products (ammonium sulfate, concentrate) were at the level 148.0–213.0 kWh/kgN for the evaporation, stripping, and reverse osmosis processes. The digestate liquid treatment systems were able to concentrate up to 67% of the feedstock nitrogen into transportable fertilizer products with low mass. The authors obtained the high nitrogen and potassium and low phosphorus concentrations within the concentrate (18.0 kgN/Mg, 12.0 kgNH$_4$-N/Mg, 0.3 kgP/Mg, and 9.0 kgK/Mg) compared with the untreated digestate liquid (4 kgN/Mg, 2.7 kgNH$_4$-N/Mg, 0.1 kgP/Mg, and 1.8 kgK/Mg), and they were dependent on the mass and nutrient recovery and characteristics of the feedstock [65]. In other studies, processing of swine manure slurry to liquid fertilizer required electrical energy at the level 102.35–1462.46 kWh/m^3 [66].

3. Legal Regulations on the Use of Fertilizers in Poland

The basic legal act on fertilizer management in Poland is the Act of 10 July 2007 on Fertilizers and Fertilization [67]. This is a document that regulates in detail the rules for obtaining permits for placing fertilizer on the market and also contains important information on when the said permit may be revoked. It also defines regulations on packaging, storage, transportation, or information labels placed on fertilizer products. In addition, it includes restrictions on the use of fertilizers on frozen, flooded, water-saturated, or snow-covered soils, as well as the use of liquid natural fertilizers during the growth of plants intended for direct human consumption. It should be noted that this law, within the scope of its regulations, includes the implementation of Regulation (EC) No. 2003/2003 of the European Parliament and of the Council of 13 October 2003 on fertilizers [68].

The most important legal act on obtaining new fertilizers in Poland is the Regulation of the Minister of Agriculture and Rural Development of 18 June 2008, on the implementation of certain provisions of the Law on Fertilizers and Fertilization [69]. This document primarily defines four main groups of fertilizers (Table 5), as well as which fertilizers are exempt from the requirement to obtain a permit, and for which one is necessary (most fertilizers placed on the market, must have a permit from the Minister of Agriculture and Rural Development).

Table 5. Fertilizer groups with an indication of the need for a permit (own elaboration based on [69]).

Type	Characteristic	Required Permit
Mineral fertilizers	inorganic fertilizers, produced by chemical transformation, physical transformation or processing of mineral raw materials, including fertilizer lime, which includes fertilizer lime containing magnesium, as well as some fertilizers of organic origin	Yes—with the exception of fertilizers marked "EC FERTILIZER" and types of fertilizer lime in which impurities do not exceed the permissible values of impurities
Natural fertilizers	fertilizers intended for agricultural use without the addition of other substances, such as manure, guano, slurry	no
Organic fertilizers	fertilizers made from organic matter or from mixtures of organic matter, including composts, as well as composts produced using earthworms	yes
Organic-mineral fertilizers	mineral and organic fertilizer mixtures	yes

The document also specifies minimum percentages of nitrogen, phosphorus, and potassium for mineral, organic, and organic–mineral fertilizers in liquid and solid form. Table 6 summarizes these data for the liquid form of fertilizers. It is worth noting that this regulation indicates the permissible values of contaminants, mainly heavy metals, but only for fertilizers in solid form.

Table 6. Minimum quality requirements to be met by liquid fertilizers (own elaboration based on [69]).

Indicator	Fertilizer in Liquid Form		
	Mineral	Organic	Organic-Mineral
Nitrogen (N)	min. 1.0% (m/m) of total nitrogen	min. 0.08% (m/m) of total nitrogen	min. 0.5% (m/m) of total nitrogen
Phosphorus (P)	min. 1.0% (m/m) phosphorus per P_2O_5	min. 0.05% (m/m) phosphorus per P_2O_5	min. 0.2% (m/m) phosphorus per P_2O_5
Potassium (K)	min. 1.0% (m/m) potassium per K_2O	min. 0.12% (m/m) potassium per K_2O	min. 0.5% (m/m) potassium per K_2O

Sizable changes for the production and distribution of fertilizers within the European Union (including Poland) are being introduced by a new piece of legislation effective on 16 July 2022, which is Regulation (EU) 2019/1009 of the European Parliament and of the Council of 5 June 2019, laying down rules for making EU fertilizer products available on the market, amending Regulation (EC) No. 1069/2009 and (EC) No. 1107/2009, and repealing Regulation (EC) No. 2003/2003 [37]. Malińska (2020) [70] pointed out that the hitherto existing Fertilizer Regulation (EC No. 2003/2003) [68], focused on conventional mineral fertilizers, specifies, among other things, requirements for their quality In contrast, the new document (EU 2019/1009) [37] targets elements of a circular economy and points to the need to source fertilizers containing valuable plant nutrients (e.g., soil improvers, organic fertilizers) from organic waste or recycled materials. In addition, it is intended to encourage fertilizer manufacturers to develop new, innovative fertilizers from organic waste and bring them to the EU market. A study by Malińska (2020) [70] explained that once the new regulations are in place, a fertilizer producer in Poland will be able to act in two ways. The first action will be based on meeting the requirements of the new regulation and "CE" marking of the fertilizer product, which will allow it to enter the EU market. It should be noted here that the quality requirements for the various types of fertilizers in solid and liquid form are different from those in Polish legislation. In turn, the second way of proceeding will be based on the requirements of national legislation and the sale of the fertilizer product to another EU country based on the principles of mutual recognition.

4. Liquid Fertilizers Developed and Used in Poland

The use of conventional mineral fertilizers is increasing at an alarming rate due to the large and rapid growth of the world's population and the ever-increasing demand for food. Synthetic fertilizers can increase crop yields and development; however, their widespread use has serious negative consequences, such as salinization and soil hardening, which can lead to reduced soil fertility, increased pesticide accumulation, and water pollution [71]. Consequently, there is a great need to develop and exploit innovative alternative crop inputs; for example, liquid fertilizers that are produced from organic waste or recycled materials [72]. Such action is significant for organic farming, which is now a farming method widely used around the world. One of the new technologies used in organic farming is the mixing of agricultural biostimulants with mineral fertilizers. Agricultural biostimulants are substances of natural origin along with beneficial microorganisms. They can be used to activate seeds, plants, and soil. They improve nutritional efficiency, affect plant growth, and increase yield, and improve product quality [73].

On the Polish market there are many fertilizer products available in liquid form. Table 7 presents a selection of organic fertilizers in liquid form, giving their brief characteristics, fertilizer composition, and the number of the decision allowing the products to be marketed. Based on the collected data, several main components used in their production were extracted (Figure 2a). As can be observed, for the production of liquid organic fertilizers, the most common is the digest of various batch products (50% of cases). Algae are an equally important substrate; however, their use is much smaller than in the case of digestate. Molasses decoction and mine minerals have also been singled out for less intensive processing into these types of fertilizers. A small proportion of fertilizers are produced from baker's yeast. In the composition of liquid organic fertilizers, nitrogen, potassium oxide, and phosphorus pentoxide dominate, with the other components usually being a minor addition.

Table 8 shows a selection of mineral (inorganic) fertilizers in liquid form, along with their brief characteristics and composition, and it gives the number of the decision allowing the products to be marketed. Sulfur is one of the main substrates in the manufacture of these fertilizers (Figure 2b). Many liquid mineral fertilizers are also enriched with the ionic form of nitrogen. In addition, there are also magnesium, calcium, or iodine and silicon fertilizers (Figure 2b). In the case of mineral fertilizers in liquid form, nitrogen is the dominant component. These fertilizers consist mainly of ammonia water, calcium silicate, or sulfur-laced nitrate–urea solution. Of the fertilizers shown in Table 8, only mineral ammonium sulphate is made under anaerobic conditions from distillers' stock with sulfuric acid added.

The production of organic–mineral fertilizers in liquid form is mainly based on algae extracts, mine minerals, and plant extracts (Table 9, Figure 2c). To produce this type of fertilizer, digestate is also used. The composition of organic–mineral fertilizers is most often nitrogen, and these fertilizers are equally wealthy in organic matter and potassium oxide. It is also possible to separate out phosphorus pentoxide. More than 50% of the analyzed group of fertilizers also have an addition in the form of trace amounts of micronutrients in their composition.

The most numerous groups of liquid fertilizer products analyzed are soil conditioners (Table 10). They are mainly made from digestate; however, algae, mine minerals, micronutrients, and humic substances also make up a sizable share (Figure 2d). Such agents are rich in organic matter, potassium oxide, and nitrogen and its forms. Phosphorus pentoxide is slightly less common in the analyzed group of liquid products. As in the analysis of liquid organic–mineral fertilizers, soil conditioners are enriched in micronutrients. In addition, humic substances and even bacteria can be found in their composition.

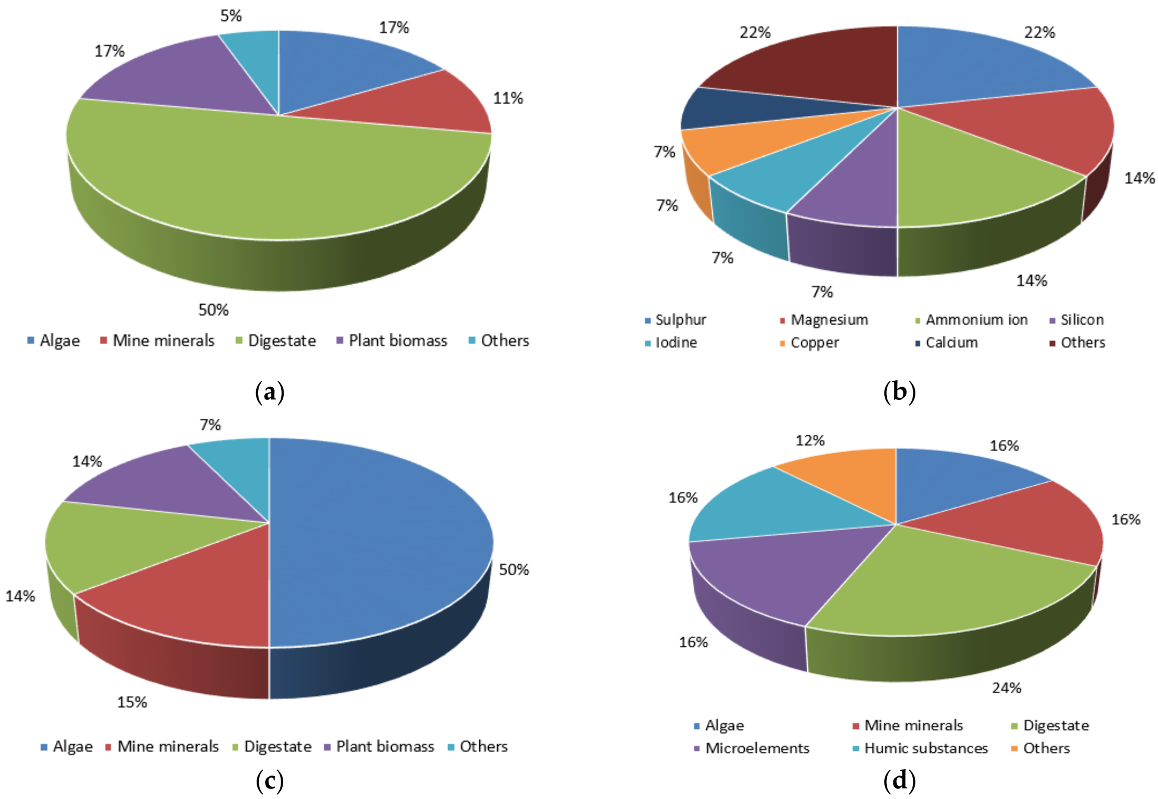

Figure 2. Input materials (micronutrients in the case of mineral fertilizers) used in the production of liquid organic fertilizers (**a**), mineral fertilizers (**b**), organic–mineral fertilizers (**c**) and in the production of soil conditioners (**d**) (authors' own elaboration based on Tables 7–10).

Table 7. Selected organic fertilizers in liquid form (authors' own elaboration based on [74]).

Commercial Name	Producer	Decision No.	Additional Information/Fertilizer Composition
AlfaMax	Agro Varichem Distribution LLC	313/12 from year 2012	Produced from algae. Contains: L-amino acids, hormones, auxins, gibberellins, cytokinins. Minimum parameters: N—1.0%, K_2O—2.5%, dry matter content—26%, TOC—5.5%.
AlgaPlant	VARICHEM LLC	284/11 from year 2011	Algae extract 36%. Contains: auxins, gibberellins, cytokinins. Minimum parameters: N—0.15%, K_2O—5.5%.
AlgaminoPlant	VARICHEM LLC	316/13 from year 2013	Brown algae extract, sargassum type and alphaaminoacids. Composition: N—1.56%, K_2O—2.94%.
DARINA	TORTRANS LLC	363/15 from year 2015	Minimum parameters: N—4.0%, P_2O_5—2.5%, K_2O—6.5%, organic matter content—30.0%.
FertiBio 48	Moolenaar BV	NE/338/2017 year 2017	Produced from corn grain. Composition: N—3.5%, P_2O_5—3.8, K_2O—3.0%.
FERMROL	IMA Poland S.A.	615/20 from year 2020	Produced by methane fermentation of distillers' stock. Composition: N—0.15%, K_2O <

			0.5%, TOC—26.9%, organic matter content—48.0%.
Gärrest	Biomethan Schöpstal GmbH & Co. KG	350/14 from year 2014	Produced from corn silage digestate, grass and GPS. Composition: N—0.47%, P_2O_5—0.18%, K_2O—0.53%, MgO—0.07%, organic matter content—76.9%.
Green Plon NPK	Bio-Wat LLC	371/15 from year 2015	Produced from the remains of methane fermentation of silage from agricultural raw materials, i.e., corn, rye, haylage, beet pulp, waste from oil plants, vegetable waste. Composition: N—0.43%, N-NH_4—0.15%, P_2O_5—0.18%, K_2O—0.35%, organic matter content—74.4%.
HUMI BROWN GOLD	Generiks LLC	549/19 from year 2019	Composition: N—0.29%, K_2O—1.13%, humic acids—79.0%, fulvic acids—21.0%, organic matter content—63.2%.
HUMIACID	"TOMATEX"	372/15 from year 2015	Produced from biogas digestate with a water content of 30%. Composition: N—0.15%, K_2O—0.58%, organic matter content—63.2%.
INNBIO	Laseffre Polish JSC	449/17 from year 2017	Produced from baker's yeast with the addition of bacteria Bacillus amyloloqiefaciens. Minimum parameters: N—2.4%, K_2O—3.5%, organic matter content—55.0%.
Konzentrat	GENO Bioenergie Leasingfonds Erste GmbH&Co. KG	257/11 from year 2011	Produced from corn silage digestate 82.2%, rye—5.1%, barley—1.4% and water—11.3%. Composition: N—0.6%, P_2O_5—0.15%, K_2O—0.45%, MgO—0.05%.
Nettle fertilizer	CDN Ireneusz Cal	479/18 from year 2018	Composition: N—0.2%, P_2O_5—0.1%, K_2O—0.2%, organic matter content—30.0%.
PLANTEO	Green Energy LLC	556a/19 from year 2019	Corn silage digestate, haylage and beet pulp. Composition: N—0.45%, N-NH_4—0.27%, P_2O_5—0.14%, K_2O—0.32%.
Biogas digestate, liquid form	Pfeifer & Langen Poland S.A.	491/19 from year 2019	Digestate from beet root fragments and pulp. Composition: N—0.34%, N-NH_4—0.17%, P_2O_5—0.07%, K_2O—0.19%, organic matter content—72.6%.
Presswasser	Biomethan Schöpstal GmbH & Co. KG	277/11 from year 2011	Plant pulp digestate. Composition: N—0.44%, P_2O_5—0.15%, K_2O—0.31%, organic matter content—73.2%.
GREEN ORGANIK	MAK Organic LLC	521a/19 from year 2019	Decoction of molasses with the addition of vegetable protein hydrolyzate. Composition: N—4.52%, P_2O_5—0.32%, K_2O—6.94%, CaO—0.35%.

Table 8. Selected mineral fertilizers in liquid form (authors' own elaboration based on [74]).

Commercial Name	Producer	Decision No.	Additional Information/Fertilizer Composition
Actifos	AGROPAK Ordinary Partnership; B. Pluta, G. Brzeziński, and Partners	241/10 from year 2010	Composition: N—10.2%, B—0.02%, Cu—0.08%, Fe—0.06%, Mn—0.04%, Mo—0.004%, Zn—0.02%.
ADIMIKS 7—solution 20%	Azoty-Adipol JSC	272/12 from year 2012	Composition: N—3.60%, $N\text{-}NH_4$—0.80%, $N\text{-}NH_2$—1.04%, $N\text{-}NO_3$—1.76%, P_2O_5—1.7%, K_2O—4.7%.
Aloes	BIOPON® Grzegorz Sobański	73/04 from year 2004	Minimum parameters: N—1.6%, $N\text{-}NO_3$—1.0%, P_2O_5—4.6%, K_2O—4.1%.
AMMIAK	TRANS-AMMIAK LLC	169/06 from year 2006	Ammonia water with a minimum $N\text{-}NH_4$ content of 20%.
BARRIER Si-Ca	Osadkowski S.A.	522/19 from year 2019	Produced from calcium silicate. Composition: CaO—1.11%, SiO_2—20.97%.
Bioflor popular	BIOPON® Grzegorz Sobański	55/04 from year 2004	Minimum parameters: N—3.0%, $N\text{-}NH_2$—2.2%, P_2O_5—1.2%, K_2O—2.4%.
FORTER	INTERMAG LLC	608/20 from year 2020	Composition: K_2O—6.31%, I—15.8%, Se—1.13%.
Insol 4	Fertilizer Research Institute	340/13 from year 2013	Composition: Mg—4.0%, B—0.5%, Cu—0.1%, Fe—0.35%, Mn—0.65%, Mo—0.005%, Zn—0.35%.
Mineral ammonium sulfate	Verbio Poland LLC	613/20 from year 2020	Distillers' stock from grain with the addition of sulfuric acid, produced under anaerobic conditions. Composition: N—8.49%, $S\text{-}SO_3$—24.4%.
NTS	Beiselen-ATR LLC	173/06 from year 2006	NS fertilizer, urea-ammonium nitrate solution with sulfur. Composition: N—27.3%, $N\text{-}NH_4$—8.0%, $N\text{-}NO_3$—5.9%, $N\text{-}NH_2$—13.4%, $S\text{-}SO_3$—3.4%.
OCTAN-PLUS	ALEKO Aleksandra Samuła	648a/21 from year 2021	Minimum parameters: CaO—6.65%, acetate content—18.9%.
PENTAKEE P-V	Agroniwa LLC	179/07 from year 2007	Composition: N—1.84%, P_2O_5—4.02%, K_2O—0.16%, CaO—3.73%, MgO—0.46%, organic matter content—41.28%.
PLONURAN LIQUID	ARYSTA LIFESCIENCE Poland LLC	118/05 from year 2005	Composition: Cu—22.4%.
RSM + S 27/3	Unibaltic Agro LLC	164/06 from year 2006	NS fertilizer, ammonium nitrate-urea solution with the addition of sulphate sulfur. Composition: N—27.6%, $N\text{-}NH_2$—13.6%, $N\text{-}NH_4$—8.2%, $N\text{-}NO_3$—5.8%, $S\text{-}SO_3$—3.1%.

Table 9. Selected organic–mineral fertilizers in liquid form (authors' own elaboration based on [74]).

Commercial Name	Producer	Decision No.	Additional Information/Fertilizer Composition
A.S.L	Verbio Poland LLC	353/14 from year 2014	Remains of methane fermentation of distillers' stock, cereal straw. Composition: N—10.2%, N-NH_4—8.28%.
ALGAREN BZn	GREEN HAS ITALIA JSC	513/18 from year 2018	Contains Ecklonia maxima sea algae extract. Composition: N—2.23%, B—2.02%, Zn—2.96%, TOC—6.58%.
BIOEKOR for geraniums and other balcony plants	EKOR WALKOWIAK Ordinary Partnership	108/04 from year 2004	Composition: N—3.6%, P_2O_5—6.0%, K_2O—7.0%, microelements.
BM Start	Laboratoires Goëmar SAS	481-18 from year 2018	Fertilizer containing MgSBMo with the addition of brown algae filtrate—Ascophyllum nodosum (GA 142). Composition: MgO—3.25%, S-SO_3—6.6%, B—2.09%, Mo—186 mg/kg, dry matter content—42.7%, organic matter content—73.8%.
CARBO'CAL	ARYSTA LIFESCIENCE Poland LLC	542/19 from year 2019	Contains Ascophyllum nodosum algae filtrate. Composition: CaO—15.4%, organic matter content—44.7%.
CARBO'FRUIT	ARYSTA LIFESCIENCE Poland LLC	543/19 from year 2019	Contains Ascophyllum nodosum algae filtrate. Composition: P_2O_5–27.02%, K_2O—7.87%, organic matter content—18.7%.
COLORADO	ARYSTA LIFESCIENCE Poland LLC	541/19 from year 2019	Contains Ascophyllum nodosum algae filtrate. Composition: CaO—2.8%, MgO—2.21%, Mn—1.86%, Zn—1.88%, organic matter content—58.3%.
FoliQ Aminovigor	Kazgod LLC	375/15 from year 2015	Fertilizer with the addition of corn extract. Composition: N—2.56%, B—0.28%, Cu—0.6026%, Fe—1.4459%, Mn—0.6148%, Mo—0.2266%, Zn—0.5466%, organic matter content—73.4%.
FoliQ® Ascovigor	Kazgod LLC	400/16 from year 2016	NK fertilizer with microelements with the addition of algae extract as an adjuvant. Composition: N—3.04%, K_2O—2.66%, B—4.15%, Mn—1.06%, Zn—0.59%, organic matter content—39.8%.
HALCZYNA	SENSO BARBARA KUKIEŁKA	616/20 from year 2020	Composition: N—1.55%, P_2O_5—0.5%, K_2O—2.05%, Mn—0.004%, Fe—0.237%, Cu—0.0002%, Zn—0.0007%, humic acids—4.69%, fulvic acids—0.69%.
HUMUS-ONE PERFEKT	TTT LLC	427/16 from year 2016	Extract of humic acids from leonardites with the addition of plant extracts. Composition: N—1.4%, P_2O_5—0.5%, K_2O—3.1%, TOC—19.0%.
Megafol	Amagro LLC	194/07 from year 2007	PK fertilizer, extract from fresh plant material—lucerne, seaweed, sugar beet molasses. Composition: N—3.2%, K_2O—9.03%, organic matter content—61.39%.

Rooter	Laboratoires Goëmar SAS	482/18 from year 2018	Phosphorus-potassium fertilizer with the addition of Ascophyllum nodosum brown algae filtrate (GA 142). Composition: P_2O_5—12.6%, K_2O—6.4%, dry matter content—23.7%, organic matter content—18.6%.
GREEN BUSH	HIMAL	273/11 from year 2011	A mixture of plant extracts with EC fertilizers. Composition: N—3.74%, P_2O_5—3.44%, K_2O—3.25%, Cu—895 mg/kg.

Table 10. Selected soil conditioners in liquid form (authors' own elaboration based on [74]).

Commercial Name	Producer	Decision No.	Additional Information/Fertilizer Composition
Acti Humus Pro	AGROSIMEX LLC	S-878/19 from year 2019	Humic acids from leonardites. Composition: K_2O—0.22%, Fe—0.013%, organic matter content—61.7%, humic acids—0.99%.
AGRO-plant	Producer Group Agro-Żabice LLC	G-1063/21 from year 2021	Digestate from a biogas plant that uses distillers' stock, haylage and molasses for the production of biogas. Composition: N—0.47%, K_2O—0.59%, organic matter content—54.4%, pH—7.9.
AGROVIT II	"BIOGAS SERVICE" LLC	G-183/11 from year 2011	Digestate obtained from stillage, waste plant mass. Composition: N—0.56%, K_2O—1.16%, CaO—0.14%, organic matter content—51.2%.
ALGEEN VIT	Biohumuseco LLC	696a/18 from year 2018	Minumum parameters: B—1.0–3.50 mg/kg, Zn—0.1–2.0 mg/kg, Fe—6.0-20.0 mg/kg, organic matter content—2.5%, dry mass content—6.0%.
ALGIN-PLUS	ITADAM.NET Adam Samuła	G-812/19 from year 2019	Algae extract. Composition: N—0.12%, P_2O_5—2.36%, K_2O—1.30%, TOC—14.1%, organic matter content—83.2%.
APOL-HUMUS	Poli-Farm® LLC	S-326e/20 from year 2020	Contains TOC in the form of dissolved humic substances—5.69 g/L.
ASX silicon plus	AGROSIMEX LLC	S-886a/20 from year 2020	Mineral salts (copper chloride, orthosilicic acid, boric acid) dissolved in a mixture of choline chloride, hydrochloric acid, sorbitol and Yucca extract. Composition: SiO_2—1.17%, B—0.47%, Cu—1.13%, organic matter content—85.6%.
Bactim soil	INTERMAG LLC	G-816/19 from year 2019	Minumum prameters: Fe—0.007%, Zn—0.007%, number of bacteria of the genus Bacillus spp. 5×10^8 cfu/mL.
Bio-algeen S90 plus 2	Service and Trade Enterprise Polger-Kido	S-3/08 from year 2008	Composition: N—0.02%, P_2O_5—0.006%, K_2O—0.096%, CaO—0.31%, MgO—0.021%, B—16 mg/kg, Fe—6.3 mg/kg, Cu—0.2 mg/kg, Mn—0.6 mg/kg, Zn—1.0 mg/kg.
Bioenergie flüssig	LINDHORST GRUPPE JLW HOLDING AG	G-810/19 from year 2019	Biogas digestate. Composition: N—0.56%, N-NH_4–0.26%, K_2O—0.55%, organic matter content—76.0%.
Biomethan - Liquid	Biomethan Zittau GmbH	G-184/10 from year 2010	Substrate after anaerobic fermentation of plant materials (corn, green rye, grass). Composition: N—0.47%, P_2O_5—0.11%, K_2O—0.67%.
Florahumus Liquid	Brown coal mine Sieniawa LLC	S-1040/21 from year 2021	Crushed brown coal from which humic acids are obtained in the form of salt. Composition: TOC–103.2 g/L, humic acids—88.8 g/L, dry mass content—21.3%, pH—9.0.
GAMAORGANIC	GAMAWIND LLC	G-1052/21 from year 2021	Distillers' stock from a biogas plant. Composition: N—0.43%, P_2O_5—0.12%, K_2O—0.17%, organic matter content—75.6%, pH—7.9.
Germinator SL	NaturalCrop Poland LLC	S-526/15 from year 2015	A concentrate of active humic and fulvic acids and bioactive chitosan (polymers of N-glucosamine and N-acetyl-glucosamine). Minimum parameters: TOC–7.5 g/L, macro- and microelements (N, P, K, Mg, S, Na, Cu, Zn, Mo, B).
GLEBOWIT II	ENEA Production LLC	G-323/13 from year 2013	Distillers' stock from an agricultural biogas plant. Composition: N—0.18%, K_2O—1.26%, organic matter content—8.15%.
GREVITAX	AVIS NATURALL Poland LLC	S-290/12 from year 2012	Organic grapefruit extract for watering or spraying.
HYDROHUMAT	AGROVITA LLC	G-557/16 from year 2016	Humic acids extracted from peat treated with sodium hydroxide and then with hydrochloric acid. Composition: N—0.52%, N-NH_4—0.04%, organic matter content—28.3%.
INGREEN SILVER	INWEX LLC	S-920/20 from year 2020	Hydrogen peroxide stabilized with silver. Composition: Ag—0.04%.
KELPAK	PUH CHEMIROL LLC	S-220d/19 from year 2019	Composition: TOC—0.36%, organic matter content—32.9%.
PERFEKT	ITADAM.NET Adam Samuła	G-813/19 from year 2019	Produced from leonardite. Composition: N—1.09%, P_2O_5—0.12%, K_2O—2.03%, TOC—18.0%, organic matter content—86.7%.
SEPTOVITAL 200	AGROSIMEX LLC	S-297/12 from year 2012	Crushed grapefruit, extracted with a solution of zucrroli. Composition: TOC—10.66%.
Synbio 600	AGROL Krzysztof Świerzewski	S-1049/21 from year 2021	Extract of humic acids from leonardites. Composition: dry matter content—5.1%, organic matter content—32.4%, pH—7.15.

TOTALSOIL	THE LLC	G-716/17 from year 2017	Composition: K_2O—2.62%, TOC—5.0%.
VANADOO	INTERMAG LLC	S-949/20 from year 2020	A mixture of ascorbic acid, vanadyl sulfate and sodium hydroxide. Composition: V—2.40%, organic matter content—46.50%.
ZumSil®	EMC DENARIUS D. Lempkowski	S-717/18 from year 2018	Contains silicon in the form of orthosilicic acid. Composition: SiO_2—18.83%.

The abovementioned data indicate that the main substrates, which are waste materials used in the production of fertilizers, are digestate and marine algae. Bioactive molecules derived from seaweed extracts are revolutionary biostimulants used to enhance plant growth and increase productivity. One of the organic fertilizers made specifically from seaweed is "True-Algae-Max" (TAM®), called a liquid extract, and a patent has been filed with the Egyptian Patent Office of the Academy of Scientific Research and Technology (application number: 2046/2019). It features nutrient values of 12%, 2.4%, and 1400 mg/kg, respectively, for total potassium, phosphorus, and nitrogen. According to ongoing research, this fertilizer is a good growth promoter for arugula, cucumber, and hot peppers [75–77]. Another use of seaweed, in terms of producing liquid fertilizers from waste, is the extraction of algae meal with water. The resulting extracts are rich in antioxidant properties. Therefore, an extraction step could be added to part of the seaweed meal processing to recover valuable compounds from fresh biomass and then used for fertilizer purposes [78].

A product developed specifically to meet the needs of sandy soil is DewEco. It is a liquid-type soil conditioning product that consists of low-molecular-weight organic materials produced by fermentation, developed by CJ (CJ CheilJedang Corp.; Seoul, Republic of Korea). It is characterized by its high water retention and cementing ability, as well as its high amino acid content. While on top, it is fully environmentally safe. It consists mainly of L-lysine and citric acid salt, which contains 50% organic matter and 4% nitrogen [79].

A waste material is also the digestate from biogas plants, and its use fits into the circular economy, as well as enabling a certain part of energy transformation. The organic waste produced after anaerobic digestion contains large amounts of nutrients. As research shows, during the separation of solids from liquids, more than 80% of nitrogen and 87% of potassium flows into the liquid parts [80].

A novel process to achieve a slow-release fertilizer is to acidify the digestate. This is a necessary process prior to the addition of wood ash to achieve a zero-charge point pH in the mixture [81]. In turn, Kovačević'ia's [82] research showed that the digestate can be used as a valuable source of nutrients for kohlrabi production, with a low risk of heavy metal contamination of the soil and plants. It was noted that the liquid phase of digest increased the leaf weight of kohlrabi, similar to mineral fertilizers. Other research shows that the use of digestate from agricultural biogas plants reduces the environmental risks that are associated with the use of mineral fertilizers while achieving comparable yield parameters for agricultural plants. The liquid phase of the digestate was also used to improve hemp production, and it was characterized by about twice the total nitrogen content compared to the solid phase. According to the research of Velechovský et al. [83], fertilization with the liquid phase of the digestate (qualitative composition in Table 11) showed the second highest increase in hemp, whereas the highest growth was recorded for joint fertilization—initially with the solid phase and then with the liquid phase [83]. Similar results were obtained by Yi Ran et al. [84], who studied the effect of the digestate on the growth, yield, and quality of rice. In this case, too, the best results were achieved when both phases of the digestate were used. Moreover, it was shown that liquid digest can increase the number of rice spikelets and thus grain yield [84].

Table 11. Quality composition of liquid phase of digest for hemp fertilization [83].

Dry matter %	pH_{H2O}	EC mS/cm	TN mg/kg	P mg/kg	K mg/kg	Ca mg/kg	Mg mg/kg	S mg/kg
6.04 ± 0.127	8.35 ± 0.353	>4000.0 ± 0.0	57,800.0 ± 1265.0	12,912.0 ± 562.0	42,988.0 ± 1214.0	39,996.0 ± 25,860	4268.0 ± 272.0	3228.0 ± 342.0
Fe mg/kg	**Zn mg/kg**	**Cu mg/kg**	**B mg/kg**	**Mn mg/kg**	**Pb mg/kg**	**Cd mg/kg**	**Cr mg/kg**	**As mg/kg**
267.0 ± 96.0	251.0 ± 68.0	6.1 ± 0.52	76.5 ± 12.5	189.0 ± 15.7	0.9 ± 0.02	0.09 ± 0.001	1.01 ± 0.02	3.79 ± 0.12

The fertilizer properties of liquid digestate have also been studied in terms of hydroponic cultivation of young lettuce in greenhouses. The results of a study published by Ntinas et al. [85] indicate the effective use of liquid digestate (qualitative composition in Table 12) as a fertilizer in hydroponic cultivation of young lettuce in a greenhouse using a floating system. It was noted that the quality characteristics of young lettuce showed increased antioxidant capacity and efficient production of secondary metabolites. It should be noted that the liquid fertilizers discussed above and available on the Polish market do not contain animal by-products, which are also the substrate in the production of fertilizers in liquid form. As a supplement, it is worth pointing out that there are two fertilizer products available in liquid form in Poland, developed, among others, based on sewage sludge (OBORNIAK_P and ELKA-AGRO [74]), but they also contain animal by-products, so these products were not included in the study. The reduction of nutrient concentrations in the growth media showed increased recovery of residual resources, which may suggest that the use of digestate is capable of partially replacing some inorganic fertilizers.

Table 12. Quality composition of liquid phase of digest for lettuce fertilization [85].

N mg/dm^3	P mg/dm^3	K mg/dm^3	Ca mg/dm^3	Mg mg/dm^3	Na mg/dm^3	Fe mg/dm^3
331.33 ± 47.65	153.62 ± 12.89	470.25 ± 2.05	12.9 ± 3.25	3.38 ± 0.31	106.2 ± 1.13	4.2 ± 1.56
Cd mg/dm^3	**Cu mg/dm^3**	**Cr mg/dm^3**	**Ni mg/dm^3**	**Mn mg/dm^3**	**Pb mg/dm^3**	**Zn mg/dm^3**
0.01 ± 0.0	0.4 ± 0.1	0.05 ± 0.01	0.28 ± 0.01	0.02 ± 0.0	<0.042	2.42 ± 0.1

The analysis of the topic indicates that the properties of the substrates used in the production of fertilizers (algae, digestate, mine minerals) determine the result of the finished product. Fertilizer properties are determined first by the qualitative characteristics of the feedstock, and in the next degree by the technological process of their processing. In the following section, the qualitative characteristics of the most used waste feedstocks in liquid fertilizer production are presented.

5. Characteristics of the Most Used Waste Materials in the Production of Liquid Fertilizers in Terms of Their Fertilizer Properties

5.1. Algae

The development of methods for processing algae, especially the improvement of liquefaction technology, has made it possible to use them as a product with fertilizer properties on a larger scale and primarily outside coastal areas [86]. It should be kept in mind that in the natural environment, algae also pose a threat, as their growth is caused by excessive eutrophication, which leads to the dying of seas and bays. In addition, algae carried by waves linger on surrounding beaches, causing pollution [87]. However, the collection and use of algal biomass, which is a renewable resource rich in valuable active ingredients for fertilizer purposes fits in with the principles of sustainable agriculture and processing, while reducing the energy and emission intensity of fertilizer production. However, it should be remembered that the availability of this raw material is not regular [87,88]. Due to the occurrence of algae extracts mainly in liquid form, they can provide a good base to produce fertilizers of this consistency. According to Battacharyya et al. [89], algae have a positive effect on the yield of vegetable plants; moreover, they can positively influence their shape or support development processes [89]. Mukherjee and Patel [90] showed that algae extracts can be used for seed treatment, soil fertilization, or foliar application, the latter form of application can leave spots on the leaves, which can negatively affect the appearance of the leafy part of the vegetable (Mukherjee and Patel, 2019). A research study shows that the application of algae extracts has a positive effect on the growth of hydroponic leaf lettuce [91]. The types and characteristics of chemical compounds present in algae, along with their role in plant fertilization, are included in Table 13.

Table 13. Chemical compounds present in algae with an indication of their role in fertilization (authors' own elaboration).

Parameter	Example of Compounds	Role	References
Phytohormones	auxins, cytokinins, gibberellins, abscisic acid, ethylene	stimulation of stem elongation and leaf bud opening, regulation of RNA protein synthesis, enzyme activity, stimulation of flower production, increasing pollen viability and zygote viability, induction of seed germination, inhibition of lateral shoot growth	[92–94]
Polyamines	putrescine, spermidine	growth regulator, seed germination stimulation, pollen tube growth, anti-cellular aging, resistance to stressors	[95,96]
Polysaccharides	alginic acid	rheological properties that allow the fertilizer to adhere to the leaves	[97]
Elements (micro- and macroelements)	zinc, copper, bromine, iodine, iron, magnesium, manganese, calcium, phosphorus	properties that encourage bees to pollinate flowers, chlorophyll synthesis, electron transport to produce organic parts of carbon	[98,99]
Sugar alcohols	mannitol	improved uptake and transport of nutrients in the plant, stimulation of polyamine synthesis	[98,100]
Isoflavonoids	phytoalexins	inhibition of pathogen growth, protection against UV radiation and heavy metal ions and thermal shock	[100,101]
Amino-acids	glycoproteins, alanine, glycine, lysine, serine, leucine, methionine, tryptophan, valine	increasing the assimilation of fertilizer by plants, forming organic connections with nutrients, increasing the efficiency of photosynthesis	[98,102]
Vitamins	A, E, C, D, β-karoten	resistance to low temperatures, increased smog tolerance, intensification of photosynthesis, improved fruit quality, root system formation and germination	[98,103]

5.2. Digestate

The main purpose of methane fermentation of waste is to produce biogas. However, this process contributes large amounts of digestate. It is assumed that a 1 MW biogas plant produces about 20,000 m^3 of digestate per year [104]. The composition of the digestate will be closely related to the type of co-substrate added to the anaerobic digester [105]. The process of anaerobic digestion is strongly influenced by the pH and temperature of the substrate, the type of substrate, and the amount of water in relation to the organic substrate [106]. The digestate, or liquid produced by the anaerobic digestion of green plant waste, can be rich in ammonium nitrogen and other nutrients important for plant growth, and can therefore be used as an organic fertilizer. Whether the digestate or liquid resulting from anaerobic digestion can be used as a fertilizer or soil conditioner is determined, among other things, by the type and properties of the substrate, the concentration and form of nutrients (mainly N, P, and K) in the digestate or liquid, and the nutrient requirements of the target crop [107]. Nevertheless, the digestate, a byproduct of anaerobic digestion, can often exhibit characteristics that limit its recycling through direct use in agricultural soils [108,109]. Consequently, anaerobic fermentates require post-treatment to increase their fertilizer value and use as a soil conditioner [110,111]. One option is to separate the digestate into a liquid and solid fraction, with the latter being composted to produce valuable and marketable agricultural end products [112]. For example, high humidity and high volatile fatty acid content can be phytotoxic [113] and may limit its use on agricultural soils without treatment [110]. Furthermore, fermentates can be a source of pathogens if the fermentation process was not carried out under thermophilic conditions [113]. Digestate treatment by solid–liquid separation is increasingly used to produce phosphorus-containing solid digestate and liquid digestate, containing water-soluble nitrogen and potassium. The solid–liquid separation of the digestate divides most of the mass into the liquid fraction, decreasing its nutrient concentrations [114]. Low nutrient concentrations and large mass complicate the use of the liquid digestate in agriculture and increase transportation requirements [115]. To efficiently utilize the nutrients, treatment of liquid digestate is needed to decrease its mass and increase nutrient concentrations [65].

In the present article, the digest resulting from a feedstock devoid of zoonotic products is analyzed. Table 14 lists the macro- and micronutrients present in the digestate, along with a brief characterization of those relevant to fertilizing plants and soils.

Table 14. Composition and role of elements present in the digestate (authors' own elaboration).

Parameter	Role	References
Nitrogen (including the ionic form of NH_4^+) *	extension of the vegetation period, stimulation of proper plant development and growth of aboveground and underground parts, maintenance of proper green color	[116–118]
Phosphorus (including the ionic form of PO_4^{3-}) *	formation and growth of the root, increase the ability to form flowers and fruit, participation in ATP production	[118,119]
Potassium	increase disease and pest resistance, stimulation root system growth, resist cold, regulation plant water management, stimulation starch and sugar production	[120,121]
Calcium	strengthening of the root system, resistance to stress factors such as drought and frost, strengthening of mechanical tissues	[122]
Magnesium	participation in photosynthesis, mineral uptake, chlorophyll component, stimulation root system development	[99,123]
Iron	reducing the action of nitrates, enabling normal growth and development, participation in the formation of chlorophyll, transporting electrons to produce organic carbon compounds, participation in the process of photosynthesis	[124]

Copper	influence on the growth and development of the plant, influence on tissue structure, protein and vitamin C synthesis, develop more grain, strengthen resistance to permanent bending of stems	[125]
Manganese	influence on nitrogen management, support root growth deep into the soil profile, improve resistance to stress factors, toxic effect on soil pathogens, participation in photosynthesis and chlorophyll formation process	[99,126]
Zinc	increase plant resistance to diseases, influence on the yield, increase plant growth dynamics, enhance biological activity of roots	[127,128]
Organic carbon, organic matter	water retention in soil, source of humus in soil, renewable source of nutrients for plants	[129]

* ionic forms are much more easily absorbed by plants (according to information in [130]).

Table 15 summarizes the quality parameters of chosen feedstock materials used in the fermentation process and the obtained digestates.

Table 15. Average values for individual parameters characterizing the feedstock and the resulting digest (own elaboration based on [131]).

Parameter	**Distillers' Stock**		**Maize Silage**		**Maize Silage + Beet Pulp + Apple Pomace**		**Beet Pulp + Maize Silage + Distillers' Stock**		**Maize Silage + Beet Pulp**	
	F *	**D ****	**F ***	**D ****	**F ***	**D ****	**F ***	**D ****	**F ***	**D ****
Unit	**[mg/g s.m.] [%] ^**	**[g/dm^3]**	**[mg/g s.m.]**	**[g/dm^3]**	**[mg/g s.m.]**	**[g/dm^3]**	**[mg/g s.m.]**	**[g/dm^3]**	**[mg/g s.m.]**	**[g/dm^3]**
Mg	22.1	0.14	2.4	0.04	2.3	0.05	2.2	0.03	2.3	0.02
Ca	20.2	0.15	4.5	0.02	9.2	0.06	9.2	0.04	9.2	0.07
K	70.6	1.14	9.3	0.15	9.0	0.17	8.6	0.31	7.1	0.19
Fe	4.1	0.03	1.4	0.02	0.9	0.02	0.7	0.01	0.5	0.02
TN NH_4^+ ***	75.4	2.18 1.91	2.1	1.50 1.44	1.6	1.29 1.18	2.7	1.53 1.44	1.5	1.47 1.38
DM ^ TSS ^^	4.1	16.2	27.3	10.7	26.4	10.5	19.3	13.8	23.2	20.5
OM ^ OS ^^	82.1	15.6	88.4	10.5	84.8	9.60	88.8	12.8	89.1	18.7

* feedstock; ** digestate; *** value for the ionic form; ^ unit/parameter relating to the feedstock; ^^ parameter for digestate.

Based on the data in Table 15, it is recognized that the feedstock with the highest content of Mg, Ca, K, Fe, TN, and NH_4^+ is distillers' stock. On the other hand, the most organic matter is contained in mixing maize silage together with beet pulp, but it is worth noting that this parameter is comparable for the juxtaposed waste materials. In addition, it can be concluded that the composition of the input materials used translates this into the composition of the digestate, and the highest values of micro and macronutrients were recorded just for the digestate from distillers' stock. The most favorable content of organic suspended solids is characterized by the digestate from a mixture of maize silage together with beet pulp.

An analysis of the scientific literature also indicates that it is possible to convert digestate from anaerobic digestion into fertilizer by composting. Then, it is possible to obtain organic fertilizer in a two-stage process: first fermentation and then composting under aerobic conditions. In such a technological system, composting may be a feasible treatment to stabilize the digestate and thus improve its properties for use as a soil conditioner or substrate [109,111,132]. For example, the direct use of digestate from food waste fermentation leads to a 60–70% nitrogen loss through NH_3 volatilization due to its properties, such as high levels of ammonium nitrogen (NH_4^+–N) (~6000 mg/kg dry weight) and high moisture levels (~75%). Therefore, biostabilization of digestate through composting is a promising solution to reduce environmental risks and improve fertilizer efficiency [133].

5.3. Mine Minerals

To produce fertilizers, waste mineral raw materials—minerals, which include peat, lignite, or leonardite—are also used. In fertilizers they are present in crushed form in suspension or liquid form. The content of humic acids separated from leonardite is several times higher than that of peat and lignite [134]. An aqueous suspension of leonardite applied at the early stage of onion growth improves root growth and development, as well as equalizing plant emergence [135]. Research also shows that fertilization with leonardite, combined with algae extract, has a positive effect on the chemical composition of carrots and reduces nitrate content by more than 30% [134]. Humic substances, which include humic acids, fulvic acids, humins, and ulmins, are the main component of min minerals. Gawroński [136] reports that these compounds increase the sorption capacity of the soil, bind micronutrients in the soil profile, which facilitates their uptake by plants, and also contribute to the sorption of heavy metals. In addition, according to the literature, they are involved in improving the transport of mineral compounds and have a positive effect on seed germination and seedling development. In seed treatment, they affect the rate of germination and increase the amount of chlorophyll in the leaves. They exhibit protective properties against the toxic effects of hydrogen peroxide and free radicals and increase the microbial activity of the soil [92,137]. It is worth noting that humic and fulvic acids sorb PAHs much faster compared to humins [138]. Humic substances, as a component of liquid fertilizers, are also responsible for the formation of chelating compounds that determine the utilization of nutrients by plants, reduce the activity of iron and aluminum ions, reduce the mobility of heavy metals, and further affect the thermal properties of the soil and optimize air–water relations [136].

6. Conclusions

The conditions of the market economy and the fact that the cost of fertilization in plant-growing technologies is a significant item in the structure of direct costs, determine the need to look for more effective and, at the same time, environmentally safe ways to fertilize cultivated plants. There is currently an opportunity to provide agriculture with a new generation of fertilizers with greater efficiency and controlled action amd having maximum limited negative impact on the environment. Fertilizers that meet such requirements are liquid fertilizers. The system of liquid fertilization of crops provides precise dosage of plant nutrients; greater possibility of adjusting the composition of fertilizer to the nutritional needs of plants; high flexibility in the selection of fertilizer mixtures; lower production costs compared to solid fertilizers; and reduced losses associated with storage, transport, and application. This paper provides examples of the use of the above-mentioned substrates, processed into liquid fertilizers, emphatically demonstrating their positive impact for agricultural and, moreover, in line with the principles of sustainable development.

The main conclusions of the study are as follows:

- There is an opportunity to use waste products to produce liquid fertilizers due to their plentiful composition in plant and soil nutrients. In addition, managing waste products and demonstrating their reuse fits perfectly with the principles of a circular economy;
- In Poland the main substrates for liquid fertilizer production are mine minerals, algae, and digestate. The analysis shows that the latter substrate is most often used to produce organic liquid fertilizers (in 50% of cases), whereas in the production of organic–mineral fertilizers, the dominant base is algae. The largest group of fertilizer products are soil conditioners, produced most often from digestate, but also from mine minerals, algae, humic substances, or with the addition of micronutrients;

- The production of liquid fertilizers from waste materials seems to be an alternative to mineral solid fertilizers, as less energy is required to produce them and other mineral resources are not required;
- A sizable portion of this type of fertilizer is produced through the operation of biogas plants and can be used locally for fertilizer purposes, which is important in reducing carbon emissions and energy consumption for transportation;
- A major limitation during the creation of this work was the lack of research on the energy intensity of the liquid fertilizer industry, which may be a direction for future research, as this field is expected to grow significantly;
- Production of liquid fertilizer from waste is an economical solution for liquid fertilizer production due to the rather high cost determined by electricity consumption;
- It seems that a good direction for research now is to learn about the properties of different groups of wastes and the possibilities for their transformation and reuse;
- Management of the liquid form of sewage sludge free of animal products for fertilizer purposes may also be a correct direction of research in Poland.

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Abbreviations

AN	Ammonium Nitrate
AS	Ammonium Sulfate
ATP	Adenosine Triphosphate
BAT	Best Available Techniques
BTU	British Thermal Unit
CAN	Calcium Ammonium Nitrate
CE	Conformité Européenne
CJ	CheilJedang Corporation
D	Digestate
DM	Dry Matter
EC	Electrical Conductivity
F	Feedstock
HHV	Higher Heating Value
KN	Pottasium Nitrate
LHV	Lower Heating Value
MAP/DAP	Mono-and Diammonium Phosphate
MOP	Muriate of Potash
OM	Organic Matter
OS	Organic Suspension
RNA	Ribonucleic Acid
SOP	Sulphate of Potash
SSP	Single Superphosphate
TAM®	True Algae Max
TN	Total Nitrogen
TOC	Total Organic Carbon
TSP	Triple Superphosphate
TSS	Total Suspended Solids
UAN	Urea Ammonium Nitrate

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