

Use of Fatty Acids in Fertilizer Formulation: A Systematic Review

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Abstract

Synthetic fertilizers have been a subject of socio-environmental challenges. A more sustainable approach is necessary to develop these farm products. Thus, this review presents a strategy for fertilizer production by utilizing fatty acids and by-products derived from renewable sources. However, given the scarcity of data on the topic in scientific journals, this review used the PRISMA report methodology from patent databases. Results show that China is this field's most significant intellectual property holder. Patents were predominantly vegetable-based (60%), mixed (14%), and animal-based (8.47%), with innovations including liquid fertilizers of plant and animal-based fatty acid esters, as well as the use of controlled-release technology. 80.60% of fertilizers were applied to the soil, followed by foliar application (12.75%) and seed application (0.60%). Notable contributions included fertilizers acting as pesticides and anti-caking agents. Thus, we realize the urgency of continuing scientific research to pursue more responsible and efficient agricultural practices.

Introduction

Fertilizers are fundamental in food quality, agriculture productivity, and soil nutrient deficiency mitigation (Aghai et al., 2019; Brasil, 2004; Maciel & Tunes, 2021; Sinha et al., 2022; Yin et al., 2023). However, one of the challenges in agricultural practices is using sustainable products. The demand for food (Sekhon, 2014; Vejan et al., 2021) faces environmental limitations and the search for innovative fertilizers while avoiding synthetic chemical fertilizers. Furthermore, the excessive usage of fertilizers results in a drastic efficiency reduction and causes severe environmental and ecological issues (González et al., 2015). Therefore, developing proper cultivation techniques and a better understanding of the soil microbiome is imperative to guarantee nutrient availability, pathogen resistance, and ecophysiological functionality while facing biotic and abiotic stress (Aghai et al., 2019). This approach could facilitate the restructuring of deteriorated zones through reforestation and restoration. A promising strategy for facing environmental challenges associated with using conventional fertilizers is to utilize plant-based oils or their by-products in the composition or mixture of fertilizers.

Plant-based oils are mainly composed of triacylglycerol, with minimal quantities of diacylglycerol and monoacylglycerol, while also composed of phospholipid, free sterols, tocopherols and tocotrienols, triterpene alcohol, hydrocarbons, and small amounts of liposoluble vitamins, either saturated or unsaturated (Guidoni et al., 2019). The global production and consumption of vegetable oils has experienced notable growth from 2013 to 2021, as Teixeira et al. (2022) concluded. Palm oil (77,56), soy oil (60,21), canola oil (32,11), sunflower oil (20,58), and others (Murphy et al., 2021; Zeferino & Ramos, 2023) compose most of the plant oil production in millions of tons during 2022-2023. These oils perform an essential role and potential in many pillars of the economy (Gomes et al., 2022; Pinto et al., 2014) (Finlay & Andrew, 2018) (De Lima Da Silva et al., 2010; Pantoja et al., 2019). In agriculture, they represent an essential progress, having many utilities: manual fruit thinning Moran et al. (2000), nutrient coating (S. Yuan et al., 2022), controlled nutrient release, and quick decomposition (Feng et al., 2019). Moreover, plant oils represent a valuable source of essential predecessors for synthesizing a variety of fatty acid esters.

These compounds have been identified as viable components to be integrated into fertilizer formulation, which is obtained through the processes of esterification and transesterification (Li et al., 2023; Oo et al., 2021). It is fundamental to reiterate that chemical-physical and Biotechnological methods have been investigated as sustainable means of producing these compounds (Li et al., 2023; Oo et al., 2021).

Fatty acid esters are considered surfactants, resulting in a more considerable fertilizer scattering. They are also biodegradable, which is highly desirable for direct environmental application. Furthermore, they are compatible with the nutrients, allowing a slow and efficient release of the fertilizer, amplifying absorption, stability, and solubility (Ríos et al., 2024). This approach aims to produce ecologically friendly fertilizers, allowing for less usage of non-renewable resources.

The integration of oils in fertilizer composition represents not only a sustainable option for fertilizer additives but can also diminish the environmental issue of indiscriminate oil dumping. In Brazil, only 2.5% of kitchen oil residue is submitted to recycling processes, while the majority is dumped in sewer systems, generating considerable consequences. For example, during the rainy season, there's a 26% increase in flood cases due to the inappropriate unloading of said oils (Abiove, 2023; Sabesp, 2016).

The inadequate disposal of oil residues significantly reduces the diameter of domestic plumbing and blockage of sewer systems when the oil cools and hardens, forming a solid barrier that demands complex procedures to unblock said sewage system. (Sabesp, 2016; Thode Filho et al., 2017). Thode Filho et al. (2017) highlight that the improper disposal of oils and fat, both in a domestic and industrial context, leads to the pollution of water sources, impermeabilization of the soil, and negative impacts on wildlife of these contaminated aquatic environments, among other harmful effects. Considering the lack of information in our current literature regarding such an approach, this paper seeks to elucidate some scientific gaps in the potential applications of oils, specifically their fatty acid by-products, as a material or ingredient for fertilizers using a systematic review in patents. The patents are intellectual property derived from an incentive for innovation, assigning inventors or owners exclusive rights to their discoveries for a limited time. (Khalil & Onyango, 2022).

Methodology

The selection of patents was performed on the 5th of October 2023, through a systematic review methodology based on the Preferred Reporting Items for Systematic Reviews and Meta-Analyses method (PRISMA) (Page et al., 2021), which guided a search in the following databases: Lens, Espacenet, and Patentscope with the keywords “fatty acid AND fertilizer.” They were directly removed from the database by separating

each patent family to avoid duplicates. The data of each document was formatted in CSV, and missing or contradictory were manually added to improve the database. Patents were selected through specific criteria: all the years available in the databases, exclusively in English, and fertilizer technology based on fatty acid. Excluded patents were either inconsistent, lacked clarity in their invention or its description, lacked a publication date, and, although they contained the keywords, were unrelated to fatty acid-based fertilizers.

Results and Discussion

General Characteristics of The Patents

Study selection

In this systematic review, a total of 1497 results were identified in the databases Lens (702), Espacenet (333), and Wipo (462). After an automatic screening, 225 results were excluded, which contained duplicates and non-encountered files. After manual evaluation with specific criteria, 796 patents ended up being removed. In the end, 259 texts were carefully evaluated. These documents included fertilizer inventions that incorporated fatty acids, or fatty acids reacted with salts, sugars, and other compounds for many purposes. The flowchart of this screening process and selection of patents can be observed in Figure 1.

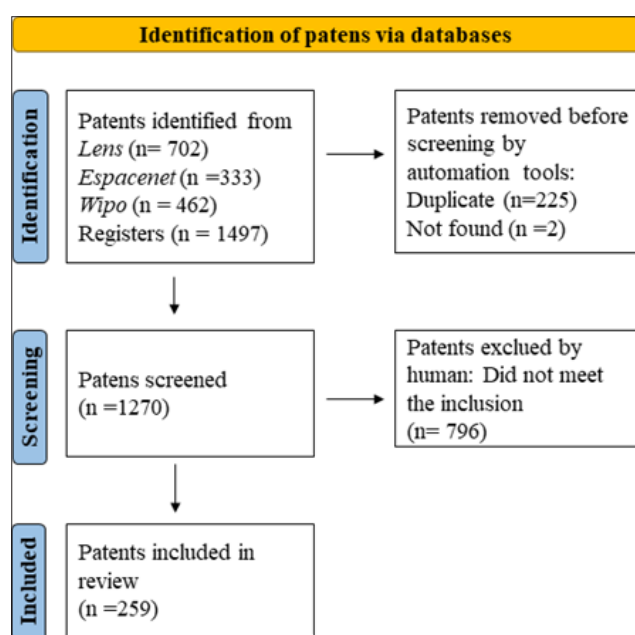


Figure 1: Flowchart of screening and selection of patents

Patents per country

Patents included in this systematic review are distributed between North America (United States and Canada, n = 15), Asia (Japan and China, n = 199), Europe (France, Spain, Germany, United Kingdom, and Holland, n = 26), Europe or Asia (n = 2), and non- identified (n = 7), as shown in Figure 2, a map of the distribution of countries that registered patents related to fatty acid-based fertilizers.



Figure 2: Number of patents per country

China had the most considerable registered patents on fatty acid-based fertilizers ($n=169$). This phenomenon can be explained by the need for China to expand its agricultural practices to provide food for approximately a quarter of the world's population while having less than 10% of the world's cultivable soil (Guo et al., 2022; HU et al., 2019). Due to this, China has become the largest consumer of fertilizer, with around 40% of the world's total consumption (Good & Beatty, 2011; Guo et al., 2022; HU et al., 2019). Furthermore, they also produce most of the essential components for fertilizers, notably nitrogen, partaking in 40% of the world's production and 30% of exports (Palhares et al., 2022). However, the excessive usage of fertilizers in China between 2008 and 2015 has significantly surpassed safety limits determined by international security norms (Cai et al., 2018; HU et al., 2019). Furthermore, the efficiency of fertilizer usage in China is below 50% (HU et al., 2019), which could motivate the development of patents for more efficient and sustainable fertilizers.

The haphazard usage of fertilizer and its inefficiency could cause air and water pollution and soil saturation (Cai et al., 2018; Feng et al., 2019; Guo et al., 2022). Within the selection of patents originating from China, it has been found that 18,34% of fatty acid-based fertilizers are classified as anti-caking. These compounds can prevent the formation of lumps, allowing a higher efficiency in the spreading and absorption of said compounds. These effects reduce the loss and degradation of the materials (Tyc et al., 2020). Lump formation is significantly mitigated by the presence of amphiphilic compounds, including fatty amines and acids, used to formulate anti-caking agents (Umerska et al., 2016). These components demonstrate a capacity to reduce interfacial energy both on the crystal's surface and in its solution, resulting in an effective blockage of crystalline nuclei (Tyc et al., 2021a).

Patents per year

As shown in Figure 3, patents related to fatty acid-based fertilizers increased progressively from 1957 to 2023.

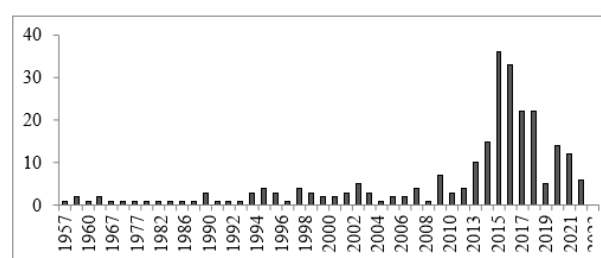


Figure 3: Number of patents per year

Up to 1986, the registration of patents remained relatively low, with unremarkable variations. Between 1990-1993, this scenery changed, with an increase and a reduction. Starting from 1994, a new increase was registered, presenting oscillations every four years up to 2013. In the global context, mineral fertilizers showed a rise of about 13,57% between the years 2000/2001 and 2011/2012, with a notable reduction in 2008/2009 due to the financial crisis, which had a negative impact in all sectors of the economy, including the mineral fertilizer (Lubkowski et al., 2015). Over time, these events demonstrate the complex relation between factors that move forward or backward the flow of innovation and development on patents for fatty acid-based fertilizers.

In the context of our study, 2014 was marked by the most extensive listing of patents associated with this subject, maintaining a linear growth until 2016, followed by a reduction in the following years. In 2020, there was a significant reduction in the registration of patents linked to the COVID-19 pandemic, which could have impacted the development of new fertilizers, with companies focusing on the research of vaccines (Sousa Neto et al., 2023). Subsequently, there was an increase followed by a reduction in 2022, probably due to a cyclical behavior. An increase in fertilizer technology development is expected for 2024-2025 due to the war in Ukraine, which began in 2022. The war caused an increase in the inorganic fertilizer supply (Shahini et al., 2022), which forced the search for new alternative formulations. This unraveling illustrates the complexities involved in the dynamic of patents during different historical events and specific contexts.

Emerging Technologies for The Production of Fertilizers

The conventional processes for fertilizer fabrication, such as Haber-Bosch, Ostwald, and granulation, have been fundamental in the large-scale production of fertilizers, providing the basis for modern agriculture (Alhasan et al., 2024; Chu et al., 2022; Goodwin et al., 2024; Haber & Le Rossignol, 1913). However, these methods have faced efficiency challenges due to the excessive usage of nutrients in agriculture (González et al., 2015). To face these challenges, microencapsulation, nanoencapsulation, and hydrolysis are innovations that represent a significant evolution in fertilizer production. These approaches provide efficient nutrient delivery, contributing to sustainable and efficient agricultural practices.

Microencapsulation and nanoencapsulation are framed in encapsulation, which consists of withholding several biological substances with the finality of slow and controlled release in specific conditions (Akhavan et al., 2018).

Microencapsulation involves coating particles with a polymeric film, which is widely used for the prolonged release of compounds, such as pharmaceuticals and fertilizers. It aims to optimize efficiency, converting liquids into powder, stabilizing substances, avoiding incompatibilities, and reducing toxicities to benefit various applications (Kalkumbe et al., 2022). Pour et al. (2022) conducted microencapsulation of *Bacillus velezensis* utilizing alginate polymer enriched with TiO₂ and SiO₂ nanoparticles. Results indicated that these compounds demonstrated remarkable efficiency, reaching bacteria encapsulation and release rate of 97,3%. According to the authors, this process might have elevated efficiency when applied to the soil. Fatty acid usage in this formulation can be due to the capacity of lipid structures to increase the lifetime of encapsulated microorganisms compared to free microorganisms (Pedroso et al., 2012; Vaziri et al., 2018). Vaziri et al. (2018) point out that co-microencapsulation between bacteria of the species *L. Plantarum* and fatty acids, such as Docosahexaenoic Acid (DHA), could optimize the release of nutrients, presenting better economic viability when considering the reduction of processing costs. Fatty acid contributes to the stability and efficiency of microencapsulation, assuring a more efficient delivery of essential nutrients. When applied to fertilizer production, this synergy emerges as a promising strategy for preserving bacteria viability, potentializing its capacity for plant growth stimulation, and facilitating plant nutrient absorption.

Nanoencapsulation from lipid-based formulas are nanometric structures that can possess active substances, providing protection, higher solubility, bioavailability, and controlled release of encapsulated components (Akhavan et al., 2018). In a study by Umerska et al. (2016), lecithin or fatty acid with less than ten carbons was added to lipidic nanostructures, arranging higher particle stability, which avoids caking and is essential for maintaining uniform dispersal of nanostructures in liquid systems, such as emulsions or suspensions.

On the other hand, hydrolysis is a chemical reaction in which

one substance reacts with a solvent, resulting in the severing of the original substance's chemical bonds.

Hydrolysis is a process that converts triglycerides and fatty acid esters into products such as free fatty acids (Huang et al., 2023). This dynamic depends on various factors, including the concentration of catalysts, the ratio of oil to water, temperature, and pH.

The hydrolysis of fatty acids commonly follows first-order kinetics, as observed by Kocsisová et al. (2006), who found that triacylglycerols and methyl esters are hydrolyzed according to the first-order reaction equation. Khuwijitjaru et al. (2004) showed that the energy required to initiate the hydrolysis reaction can vary according to the spatial configuration of the acyl and alkyl chains. On the other hand, Anozie & Dzobo (2006) observed that the kinetics of palm oil hydrolysis were variable depending on the oil/water ratio, i.e., the concentration of triglycerides. It was also observed by Anozie & Dzobo (2006) that the reaction rate is proportional to the initial catalyst concentration, which can influence the mass transfer and chemical aspects of the reaction. Increasing temperature and pressure can improve the efficiency of commercial processes for separating oils and fats by dissolving these hydrophobic solutions (Gervajio, 2005). In addition, supercritical and subcritical temperature conditions can provide advantages that increase efficiency in hydrolysis processes, such as carrying out reactions in a short time (Kocsisová et al. 2006). It has been shown by Kocsisová et al. (2006) that it is possible to obtain conversion yields of over 95% in the hydrolysis of fatty acids in water in a relatively short time (12 minutes) at a temperature of 340°C. Milliren et al. (2013) obtained yields of 85% of free fatty acids in the hydrolysis of soybean oil at 300°C in 60 minutes.

pH is another parameter that can influence the solubility of fatty acids in aqueous media. Vorum et al. (1992) showed that the low solubility of fatty acids at pH close to neutral can facilitate the direct transfer of free, unbound fatty acid ions in a monometric manner (Leplingard et al., 2003). (Szopa et al., 2023).

In agricultural practices, the hydrolysis can be applied as pre-treatment to organic residue (Tang et al., 2022; Zhang a, 2015). Tang et al. (2022) investigated the effects of alkaline thermic hydrolysis in sewer sludge, aiming to produce a liquid fertilizer. The results showed a reduction in pH derived from temperatures increasing to 140° C, resulting in a release of amino acids and fatty acids through the depolarization and cleaving of chemical bonds, which is beneficial due to the increase of organic carbon in the soil, stimulating microbial activity and improving soil texture. This approach drives an efficient method for generating essential plant nutrients, promoting plant growth without harming the soil.

Formulation of Fatty Acid-Based Fertilizers and Use of Lignocellulosic Biomass

Origin of Fatty Acid

Fatty acids in fertilizer fabrication can be derived from many

sources, including plants and animals. In contemporary agriculture, fertilizer patents formed from fatty acids represent a significant technological advance. Fatty acids are highly versatile in different chemical reactions, resulting in value compounds for the formulation of fertilizers (Tyc et al., 2021b). The specific region to apply the compound (leaf, root,

soil, and others) of fatty acid-based compounds is a crucial element that determines the activity of fertilizers. Table 1 cites the patents that utilize fatty acids and their byproducts, such as esters, from plants or animals, the local application, and the corresponding activity. This table presents results only from patents that provided all the information.

Display Key	Origin	Fatty acid derivates	Application local
AU2019/428312A1	castor bean oilseed	ricinoleic acid	leaf
CN101811916A	soy oil	fatty acid salt	soil
CN103483053A	vegetable	fatty acid membrane emulsion	leaves
CN104276884A	animal fat	oil residue	soil
CN104496710A	linseed and peanut oil	fatty acid and glycerol fatty acid	soil
CN104725144A	coconut oil	fatty acid methyl ester	soil
CN105859434A	citrus fruit	sucrose fatty acid ester	soil
CN106520364A	coix seed crude oil	fatty acid ethyl ester	soil
CN106748241A	vegetable oils, fatty acid oils, oil-containing tree seeds and mixtures	epoxidation fatty acid triglyceride oil	soil
CN107867956A	bivalve mollusk	fatty acid ethanol amide	soil
CN108069775A	oil shale ash dregs	poly glycerine fatty acid ester	soil
CN113512172A	sebacic acid	fatty acid glyceride	soil
CN115925473A	pupa extract	saturated fatty acid	soil
CN208857166U	waste liquid	lutein fatty ester	soil
GB1022106A	myristic, lauric, palmitic, stearic, oleic, or 9- dodecylenic acid	fatty acid salt	soil
JP2008024552A	coconut oil	higher fatty acid	soil
JPH02267180A	animal feces	fatty acid calcium	soil
JPH07232982A	coconut oil, beef tallow, castor oil, lard, palm oil, soybean oil, rapeseed oil, olive oil	fatty acid, calcium, salt	leaf
JPH101381A	animal	fatty acid amide	soil
KR92235435	vegetable	omega 3 fatty acid	soil
US5424270A	lard, beef tallow, cottonseed oil, and palm oil	alkali metal fatty acid salt	foliage
US5489569A	vegetable oil (tall oil, palm oil, and soybean oil)	fatty acid residue	leaf
		myristic acid (c14:0)	
		palmititic acid (c16:0)	
		stearic acid (c18:0)	
		behenic acid (c22:0)	
	lignoceric acid (c24:0) and palmitoleic acid (c16:1)		
US9796896B2	biodiesel	margaric acid (c17:0)	soil
		oleic acid (c18:1)	
		linoleic acid (c18:2)	
		linolenic acid (c18:3)	
		arachidonic acid (c20:4)	
		eicosenoic acid (c20:1)	
		tetracosenoic acid (c24:1)	
WO2007/030885A1	castor oil	fatty acid ester	soil

		methyl palmitate, methyl palmitate, octadecanoic acid methyl esters and linderic acid methyl esters, methyl myristate, 7-tetradecenoyl acid methyl esters, palmitoleic acid ester	
	11-octadecenoic	acid acid methyl esters	

Table 1: Identification of patents in the study concerning the origin and type of fatty acids and application site

In this study, we identified that the % of patents was 60% plant-based, 8,47% animal-based, and 14% animal and plant. Hidekatsu (2000) developed a liquid fertilizer from raw animal material composed mainly of fatty acid (sorbitan fatty acid ester) and soluble proteins. This product aims to be a source of plant nutrients with stable quality and extended lifespan while offering ease of application and being directly absorbed by plant roots.

The patent from (Xiuli et al., 2018) proposes a multifactorial fertilizer made from animals, aiming to optimize efficiency and avoid waste, removing the excess radicular system in plants and soil flattening. This invention also possesses sorbitan fatty acid ester in its composition. Sorbitan fatty acid ester is a complex mixture of fatty acid and polyolester derived from sorbitol (Sahasrabudhe & Chadha, 1969).

Gonzalez et al. (2019) evaluated the impact of irrigation with many hydrophobic organic additives, including Tween 80, a surfactant made from polyoxyethylene 20 sorbitan fatty acid ester, on the lixiviation, availability, and degradation of DDT (dichloro-diphenyl-trichloroethane) residues. Its conclusions emphasize the significant relevance of Tween 80 in assembling fulvic acids and the desorption of DDT in the soil.

Han-Yong (1996) also developed an anti-foaming animal-based fertilizer based on fatty acid ester from fish oil to avoid auto deterioration during prolonged storage. Foam formation can create a surface promoting bacteria and fungi growth, accelerating deterioration. Although this innovation has expired, this approach aligns with the discovery of (Gallagher et al., 2019), in which the dihydro γ linoleic acid (DGLA), a specific member of the omega six families, demonstrated its capacity to inhibit the modified harnessing of low-density lipoprotein (LDL) and stimulating an efflux of cholesterol from foamy cells, characterizing as an anti-foaming agent.

On the other hand, fertilizer can be derived from many plant sources, such as palm oil, soy, olive oil, corn oil, grape seed oil, coconut oil, and butter. (Geng et al., 2010) been evaluated so that plants can both properly receive nutrients but not in excess, which can be toxic and lost through lixiviation. This innovation pulverizes the surface, accelerating the reaction with film-forming components and resulting in quick solidification. Furthermore, the surface is laced with large particles, which allows this release mechanism. Baozhong et al. (2019) innovated in developing a controlled-release fertilizer, focusing on improving its durability and mechanical resistance. Their study showed that including epoxidated fatty acid from triglyceride as an additive significantly reduced adverse reactions during

handling, improving the release profile of the product. This unique additive acts as a plasticizer and compatibility agent, effectively mitigating the mechanical impact. Yuan et al. (2022) demonstrated that vegetable oils can be utilized in agriculture as a nutrient coating (fertilizer encapsulation) due to being able to make the fertilizer hydrophobic due to its alkyl chain of long fatty acids. Vegetable oils are also highly biodegradable (Feng et al., 2019). Feng et al. (2019) formulated a fertilizer with a controlled release made from soy oil and epoxidated oleic oil and observed that after 180 days, there was a degradation of 21,85%. Many physical and biological factors, such as water, light, temperature, and microorganisms, can influence this percentage.

Therefore, soy oil can be utilized to induce thinning. In a study conducted by (Moran et al., 2000), it was observed that the application of soil oil in peach trees, a component not mentioned by the regulation of the Environmental Protection Agency (EPA), due to its shared nature as a food constituent, as much as its nontoxic and nonpersistent characteristic in the environment, revealed it to be an effective alternative to manual thinning. This constant practice resulted in a more significant survival of trees than control trees, which, in their case, led to a substantial reduction in cost associated with this cultivation. Fertilizer can also be obtained from biodiesel residue, triglyceride, plant oil refinery residue, fatty acid combined with glycerol, mushroom residue and even the plant *Portulaca oleracea* L (Baozhong et al., 2016; Bijpost et al., 2021; Cantizani, 2013; Dehai et al., 2016; Ho and Soo, 2013; Joan and Bo, 2017; Qihua, 2013; Yuan et al., 2014; Zhengzhu et al., 2014).

Application Area of Fatty Acid

Fertilizers have different zones of application, such as seed and leaves, to supply resistance against pests and promote the vigor of plants (Amruthesh et al., 2005; Ellinger et al., 2014), on the roots or soil, with the potential of increasing permeability, improving water and soil retention. Depending on the type of fertilizer, this compound can also stimulate microbial activity in the soil, accelerating decomposition and releasing nutrients essential for plant growth. This study observed that 63,70% of patents specified where to apply the fertilizer, of which 80,60% are used in the soil, 12,75% on leaves, and just 0,60% on seeds. The innovation of (Jie et al., 2017) proposes fertilizers that can significantly improve the granular structure of the soil, facilitating water penetration and air circulation and appropriately protecting against hardening. This fertilizer is composed of sucrose fatty ester derived from aliphatic fatty acid esterification, acting as a non-ionic surfactant, which is safe and highly degradable. Furthermore, due to its high

viscosity and hygroscopic properties, it contains propanediol, acting as a humectant and anti-caking agent.

In addition, the presence of polyaspartate amplifies the activities of these components, resulting in harvests with greater productivity and higher quality. Soil treatment with salt and caustic soda can cause significant damage. The salt's osmotic stress reduces the soil's capacity to absorb water, leading to photosynthesis inhibition and hindering plant growth (Yung et al., 2021).

The invention of Winston (1995) proposes a water-based fungicide fertilizer for application on foliage, fruits, or seeds. This formulation includes a bicarbonate salt added to a combination of fatty acid salt and pseudo-plastic thickener. Fungicide activity is attributed to bicarbonate, while fatty acid salt plays a crucial role in the applied region's dispersion and adherence of fungicide components. Furthermore, the pseudo-plastic thickener increments the quantity of the fungicide product that adheres to the plant's surface due to its static heightened viscosity. Although this technology uses fatty acid salt as an adhesive component, there is evidence that it can cause the rupturing of an organism's cellular membrane (Hayes & Roden, 1990), possibly resulting in fungicide activity. Additionally, using fatty acids without saponification can present fungicide effects (Amruthesh et al., 2005; Ellinger et al., 2014).

Amruthesh et al. (2005) and Ellinger et al. (2014) did a study in which they treated millet seeds with a mixture of fatty acid, docosahexaenoic acid, eicosapentaenoic acid, arachidonic acid, linolenic acid, linoleic acid, and oleic acid, to prevent mildew. The authors observed that the treatment with any of these acids reduced the incidence of the disease in comparison to untreated seeds, with higher protection associated with eicosapentaenoic acid (78,6%) and arachidonic acid (76,5%) and minor protection after treating with oleic acid (5,1%). Furthermore, they observed that the vigor index of the plants increased significantly with all fatty acids, except for oleic acid, compared to the control plants. The efficiency of oleic acid was also reported as a component of reactive activity insecticide for *Leptinotarsa decemlineata*, a significant pest affecting Solanaceae cultivation in the United States (Clements et al., 2019).

Characterizing the formulation of fertilizers

The patent classification from the International Patents Classification (IPC), which categorizes patent information into specific groups based on themes and technical areas (Lim & Kwon, 2017), revealed a significant disparity, as shown in Image 4. It is crucial to observe that, in certain situations, certain patents were classified into more than one group and specification, which can influence an analysis of the results. These findings were expected due to the similarity between these areas and employed search criteria. However, a more profound analysis of these results could reveal additional insights about tendencies and specific patterns within this field. The C group (chemistry and metallurgy) emerged as the most present, contributing to 286 documents, representing

83,87% of patent descriptions. On the other hand, the A group (human needs) was in second place, with 36 patents (10,36%), considerably less than group C. Furthermore, groups B, D, and H showed a minor contribution, with 4,69%, 0,59%, and 0,29%, respectively.

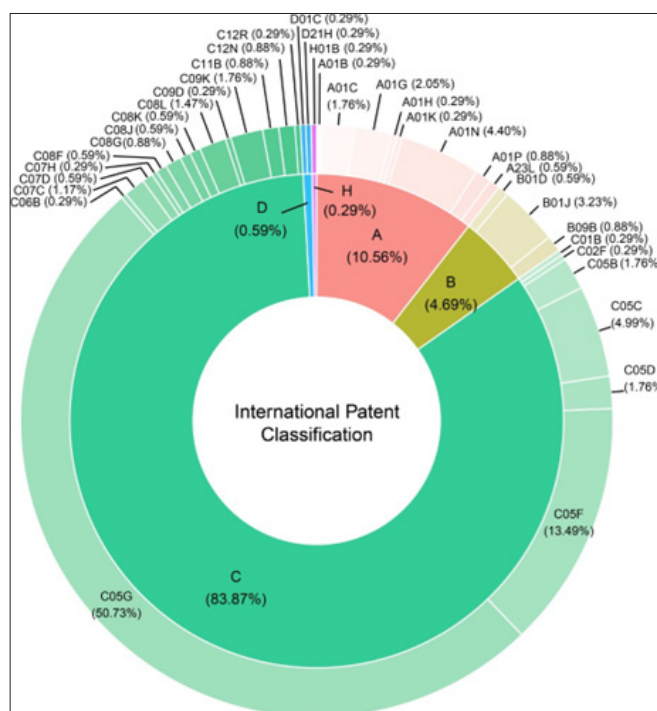


Figure 4: Percentage of patents per International Patents Classification criteria

On a more specific level, code C05G (fertilizer mixture) was mentioned in 50,73% of analyzed patents.

On the other hand, the code C05F (organic fertilizers not covered by subclasses c05b, c05c, e.g., fertilizer from waste or refuse) was mentioned at 13,49%, while C05C (nitrogenous fertilizers) reached 4,99%. It is also essential to inform the notable relevance of the group A01N (preservation of bodies of humans or animals or plants or parts thereof), referring to disinfectants such as herbicides and pesticides, present in 4,40% of the analyzed patents.

Although inorganic fertilizers still maintain a significant importance in the sector, we can observe that the code C05D (inorganic fertilizers not covered by subclasses c05b, c05c; fertilizers producing carbon dioxide) was cited in just 1,75% of the analyzed patents, the same as C05B (phosphatic fertilizer).

Fatty acid for fertilizer in slow or controlled nutrient release

The inefficiency of fertilizer absorption leads to severe environmental issues, impacting animal and human health and causing severe economic problems due to loss of material, energetic loss, and waste of human resources (Lubkowski et al., 2015). Since the beginning of the 20th century, fertilizers with controlled or slow-release (S/CRFs) have been developed to reduce the impacts of applying fertilizers (Liu et al., 2022).

There are two categories of coated fertilizers: organic and inorganic. The organic coating comprises biodegradable material with plant oil, recognized for its availability, ecologic aspect, renewable source, and hydrophobic properties (Yuan et al., 2022). In this context, (Zhengzhu et al., 2014) presented an innovative approach for developing a coating for controlled-release fertilizers. This coating is based on polyester polyol derived from dimer fatty acid C36, extracted from soy oil, demonstrating a pioneering and advantageous method. First, compound A was mixed (fatty acid dimer) with compound B (isocyanic ester) at high temperatures (65°C-85°C). Finally, the coating was applied to the heated and granulated fertilizer; the process was repeated until it reached the desired quality. This method is notable due to its abundant source, simple synthesis method, reduced cost, and remarkable properties, such as high resistance to water, heat resistance, and elevated flexibility. During the tests, for 60 days, there was an 80,46% release of nitrogen. In the first stages, the release rates were below the national standard, registering 0,96%, 7,04%, and 52,41% in 24h, seven days, and 28 days, respectively, demonstrating satisfying results.

Research conducted by Lubkowski et al. (2015) used poly-butylene succinate and fatty acid dimer as the basis for fertilizer coating. During their investigation, they noticed an initial quick release of phosphate nutrients compared to ammonia, reaching 15% release in 24 hours. It is worth noting that this experiment was made using the water release test, a more accelerated evaluation method. The researchers observed that the thickness of the coating is directly related to the diffusion speed, influencing the release rate. The concentration of mineral components on the grain also had a significant task in determining this release rate. Furthermore, no fractures were found on the surface of the fertilizer, which suggests that the predominant method was diffusion, explaining the reduced rate of nutrient release. Geng et al. (2010) created a formula to significantly improve the control of nutrient release and reach an efficiency of 1,5 to 2 times over a conventional fertilizer. This innovation combines salt from ricin acid, a component for fertilizer, with a polymer derived from carbon dioxide and calcium chloride. In a related study, (Liang et al., 2019) investigated the impact of the polyurethane coating made from castor oil, rich in ricin oil, to be applied on fertilizers. Their discoveries revealed that polyurethane from biological matter can increase the robustness of the coating, resulting in a material with excellent properties for controlled nutrient release.

Fatty acid in anti-caking compounds

One of the main objectives of the fertilizer industry is to ensure product stability during storage. One adopted strategy is creating a hydrophobic barrier on the granule's surface. (Szlek et al., 2022) reviewed chemical treatments destined to make hydrophobic coats from cellulose and polysaccharides. A review highlighted promising therapies, including silanes, ester formation, and plasma treatment. This technique reduces nucleation and crystallization, reducing surface tension and crystalline gap resistance. Furthermore, it aims to prevent

the adverse effects of environmental conditions, such as temperatures, humidity, and pressure (Tyc et al., 2021b; Zhang et al., 2016).

Fertilizer with anti-microbial anti-pesticide activity and fatty acid effects

In agriculture, notable advancements have been made in developing cultivation protection agents. (Haibing et al., 2018) proposed a three-layer coating for Konjaku plantations (a medicinal plant from Asia), presenting a multifunctional structure: one bacteriostatic and insect-repellant coating, one nutritional coating, and a third pressure-resistant one. Notably, the first coating incorporates antimicrobial components, such as a mixture of bacteria in azoles chela chains, phoxim Raytheon, fatty acid soap, sodium carboxymethyl amide, polyethyleneglycol, and water. The second coating supplies nutrients, facilitating growth and contributing to plant resistance. Finally, the third layer of coating adjusts the pH of the Konjaku epidermis and creates a more resistant shell.

The contribution of Aristos et al. (2007) introduced a concentrated emulsive compound and a method of pest control using active agrochemical agents, ester fosfate surfactants, solvents non-mixable in water, and emulsifying compounds with alquilarisulfonates and emulsifying nonionic components (surfactant). Furthermore, Hualian (2015) introduced an organic pesticide that consists of an active component (like botanic pesticides derived from rotenone, piretro, sabadilla, Melia azedarach, ryania, or a mixture of those) used to stabilize an organic manure aqueous extract. This pesticide is also composed of surfactants, solvents, and fatty acids.

These innovations highlight active components for antimicrobial effects and pest control, including fatty acids. These components can adhere to plant tissues, overcome barriers for better diffusion, promote efficient dispersion, and increase antimicrobial component solubility (Ahad et al., 2009; Aspenström-Fagerlund et al., 2007; Krawczyk, 2018). Focus directly on the potential of fatty acids as a means to intensify the effects of active components, studies like that of (Ramadan et al., 2022) suggest promising synergic effects with low to moderate oral toxicity for mammal and non-target organisms when fatty acids are combined with pyrethroid compounds (Soderlund, 2020), such as deltrametine on resistant beetles. These discoveries are evidence of the importance of fatty acid in making cultivation protection and indicate a promising path for future innovation, exploring its synergistic properties and potential for enhancing the efficacy and sustainability of agriculture practices.

Formulation of phosphate-based fertilizers and fatty acid effects

Of the patents related to phosphate-based fertilizers, we observed that they were only 2,13%. Inorganic phosphate is a limiting essential component for the development of aquatic and land plants, as detailed by Poirier et al. (2022). According to the authors, inorganic phosphate is essential for developing land and aquatic plants.

Of the patents on phosphate fertilizers, only one stands out: the notable invention of (Poirier et al., (2022), which focused on enhancing urea fertilizer efficacy after adding sucrose fatty acid. This discovery, inserting many saturated fatty acids, such as capric acid, lauric acid, myristic acid, palmitic acid, stearic acid, and oleic acid, revealed potential compounds for enhancing the efficacy of fertilizers. Furthermore, the inclusion of potassium phosphate, which characterizes the type of fertilizer according to the IPC, not only acted as a fertilizer but also played a buffering role, controlling the pH of the fertilizer solution. This strategy focused on maintaining a safe pH for plants and avoiding the corrosion of containers during storage.

Tests monitored the absorption of nitrogen and phosphorus after applying the fertilizer. It was evident that the increase of fatty acid resulted in a 39% increase in nitrogen absorption. However, phosphorus absorption varied intriguingly: it increased until the addition of one part per weight of fatty acid (10%), reducing when the maximum quantity of fatty acid was applied, reducing 2% when compared to the part per weight addition.

It is crucial to consider the timeline as the context for this discovery. Although the invention made by Takashi et al. (1986) was relevant at the time, it would be interesting to explore the subsequent development of this field, especially when considering the increasing usage of phosphorus in fertilizer production since 1950, comparable to petroleum, due to its accumulation during millions of years and exhaustion vulnerability (Poirier et al., 2022).

Additionally, it is crucial to note that not all phosphorus employed for fertilizer composition is found in phosphate form, making it difficult for farmers with limited resources to acquire it (Haefele et al., 2013; Hong et al., 2020).

Although this patent represents a significant advance in the search for effective fertilizer solutions, the current scenario and challenges farmers face suggest the continuous need for innovative research to develop efficient and accessible fertilizers, considering the limitation of resources and the critical importance of phosphorus in agriculture.

Formulation of organic and biological fertilizer and the effects of fatty acid

Albeit the innovations searching to improve the efficiency of inorganic fertilizer are highly relevant to facing current environmental challenges, the excessive and indiscriminate use of nitrogen and phosphate compounds continues to cause considerable pollution and reduce the efficacy of productivity (Gouda et al., 2018; Lehmann & Kleber, 2015). On the other hand, the presence of organic carbon and nutrients is familiar in organic fertilizers (Fernández-Delgado et al., 2022), and also amino acids and fatty acids, when submitted to enzyme or chemical processes, essential for the balance of soil microbiome and development of plants (Tang et al., 2022). Likewise, the strategy substitution of inorganic fertilizer for soil microorganisms, like bacteria, fungi, and algae, emerges

as a possible approach to reaching sustainability in agriculture (Gouda et al., 2018; Vejan et al., 2016).

(Jiayu, 2018) developed an organic fertilizer incorporating the presence of Bacillus, seeking to enhance the microbial biodiversity of the soil, and reducing the need for chemical fertilizers. Its composition is diversified, including bovine and bird feces, stalk, soil, worn-out coal, mushrooms, algae, mussel dust, wood splinter, honey, amino acids, potassium metaphosphate, oligo-elements, potassium breeze, phosphorus mineral, humic acid, ammonium sulfate, borax, zinc sulfate, sodium carbonate, and fatty acid acetic anhydride, obtained through the esterification of acetic anhydride and fatty acid. Furthermore, it presents a mixture of the Bacillus genus microorganisms, including *B. subtilis*, *B. amyloliquefaciens*, and *B. thuringiensis*. Tests demonstrated an increase of up to 14,9% in the performance of spinach agriculture in comparison to chemical fertilizers. These results might explain why many bacteria species produce antimicrobial metabolites and how they can control many diseases, increasing plant resistance and improving development (Pour et al., 2022).

Conclusion

Research incorporating fatty acids in fertilizer has shown to be a promising alternative for the efficiency and sustainability of agriculture. Based on the systematic review of patents, in October 2023, 259 patents were identified, led by China. Innovations include animal and plant liquid fertilizers, fatty acid esters, and controlled-release formulations. Predominantly for soil (80,60%), notable contributions include fertilizers that improve soil conditions, have pesticide activity, act as anti-caking, and offer slow and controlled nutrient release, among other benefits. These fertilizers promote soil health, protect plants against pests and disease, maintain nutrient quality, and optimize agriculture productivity. The diversity in patent origin, including 60% plant, 14% mixed, and 8,47% animal, shows the growing tendency for sustainable agriculture. Including fatty acids and microorganisms from the soil for composition suggests a positive direction in agriculture practices. This is due to the urgency of developing more responsible and advanced solutions and fertilizers.

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