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Bibliographic review

Pyroligneous acid, characteristics and possible uses in agriculture

El ácido piroleñoso, características y posibles usos en la agricultura

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ABSTRACT : Pyroligneous acid is a complex mixture containing 80-90 % water and 10-20 % organic compounds, including more than 200 chemical components such as acetic acid, phenols, alkanes, alcohols and ester compounds, which can be extracted from different plant materials that contain lignin, cellulose and hemicellulose. In different countries, practices of transformation of the different vegetable materials are adopted in order to extract this product, since investigations carried out show that it has potential in different sectors such as agriculture. It has characteristics that allow it to replace synthetic products used in the food, cosmetic and agricultural industries, which alter the environment and are harmful to people's health. It is a product of which little is known about its applicability and its establishment could contribute to the generation of increasingly friendly practices with the environment. In this sense, the present work aims to collect information on pyroligneous acid and its possible effects on agriculture.

Key words: biostimulant, pesticide, pyrolysis, herbicide.

RESUMEN: El ácido piroleñoso es una mezcla compleja que contiene entre 80 y 90 % de agua y de 10 a 20 % de compuestos orgánicos, que incluyen más de 200 componentes químicos tales como el ácido acético, fenoles, alcanos, alcoholes y compuestos de éster, el cual puede ser extraído de diferentes materias vegetales que contengan lignina, celulosa y hemicelulosa. En diferentes países se adoptan prácticas de transformación de las diferentes materias vegetales con el fin de extraer este compuesto, ya que investigaciones realizadas dan a conocer que tiene potencial en diferentes sectores como el agrícola. Tiene características que permiten sustituir productos sintéticos utilizados en la industria alimentaria, cosmética y agrícola, que alteran el medio ambiente y son perjudiciales para la salud de las personas. Es un producto del cual se conoce poco sobre su aplicabilidad y su establecimiento pudiera contribuir a la generación de prácticas cada vez más amigables con el ambiente. En ese sentido, el presente trabajo pretende recopilar información sobre el ácido piroleñoso y sus posibles efectos en la agricultura.

Palabras clave: bioestimulantes, plaguicida, pirólisis, herbicidas.

INTRODUCTION

The search for and application of technologies in the acquisition of energy products and organic chemicals are of considerable interest in today's world, among which it mentions the pyrolysis of plant biomass (1).

Although pyrolysis dates back to ancient Egypt and is still under development, in the current energy scenario, it has received special attention, since it can directly convert biomass into solid, liquid and gaseous products by thermal decomposition in the absence of oxygen (2).

When biomasses are subjected to the pyrolysis process, they produce a substance known as pyroligneous acid or wood vinegar, which can be used for different agricultural purposes (3). It has characteristics that make it possible to replace synthetic products, which not only alter the environment, but also are also harmful to people's health (4).

In Cuba, some studies have been carried out at laboratory scale, among which are the works carried out on the antimicrobial evaluation of 4 products derived from pyroligneous acid for their possible use as disinfectants (5). GRAM-SCHMIDT chromatograms of pyroligneous acid obtained in the pyrolysis of different plant biomasses (6) and the comparison of Guachapelí (*Albizia guachapele*) versus Marabú (*Dichrostachys cinérea*) and the kinetics of their pyrolysis (7).

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In correspondence with the above, the present review aims to gather information on the state of knowledge regarding pyroligneous acid, its characteristics and possible uses in agriculture.

DEVELOPMENT

Pyroligneous acid

Pyrolean acid is an aqueous liquid obtained by condensation of the smoke generated during the pyrolysis of plant biomass (8). Its extraction is very simple: when charcoal is processed, the smoke is passed through a pipe or chimney; in this process the acid, which comes out as a gas, is condensed and collected. This liquid has a special smoky, light yellow to brown color (9). The yield depends on the biomass used (10).

Chemical composition of Pyroligneous Acid

Pyrolysis is a process that transforms plant biomass into by-products such as biochar, pyroligneous acid (PA) and tar (11).

In pyrolysis, complex reactions of depolymerization, hydrolysis, oxidation, dehydration and decarboxylation occur. When the volatile products condense, they give rise to a liquid containing two phases: an aqueous phase called pyroligneous acid, formed by oxygenated organic compounds of low molecular weight; and another non-aqueous phase called tar, which contains insoluble organic compounds of high molecular weight such as: pyrocatechol, guaiacol, cresol, methyl-cresol, toluene, xylene, naphthalene, and other hydrocarbons (12).

The volatile products of pyrolysis are the result of the decomposition of the macro components (cellulose, hemicellulose and lignin) and of secondary reactions between the volatile compounds formed in the primary decomposition. One of the most abundant liquid products of slow pyrolysis is pyroligneous acid, with a high content of water and acetic acid (12).

Pyroligneous acid contains 80-90 % water, 5-10 % acetic acid and more than 200 kinds of dilute chemical compounds (9). The products obtained are gases, liquids and solids. The proportion and composition of these products depends largely on the type of biomass used (13).

In the pyrolysis of sugarcane bagasse and coffee husk, a high presence of carboxylic acids and phenols is observed, as well as ketones, alcohols and aldehydes, given the high content of hemicellulose and cellulose, which upon thermal decomposition give rise to the volatilization of these types of organic compounds (12).

In the pyroligneous acid of tobacco, the predominant compounds, after acetic acid, are those of the amine group such as acetamide, propionamide and nicotine; however, the content of phenolic compounds is lower, because the lignin content is much lower than in the bagasse of cane and coffee husk (14).

The composition analysis of the pyroligneous acids of the bamboo, pisonay and cetico species yielded different organic compounds (acids, alcohols, phenols and neutral compounds). The bamboo species presented 12 organic compounds; the pisonay species resulted with 20 organic compounds and the cetico species had 23 organic compounds (10).

Analysis of the pyroligneous acid components of bamboo, oak and pine, determined that the pyroligneous acids of these are almost identical and are composed mainly of phenolic compounds and aromatic hydrocarbons (15).

Effect of Pyroligneous acid on seed germination

The use of pyroligneous acid in the germination of watermelon (*Citrullus lunatus*), cocoma (*Solanum sessiliflorum*) and cacao (*Theobroma cacao*) seeds in the District of San Gabán, Carabaya, showed significant effects on the germination of cocoma and cacao seeds; however, there were negative effects for watermelon seeds. The 10 mL dose had the best results in the germination of cocona and cacao seeds with 94.5 and 98.5 %, respectively. The 100 mL dose inhibited germination and the 1 mL dose showed no positive effect. These authors consider that pyroligneous acid from bamboo shows efficiency in the germination of seeds of perennial plants and those with dormancy problems or recalcitrant plants (16).

The application of bamboo pyroligneous acid to improve rice seed germination significantly increased the percentage of seed germination due to its ability to inhibit pathogens due to its chemical components (17).

Biostimulant effect of Pyroligneous acid

The addition of pyroligneous acid individually promotes root development of bell pepper seedlings by 45.4 - 51.6 %, and increases shoot and root biomass by up to 22.0 and 113 %, respectively (18).

In a comparative study between pyroligneous acid from *Pennisetum Clandestinum* L (kikuyo) and from Bamboo, it was demonstrated that both had similar properties and that their characteristics can increase root growth in vegetables (19).

Studies found a higher production of paprika in the plots where 6 mL of pyroligneous acid per liter of water was used, which confirms that this product also has a growth stimulator effect that enhances a higher development of the plant and therefore a higher yield (20).

In the evaluation of the components contained in pyroligneous acid, in its physical-chemical characteristics, laboratory analyses were carried out at the beginning and at the end of the research. It showed that Nitrogen, Potassium, Magnesium and Sulfur macronutrients increased their concentration, while other compounds such as Phosphorus and Calcium, in lower concentration in ppm, enhanced the vegetative development of the plant (3).

Effect of Pyroligneous acid in the soil

In the production of compost, it increases the nitrogen content and accelerates its fermentation by using it in a ratio of 200 mL per liter of water (20).

Pyroligneous acid acts as a promising soil improvement amendment because it contains multiple benefits for agricultural production, stimulates plant growth, improves soil acidity, improves nutrient absorption by plants and acts as an organic fertilizer (21). Its application raises the soil's cation exchange capacity (CEC) and, consequently, benefits the translocation of nitrogen and phosphorus from the soil to the plant. Thus, there is a reduction in N leaching and an increase in bioavailability in agricultural soils (22), which can potentially decrease the demand for nitrogen fertilizers for crop growth (23).

The application of a mixture of pyroligneous acid with Bocashi showed a better quality index in electrical conductivity, organic matter, and nitrates, in the total content of organic carbon, nitrogen, phosphorus, calcium and magnesium. This was not the case for nitrogen-ammonia, cation exchange capacity and total potassium (24).

Methyl formic acid and methyl acetate, contained in pyroligneous acid, help the development of microorganisms that improve the soil and the quality of organic fertilizer (20).

When applied to the soil, it prevents the proliferation of nematodes, viruses, gray mold, bacteria, etc. The high acidity and the methanol and phenol content have a strong bactericidal effect at high concentrations (25).

There are proven results of the efficiency and efficacy of pyroligneous acid as a source of organic fertilization. Nearly 400 small rural producers in four municipalities in Nicaragua use this substance as a source of fertilizer for their crops (26).

Effect of Pyroligneous acid in the control of pests and diseases

The liquid fraction obtained by conventional pyrolysis of wood has great utility as a fungicide, bactericide and insecticide. It is especially useful in the biological activity of fungal and termite attacks (27).

Preliminary fungicidal and antithermitic evaluation of the pyrolethal liquid showed its toxicity against the wood-rotting fungi *Coriolopsis polizona*, *Fomitella supina*, *Pycnoporus sanguineus* and *Trametes villosa*. The toxicity limit values were 3 % pyrolethal liquid per volume of medium against the fungi *Coriolopsis polyzona* and *Fomitella supina*; and 4 % pyrolethal liquid per volume of medium against the fungi *Pycnoporus sanguineus* and *Trametes villosa*. These toxicity values, once converted into their equivalent organic fraction content, coincide with adequate toxicity values found in the literature. Regarding the anti-thermitic efficiency, experiments showed that the pyrolytic liquid protects the wood from termite attack on a regular basis (28).

In a study carried out in Ecuador to evaluate the use of pyroligneous acid, obtained from rice husk (*Oriza sativa* L.) for the management of the insect known as negrita (*Prodiplosis longifila* G.) in tomato (*Solanum lycopersicum* L.) under controlled conditions. They concluded that the dose of 1.75 mL of this product in 100 liters of water, showed a 78.8 % mortality of larvae (29).

When evaluating the effect of pyroligneous acid in the control of insect pests in the paprika crop (*Capsicum annuum*), the results showed that the doses of 4 and 6 mL/ liter of water exerted a repellent effect on white flies, but as for aphids, the dose of 6 mL besides having a repellent effect was attributed a mortality effect. Thus, these authors affirmed that pyroligneous acid exerts a repellent effect on the aforementioned pests. They also pointed out that mixed with other pesticides; the same effect can be expected with half the dose of the pesticide, since the alcohol and the organic acid help the osmosis of the leaf and the dilution of the pesticide (20).

It is a product that is used as an alternative for management, it eliminate the presence of pests, but it considerably decreases the population index (30).

The fungicidal and insecticidal activity of pyroligneous acid from bamboo and mangrove wood was experimentally demonstrated (31). On the other hand, in a study carried out with vinegar obtained from coconut shell, it was shown that this liquid, with different dilutions, maintained thermitic and pesticidal activity, and that wood treated with it presented a preventive action against termites (32).

Wood vinegar against chromogenic fungi and molds present in Japanese red pine wood had greater efficacy against chromogenic fungi, in such a way that with a 1:1 dilution its inhibition was achieved during 8 weeks (33).

In soil sterilization, it works as a fungicide by rapidly reducing the oxygen level and drastically lowering the pH for one week, achieving control of nematodes, viruses, gray mold, downy mildew and bacterial wilt. It should be applied one week before sowing in a ratio of 2.8 L of pyroligneous acid/20 L of water and one week after sowing in a ratio of 200 mL of pyroligneous acid/20 Lts of water, preferably applied in the morning hours (20).

The use of biopesticides, such as pyroligneous acid is a simple technique for the use of producers, which reduces maintenance costs by 50 %, besides it does not harm the environment or human health. In foliar application, phenol, cresol, alcohols, formic acid, acetic acid, formaldehyde, methanol, among others, cause repellency in insects such as mites and aphids by its characteristic smoky odor, has fungicidal effect for powdery mildew, gray mold, downy mildew, soft rot, clerotinia rot and bacterial wilt and activates plant growth (20).

Pyroligneous acid inhibits the growth of some pathogenic fungi (*Rhizoctonia solani*, *Sclerotium oryzae*, *Helminthosporium mayis*, *Pythium* sp., *Colletotrichum gloeosporioides* and *Cucurbitarum choanephora*) and some bacteria (*Xanthomonas campestris* pv. *Citri* and *Erwinia carotovora pv.Carotovora*). The results indicate that the adequate concentrations are lower than 10 % to avoid leaf burns (34).

Herbicidal effect of Pyroligneous acid

About Pyroligneous acid or wood vinegar there are references of its use as a natural herbicide since ancient

times, but there are almost no scientific studies on the efficacy of this vinegar as herbicide (35).

The evaluation of the behavior of vinegar as an herbicide in three percentages of acidity, in the Zamorano area in Honduras, showed that there was no change in the pH of the soil remaining between 5.6 and 5.7-pre and post application. The most significant control ($p \leq 0.05$) was in *Melampodium divaricatum* 15 days after application with 84 %, in the rest of broadleaves the control was not significant and for grasses and sedges there was no control. The most significant interaction ($p \leq 0.05$) was in *Melampodium divaricatum* at 10 % acidity and 15 days of weed emergence with 96 %, in the rest of broadleaves there was no effect of the interactions. The most significant control ($p \leq 0.05$) in application volume was in *Melampodium divaricatum* at 250 L ha^{-1} with 95 %, in the rest of weeds there was no difference. The effect of vinegar on broadleaf weeds was evident, but not on grasses and sedges (36).

CONCLUSIONS

Pyroligneous acid is obtained from the pyrolysis of plant biomass; it is a complex mixture of water and organic compounds, which presents characteristics in its chemical composition that allow it to be used in agricultural activities in an environmentally friendly manner.

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