

Review Article

PHASE TRANSFER CATALYSIS: NEW TECHNOLOGY TO BOOST ORGANIC FARMING

Abstract

Introduction of Phase Transfer Catalysis (PTC) technology, which was developed in the 1970s has revolutionised the dyes and pharmaceutical industries in many ways. PTC is a process that facilitates the organic compounds to move from one phase to another phase, without any change in the chemical qualities. Application of this technology was explored in the 1980s for agriculture, by using different plant extracts as PT catalysts. The objective was to facilitate increased absorption of nutrients by plants, by stimulating plant growth and easy availability of nutrients in the soil. Introduction of nano-carbon materials with nutrients and herbal growth stimulants could further support the crop growth by facilitating increased uptake of nutrients, apart from enabling the plants to develop resilience to harsh environmental conditions, resulting in higher crop yields. Some organic bio-stimulants developed recently by Snehasrusthi Group in India have been very successful in improving the growth, yield and quality of several seasonal and perennial crops in India. These bio-stimulants have excellent potential to boost organic agricultural production and income of farmers in the future.

Key words: Phase Transfer Catalysis, PTC, Organic Farming, Plant Growth Stimulants

Introduction

Phase Transfer Catalysis is a new chemical process invented in the recent years. In synthetic organic chemistry, the major challenge has been to blend two chemicals of different nature to form a new product without allowing any intermittent reactions to alter their qualities. A common example is to mix a water soluble reagent and another non-water insoluble organic reagent. This problem is generally solved by adding a solvent that is both water-like and organic-like, which holds both the chemicals together. The efficiency of such blending is high when the catalyst has a larger area of interface. This method of promoting reactions between reagents with opposite solubility preferences is known as Phase Transfer Catalysis (PTC) technology and the chemical used to facilitate such reaction is known as Phase Transfer

Catalyst. This mechanism was first conceived in the 1950s by Henry Hennis, a process chemist at Dow Chemical (1). He outlined the extraction mechanism to explain a successful alkylation reaction which he developed and that was catalysed by a quaternary ammonium salt (2). 10 years later, Charles Starks, who was associated with Continental Oil, reinvented the extraction mechanism and provided necessary support with detailed kinetic studies. Starks coined the term “Phase-Transfer Catalysis”, and published a paper in the Journal of the American Chemical Society in 1971 (3). Since then, PTC has become a practical methodology for organic synthesis. Now PTC is a prime synthetic tool, widely used for industrial applications and manufacturing process. This technology is now being applied effectively in a wide range of organic reactions, in the synthesis of pharmaceuticals, agricultural chemicals, flavouring agents, perfumes, dyes and for polymerization reactions, monomer synthesis and polymer modifications, for environmental control processes and for many other applications (4).

The objective of this paper is to review the role of PTC in different sectors of the chemical industry and how this technology could contribute to the agricultural production, particularly to reduce the use of expensive and harmful agro-chemicals and to promote residue-free, food production. The methodology adopted was to review the basic principle involved in making use of PTC technology by different industries and how some efforts were made by different scientists to apply this technology for promoting plant growth, without affecting food safety and quality. Therefore the study included the review of research papers and industrial processes on PTC and personal interactions with the scientists and chemical professionals engaged in industrial production of organic chemicals. Field visits were also carried out to verify the response of various agricultural crops to newly generated organic compounds in producing residue-free, organic agricultural produce.

Types of Catalysts used for PTC

The principle of PT catalysis is based on the ability of certain phase-transfer catalysts to facilitate the transport of one reagent from one phase into another un-mixable phase wherein the other reagent exists. Thus, reaction is made possible by bringing together the reagents which are originally in different phases. However, it is necessary that the transferred species is in an active state for effective PT catalytic action, and that it is regenerated during the organic reaction (5).

There are many types of PTCs, such as quaternary ammonium and phosphonium salts, crown ethers, cryptands, etc. The types of catalysts used and their details are presented in Table 1.

Among these, the quaternary ammonium salts are the cheapest and hence most widely used in the industry (6-11). Despite the development of PTC in organic synthesis, the mechanistic aspects of PTC remain unclear, mainly due to the difficulty of investigating biphasic systems and the many complex parameters which are required to be analysed.

Table 1. Commonly used PT catalysts

Catalysts	Cost	Stability and Activity	Use and Recovery
Ammonium salts	Cheap	Moderately stable in basic conditions and up to 100°C. Decomposition by Hofmann elimination under basic conditions. Moderately active.	Widely used. Recovery is relatively difficult.
Phosphonium salts	Expensive than ammonium salts	Thermally more stable than ammonium salts, although less stable under basic conditions.	Widely used. Recovery is relatively difficult.
Crown ethers	Expensive	Stable and very active catalysts both under basic conditions and at higher temperatures up to even 150-200°C.	Often used. Recovery is difficult and causes environmental issues due to their toxicity.
Cryptands	Expensive	Stable and highly reactive, excluding the presence of strong acids.	Used sometimes despite high costs and toxicity, due to higher reactivity.
PEG	Very cheap	Lower activity but more stable than quaternary ammonium salts.	Often used; Larger quantities of catalyst cause no problems. Fairly easy to recover.

Source: Jagtapa and others (2)

Mechanism of Exchange

The mechanism of PTC reaction was first proposed by Dr. Charles Starks, who called this mechanism as the Extraction Mechanism (12). According to him, a quaternary ammonium halide (Q^+X^-) present in the aqueous phase undergoes anion exchange with the anion (Y^-) of the reactant dissolved in the aqueous solution. The ion pair formed (Q^+Y^-) can pass through the liquid-liquid interface as a result of its lipophilic nature, seeeee and goes from the interface into organic phase. The cycle continues with subsequent return of catalyst to the aqueous phase (13-16). In the organic phase, the anion of the ion-pair is nucleophilic, which undergoes a nucleophilic substitution reaction with the organic reagent, forming the desired product. The

catalyst subsequently returns to the original aqueous phase and the cycle continues. Thus, PTC is an important and efficient techniques for various organic transformations due to its operational simplicity, mild reaction conditions, use of safe and inexpensive reagents and solvents, and possibility of conducting reactions on a large scale (17). With this technology, it is feasible to facilitate the interphase migration of substrates making reactions between the reagents in two immiscible phases (18). PTC is also a useful method for carbohydrate synthesis, as the reactions can be performed on a large scale (19).

Choice of PT Catalyst: There are two important requirements for using any molecule as a PT catalyst (15). It should be cationic and must contain an adequate chemical structure, which is capable for splitting the nucleophilic anion in the organic phase. Further, the cation-anion bonding must be low for superior anionic reactivity. Some important factors in employing a PT catalyst are stability beneath reaction conditions, ease of formation or availability of catalyst, ease of separation or recovery and non-toxicity (16-21). Although no definite guidelines are provided for the selection of an ideal catalyst for a given reaction system, depending on some of the above factors, appropriate PT catalysts can be used. The application of PTC technology became cheaper and easily available with the use of alternative raw materials like potassium carbonate and aqueous NaOH solution, thereby avoiding the requirement of severe anhydrous conditions and expensive solvents and organo-metallic reagents. As PT catalyst, quaternary ammonium salts based on cinchona alkaloids are often used for asymmetric epoxidation of electron-deficient alkenes. Chiral crown ethers and guanidinium salts are also used for asymmetric epoxidation of electron-deficient alkenes (22, 23 and 24). Presently, temperature-controlled phase-transfer catalyst and hydrogen bond phase-transfer catalyst are regarded as better alternatives to traditional phase-transfer catalyst such as onium salt, crown ether and polyether phase-transfer catalyst. This is because of their excellent properties such as nontoxicity, well-cycling performance and low cost (25). Use of this technology was further extended to in the synthesis process for producing fine chemicals used as agrochemicals, pharmaceuticals, perfumery and fragrances, dyes, paper, etc. during the recent years (26, 27 and 28).

Application of PTC for Organic Farming

In the mid-1980s, when Indian farmers started realising the disadvantages of using higher doses of agro-chemicals, causing the pollution of soil, water and food products, apart from high cost of production, there was a strong wave of organic farming, as an alternative to high input

agriculture. Most of the farmers were directionless, while the scientists were looking for viable alternatives. The challenge was to reduce the quantity of chemical fertilizers being applied, without starving the crop for nutrients and depriving protection against pests and diseases, without using chemicals which cause environmental pollution and health hazards.

With regard to nutrients, it was a known fact that the quantity of nutrients applied in the form of chemical fertilizers was significantly higher than the actual quantity of nutrients absorbed by the crop plants. Higher doses of fertilizers affected soil pH and soil texture, reduced soil permeability and increased the salt content, thereby depleting the soil productivity. Application of fertilizers in lower doses did not maximise the crop yields, because of their inability to absorb the required quantities of nutrients. It was primarily because, a significant part of the nutrients available in the soil and fertilizers were fixed and insoluble for absorption by the plants. Secondly, the plants did not have robust vigour to absorb more nutrients. Hence the scientists were searching for two types of solutions, firstly to increase the release of nutrients and secondly to increase the absorption capacity of plants. The other challenge was to replace the chemical nutrients with organic nutrients. Any breakthrough in these areas could revolutionise the agricultural industry in many ways. With regard to plant protection, the challenge was to avoid harmful chemicals with safer botanical and safe organic products (29).

An Initiative to Tap New Technologies for Improving Agricultural Production

During the same period in the 1980s, Mr. Dhanjay Dhekane, a senior organic chemist, working on pharmaceuticals and dyes in Ahmedabad, India was using PTC technology for developing new formulations. After thoroughly reading a classic book on PTC, titled 'Phase transfer catalysis: Principles and Technique' authored by Starks and Liotta, published in 1978, he was conversant about the advantages of its application in different fields. He has been using triethyl benzyl ammonium chloride, triethyl ammonium chloride and crown ethers as PT Catalysts for producing bulk drug intermediates like n-butyl di-ethyl malonate. The use of PTC technology reduced the process time from 25-30 hours to only six minutes with improvement in the quality and yield. Impressed with this technology, he was trying to apply PTC technology in other fields.

This was the period when India had taken benefits of Green Revolution for over 25 years and the crops were not responding proportionately to increased doses of chemical fertilizers. Increasing cost of inputs and incidences of pests and diseases were bothering the policy makers

and farmers. Thus promotion of organic farming was a hot topic for discussion in the country. Hailing from the agriculturalist family, Mr. Dhekane was also trying to understand the problems of the farmers and explore suitable solutions. He was aware that several botanical extracts were used for boosting plant growth stimulation and pest control by farmers. He found out that the alkaloids and some other phytochemicals present in these plant extracts had certain molecular structures similar to the chemicals used as PT catalysts. So, he thought of mixing these extracts with micro-nutrients, organic nutrients like cow urine, humic acid, sea weed extract, etc. for spraying on plants of different vegetable crops. These plants responded to the treatment and exhibited higher growth. The results were outstanding. This motivated him to take up series of research trials by mixing herbal extracts of neem and drum-stick leaves, pongamia seed extract, etc. with humic acid, fulvic acid, protein hydrolysates, etc. for spraying on different crops at different stages. The results were spectacular (Personal communications). There was a significant improvement in plant growth, flowering intensity, size of the produce, increase in yield and improvement in the quality. The incidences of pests and diseases were also low. So he was convinced about the application of PTC technology for boosting agricultural production.

New Product Development: Mr. Dhekane went a step forward to explore the scope for helping the farmers interested in organic farming with a new and unique product. The aim was to increase the crop yield through the following approaches:

1. Increase the appetite of the plants to consume or absorb more nutrients from the soil;
2. Make more nutrients freely available for the plants to be absorbed from the soil;
3. Sustained release of nutrients to ensure steady supply, without any wastage in the soil through leaching;
4. Develop resistance or provide protection against pests and diseases;
5. Improve the yield and quality of the produce.

Focusing on the above objectives, various ingredients were introduced for different cocktails to be used for spray and soil application and tested on different seasonal and perennial crops.

Application of Nano-carbon: Nanocarbon was another important component, which was included in these products, because of its benefits to plant growth. It was fairly well known that nanocarbon has a significant role in increasing crop productivity through soil Improvement, slow release of nutrients and pesticides, growth stimulation, plant protection, environmental

sensing, etc. Nanocarbon materials were cost-effective, and less toxic to plants, unlike metal and polymers. They were also helpful in maintaining the equilibrium in the environment by targeted and sustained release of fertilizers and pesticides (30). Nanocarbon materials were immensely beneficial as biosensors, carriers, and light convertors, which could improve the sustainability of agriculture. Various benefits of nano-carbon for agriculture are presented in Table 2 (31).

Table 2. Applications of nanocarbon in agriculture.

Application area	Nanocarbon application	Benefits and impacts
Soil improvement	Nanocarbon soil additives	Improved soil structure and nutrient retention
	Nanocarbon-based soil amendments	Enhanced microbial activity and fertility
Nutrient management	Nanocarbon-coated fertilizers	Controlled nutrient release and efficiency
	Nanocarbon nutrient carriers	Better nutrient uptake and reduced leaching
Pest control	Nanocarbon-based pesticides	Targeted pest control and reduced pollution
	Nanocarbon-enhanced biopesticides	Reduced environmental impact
Water purification	Nanocarbon-based water filters	Contaminant removal and improved water quality
	Nanocarbon for heavy metal adsorption	Cleaning polluted water sources
Crop monitoring	Nanocarbon-enabled sensors	Real-time data for optimized cultivation
	Nanocarbon-enhanced imaging systems	Detailed insights into crop health and growth
Environmental remediation	Nanocarbon-based soil remediation	Contaminant adsorption and soil restoration
	Nanocarbon for air and water clean-up	Removal of pollutants and toxins
Smart delivery systems	Nanocarbon-controlled release systems	Targeted and controlled delivery of substances
	Nanocarbon-responsive sensors	Environment-triggered payload release
Precision agriculture	Nanocarbon-enabled precision farming	Tailored practices for optimized yields
	Nanocarbon-based data-driven decisions	Enhanced resource efficiency
Customized plant nutrition	Nanocarbon nutrient release systems	Customized nutrient delivery for plants
	Nanocarbon-modified soil amendments	Improved nutrient availability and plant growth

Source: Bhojiya, 2023 (31).

Support for Green Harvest: Based on the field performance, Mr. Dhekane successfully developed four new generation bio-stimulants for improving agricultural production, for the first time, by incorporating certain ingredients to facilitate the phase transfer catalysis and sustained release catalysis, which were widely used in pharmaceuticals industry. With a commitment to promote eco-friendly farming, he shifted his focus from pharmaceuticals to agriculture and established a new firm under the banner of ‘Snehasrusthi’ to take up commercial production of these bio-stimulants. The details of these products are presented in Table 3 (32). These organic products were tested on a large scale through series of field trials on different crops.

Table 3. Composition of Bio-stimulants developed by Sneha Srusti Group.

Products	Composition	Benefits
Soil Guard	Activated nano-carbon (N300), Humic acid, <i>Pongamia pinnata</i> , <i>Aloe indica</i> , <i>Moringa oleifera</i> , Trace elements, PTC, Cow urine	Increases- soil organic carbon, tolerance to salinity and climate resilience, seed germination, crop root system, nutrient uptake, crop growth and yield
Bio Shield	Activated nano-carbon (N300), Fulvic acid, <i>Pongamia pinnata</i> , <i>Aloe indica</i> , <i>Moringa oleifera</i> , Trace elements, PTC, Cow urine, and others	Improvements - in cell division, photosynthesis, plant growth, flowering, fruit set, yield and quality, shelf life, climate resilience, tolerance to pests and diseases
Sneha Sampurna	Activated nano-carbon (N300), PTC, <i>Sargassum wightii</i> , <i>Saccharum officinarum</i> , DSW extract	Increase in soil fertility, plant growth, flowering, fruit set, yield and quality
Sneha Shakti	Plant extracts rich in amino acids, organic nitrogen, natural phosphorous, sulphur, zinc and other trace elements	Improves – soil structure, soil organic carbon, water holding capacity, root system, crop yield

Source: Snehasrusthi, 2024 (32)

The effects of these organic bio-stimulants on different crops are summarised in Table 4 (Personal communications and Field records). The results highlighted phenomenal increase in healthy vegetative growth, yield and quality, without proportional increase in the cost of inputs. These bio-stimulants have received safety approval from the concerned government authorities for application on all types of crops, which are now marketed in Maharashtra and Gujarat states and the response from farmers has been overwhelming (33). It is anticipated that these products will immensely benefit the farmers across the country. With such new generation safe and eco-friendly inputs, bright days are ahead for the farmers and consumers.

Table 4. Performance of different crops in response to Snehasrushti Bio-stimulants

Agri-produce	Bio-stimulants Used	Results without Using Snehasrushti Products	Results on Using Snehasrushti Products
Banana	Soil Guard Bio Shield Sneha Sampurna Sneha Shakti	Normal Bunch of Bananas, weighing about 27-30 kg. Ave. Banana size 7-9 inch.	Bunch of Bananas weighing 42-45 kg. Average banana size 10-11 inch.
Mango (Kesar variety in Junagadh, Gujrat)	Soil Guard Bio Shield Sneha Sampurna Sneha Shakti	Each box of 10 kg contained 38-42 fruits. Size of Mangoes was decreasing from lower to upper branches on tree.	Each box of 10 kg contained 28-30 fruits. Size of Mangoes was uniform throughout the tree. Yield 60-65% higher.
Mango-100 year old Alphanso trees in Deoghad Maharashtra	Soil Guard Bio Shield, Sneha Sampurna Sneha Shakti	Trees yielded only 17-20 boxes of 5 dozen each. Shelf life: 7-9 days.	Trees yielded about 47-50 boxes of 5 dozen each. Shelf life: 15-17 days.
Lemon in Karveer block, Kolhapur, Maha	Soil Guard Bio Shield	Plants were 2.5 feet tall with smaller leaves. Yielded no fruits.	Plant were 4-4.5 feet tall with bigger leaves. Each plant had several fruits
Turmeric Selam variety	Soil Guard Bio Shield	Plants were small. Yield 500-650 gm/rhizome (17-21 qt./acre dry turmeric). Curcumin content was 3.5-3.7%.	Bigger plants, larger leaves, yielded 2.5-4.0 kg /rhizome (dry turmeric 38-42 qt/acre). Curcumin content 4.3-4.7%.
Onion	Soil Guard Bio Shield Sneha Sampurna Sneha Shakti	Production: 120 qt./acre. Onion size was medium	Production: 180-200 qt./ ac. Onion were medium and large size, fresh looking
Potato Pink variety for making chips	Soil Guard Bio Shield Sneha Sampurna Sneha Shakti	Production: 5-7 medium size potatoes/plant.	Production: 12-14 medium size potatoes/plant.
Wheat (Khapali / Emmer)	Soil Guard Bio Shield Sneha Sampurna Sneha Shakti	Production: 12-15 quintals/acre	Better vegetative growth. Production: 24-25 quintals/acre
Cotton	Soil Guard Bio Shield Sneha Sampurna Sneha Shakti	Yield: 8.5-8.7 qt./acre. Lesser staple length and tensile strength. Susceptible to pests.	Yield: 20-22 qt./acre. Better staple length and tensile strength.
Sugarcane	Soil Guard Bio Shield Sneha Sampurna Sneha Shakti	7-8 shoots/plant. Cane weight 1.5-1.8 kg and length 11-12 feet. Yield: 45 tons/ac. Sugar content: 8.5-9%.	17-18 shoots/plant. Cane weight 2.5 kg, length 17-19 feet. Yield: 75 tons/acre. Sugar content: 9.5-9.7%.

Source: Unpublished Reports and personal observations

Conclusion

Application of Phase Transfer Catalysis (PTC) technology, which had revolutionised the dyes and pharmaceutical industries in many ways was introduced in Indian agriculture, during the

mid-1980s. Herbal based bio-stimulants along with phase transfer catalysts, nano-carbon and micro-nutrients indicated their potential to boost plant growth, yield and quality. The phase transfer catalysts facilitated the increase in absorption of nutrients by stimulating plant growth and availability of nutrients in the soil. Introduction of nano-carbon particles with nutrients and herbal growth stimulants could further support agricultural crops by facilitating the increase in uptake of nutrients, apart from enabling the plants to develop resilience to harsh environmental conditions, resulting in higher crop yields. Some organic bio-stimulants developed recently in India have excellent potential to boost green agricultural production and income of farmers in the future.

Disclaimer (Artificial intelligence)

Author hereby declare that NO generative AI technologies such as Large Language Models (ChatGPT, COPILOT, etc) and text-to-image generators have been used during writing or editing of manuscripts.

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