

Flavour & Fragrance through Green Chemistry

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Fragrances over the years has always gained a mystical status in the society and thus been also linked with a lot of ritual and religious practices.

In the ancient times when science was at its infancy stage the natural raw materials such as Agarwood fondly known as 'Oudh', Frankincense, Sandalwood, Benzoin Resinoids such as Tolu and Peru Balsams, Musks from the Musk Deer were the most commonly used fragrances due to their high fragrance retentive nature. The Arabs in order to fragrant themselves used to burn Agarwood barks and then apply its ash over the body, the West particularly Europeans consider Frankincense to be most sacred fragrance as it has been traditionally used in prayer meetings whereas the Indians consider Sandalwood fragrance the most pious scent hence gained the special memory association to religious rituals. India in particular has also made its special place in the fragrance industry due its exquisite fragrance of sandal and thus sandal has become synonymous to India. Thus these fragrances therefore gained a special status in the society having a distinct cultural impression or association.

With the passage of time people become more aware on the nature of scents, and their behavioral patterns when mixed with each other. Towards the end of the 19th century, the fragrance industry increasingly targeted women belonging to the middle class and the first synthetic fragrance ingredients made their appearance. The Second Empire was marked by a brief yet excessive infatuation with vetiver and patchouli. This fad came to an end during the latter part of the 19th century when the emergence of a strong middle class brought about a more refined taste in fragrance. The trade of luxury goods blossomed and perfumery was increasingly viewed as an art. New and original fragrance notes such as coumarin, heliotropine, vanillin, ionone and the first aldehydes were created through the brand-new process of chemical synthesis causing an olfactory revolution. It marked the birth of modern perfumery.

The development of a new product in the chemical industry is driven by needs like technical properties, price, performance ratio, biodegradability and safety of the product. However, in terms of improving more and more on ecological criteria coupled with biodegradability the production process needs a greener path of production thus sighting the increasing role of green chemistry in the flavor & fragrance industry.

Of all the major definitions of green chemistry the most apt and logical principle is 'Use renewable resources as raw materials wherever it is possible.' Perfumery on the whole has its

origin in the utilization of natural resources such as essential oils and natural extracts, but after the triumphant progress in the synthetic fragrant substances the natural ingredients have a restricted usage. However, several natural raw materials consist of only natural hydrocarbons that are not suitable as smelling substances per se, but offer excellent possibilities for functionalization with oxygen containing group transformations leading to the synthesis of excellent fragrant materials the sustainable way.

India is blessed with many positive factors, which enables it to stand at unique position in agriculture-based product. After achieving self-dependence on food front now India is in position whereby it has become net exporter of agriculture based product.

Aromatic plants are very important part of agriculture and have been grown in India for their fragrance and therapeutic use from ages. In last four decade due to effort of National Scientific Laboratories such as CSIR, ICAR, CIMAP, Educational Institutions with emphasis on Research of Natural Aroma Molecules along with the industrial houses who have had the vision for Greener way to approach the manufacturing of aroma molecules; many crops have been taken on large-scale cultivation having an excellent success ratio. Mint is the very apt example of it, which has managed to make India the ace producer of same driving away very strong competing Countries like China, Brazil having equivalent agricultural strength. Many advance countries such as Germany and Japan boasts of a very strong production base of synthetics also are finding it very difficult to compete on price and quality with Indian produced natural Menthol. This progress very clearly indicates that if planned efforts are put India can be No.1 player in this field with very strong position in agriculture fields which can be considered as "LABORATORY UNDER SUN".

Post the revolution in the field of Biotechnology, the National laboratories have been able to develop strains of Cymbopogon, Ocimum species that are engineered to give high yield/acre with a higher degree of the desired component. This development shall enable India to make major break through in many terpene chemicals.

Over last few decades terpene chemicals were being replaced by synthetic equivalent petrochemicals & turpentine as starting materials for aroma chemical synthesis; and the synthetics are bound to become scarce in this New Millennium.

Therefore the need of the hour is to ensure that we have extensive plantation on millions of acres of these two species as intercrop with horticulture or on waste land which shall not only improves environment only but shall also increase the green Economy by means of rural employment and generation of rural entrepreneurs.

Recent noble prize on 4th October 2004 to Mr. Richard Axel for his contribution towards Aroma Science for medicine proves that future medicines will be based on Terpene & Sesquiterpenes for which essential Oils are best source. Synthetic molecules which often have three un-natural Character viz;

- a) Non bio-degradable
- b) Non Chiral
- c) Non natural identical;

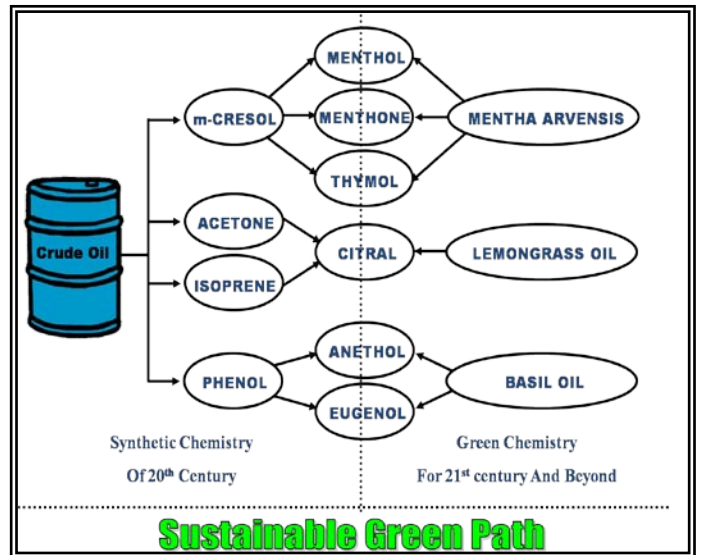
may not be accepted by human body and may be treated as toxins which has to be evaluated very carefully before allowed to enter human body. This whole new branch of science may emerge as new medical science which described beautifully in CIMAP director's report in 2003. Dedicated Laboratories of CSIR like ITRI with extensive work on such common Terpene Chemical used frequently for F & F industry along with cosmaceuticals may prove very clearly how natural Terpenes & Sesquiterpene based Chemicals are superior on above three criteria as compare to Synthetic equivalent Chemicals such work will allow entire world to shift from Synthetic to natural through green Chemistry with green path. This development puts India in whole world in unique position as production base for natural essential oils having a very solid fundamental base of long term sustainability.

Based on need of essential oils and their isolates (natural or synthetic) on global scale a planned projection is done; Thereby sighting urgent need for strategy planning of steady sustainable supply of natural essential oil & their natural isolates. In projected figure price projected may seems to be very low compare to prevailing price for same oils in market. Here we have to take in consideration competition from synthetic materials, which are derived from turpentine, and petroleum feed stock like Isoprene. These materials are processed on very large scale so economy of scale favors final prices of this synthetic derived molecule at present compare to equivalent natural isolates. However we should take in consideration following factor for future, which can favor production of these isolates, derived from natural essential oils :-

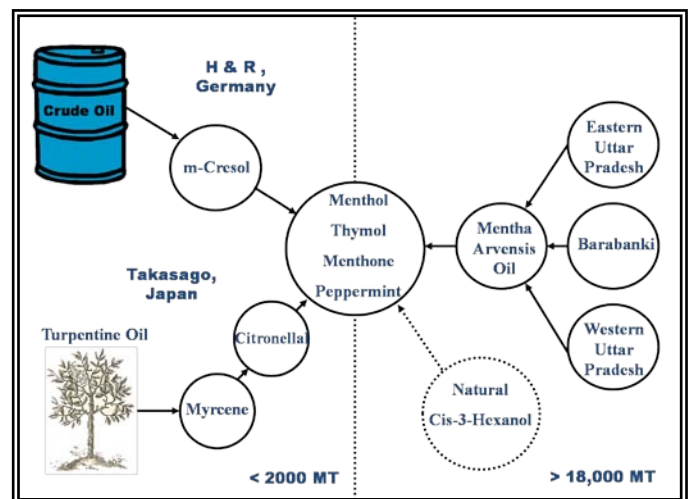
- 1) Prices of petroleum products are going up so in future with depletion of it prices are expected to rise further.
- 2) Prices of turpentine is going up gradually because of high cost of labour in producing country like China, Brazil & Indonesia. As Turpentine is obtained from gum resin which is very labor intensive & requires labor in hilly rural areas which is becoming less & less with urbanization.

3) Recovery of turpentine oil from crude sulfate turpentine liquor also require lot of energy which is derived from petroleum as fuel so prices for these are rising in last few months. It is expected that same trend is going to continue in future. Again for separation and conversion of Alfa and beta Pinene from turpentine to it's desired basic derivative like Geraniol, Citronellol, Citral, Linalool also requires lot of energy and chemicals, which are derived from petroleum feed stock.

4) Conversion of petroleum feed stock and turpentine to above mentioned derivatives require use of lot of hazardous reactions, which leads to generation of many pollutant as well as explosion hazards. Now with more emphasis world over on neat and clean technology this facility of production may find it difficult to produce derivatives like Geraniol, Citronellol, Citral, Linalool at very low cost as they may have to spend lot of money on pollution control and safety of operation.



5) Essential oil processing in form of value added product to its isolates is done through multi-component fractional distillation. In last two decades more than adequate capacity for it has been installed in producing as well as consuming area within India. This capacity is many times more than total current production of essential oils making this capacity as spare. If production of essential oil is



increased then this high capacity plant can be effectively judiciously utilized without new investment. This can make availability of value added isolate at very economic price enabling same to compete with synthetic equivalents.

6) Utilization of bi product from processing has made many essential oil economically viable. For example Sclareol from Clary sage spent biomass by solvent extraction, Cis-3 hexenol from mint terpenes and distillation water. Thus more utilization of bi product can

be looked in to so that final essential oils become economical. To illustrate unique position of Indian consuming industry we can take here example of Patchouli oil which is becoming very important oil for cultivation. Bi product of Patchouli oil cultivation and extraction in form of twigs and spent leaf can fetch more than 60% of raw material cost by Agarbatti Industry for making there raw Agarbatti making production of Patchouli economically viable. So in future India can even compete strong producing country like Indonesia and China, which are controlling maximum market share so far.

- 7) Post harvest processing of essential oil bearing biomass involves steam distillation where fuel cost is very important. Most of units operating in mint belt are working on spent biomass as fuel thus making cost of distillation per kg very economical (approx. Rs.30-35 per kg.). It can be brought down even further if same equipment is used through out year instead of 2-3 month at present. There is labor cost of distillation, which ranges Rs.18-20 per kg however if equipment is utilized through out year for other crop distillation cost per kg will come down further making essential oil more economically viable. This will develop much needed employment.

The plants chosen are carefully and very strategically categorized under the segment of the HIGH PRIORITY RATINGS as they bear the important start up molecules for large scale production of many aromatic chemicals derived from the Natural Origin which is highly a sustainable route of production in comparison with the purely synthetic route owing to the use of chemicals right from the start up molecules. These natural derivatives also help in building up overall eco-friendly industrial model whereby there is complete utilization of the plant leading to a better energy efficient/ fuel efficient system where the natural waste can act as a part substitute for modern conventional fuel systems such as coal, diesel.

These crucial listed plants are the plants chosen for a dynamic discussion in order to excel and achieve the status of world leaders in production of essential oils with unmatched quality.

These plants can be categorized according to their planting duration and with this systematic classification planting cycle and the intercropping of plants can be easily monitored.

1.) Short-term Crop :

- a. **Duration : 3-4 Months**
- b. **Species : Ocimum**

- Ocimum species are well known for being a rich source of many naturally occurring essential oils, aroma chemicals that have a great value in perfumery and flavoring industry. In Indian sub – continent around 9 species of Ocimum are available having varied sets of predominant marker compounds thus making each species a unique one to develop.

2.) Medium-term Crop :

a. **Duration** : 4 – 5 Years

b. **Species** : *Cymbopogon*

- *Cymbopogon* is one of the most important essential oil yielding genera of the Poaceae. The genus comprises ~140 species that are widely distributed in semi-temperate to tropical regions of Asia, Africa and America. Approximately 45 species have been reported to occur in India. The *Cymbopogon* species that produce volatile oils are called aromatic grasses. Different types of essential oils, such as palmarosa oil, lemongrass oil, citronella oil and ginger grass or rusa oil, are very popular in perfumery and have an ever increasing demand for the same as their oils house a galaxy of essential natural chemicals.
1. **Lemongrass:** Lemongrass is one of most important aromatic grass which can become a crop of future India based on experience among many aromatic crop. Reason for same is its application for derivatives like Vitamins which require basic molecule like Citral which is major component of this oil. Lemongrass is well adapted to Indian conditions and supplements dairy industry.
The ever increasing prices in the petrochemical industry have made it highly impossible to process citral from the synthetic route where the demand for citral is very high in the pharmaceutical industry which acts as an important precursor for the production of many vital molecules.
 2. **Palmarosa:** Palmarosa or Rosha grass of family Poaceae and species *cymbopogon*, Is an important essential oil yielding aromatic grass. Earlier it used to be collected from the forests of central India by forest product traders but to establish a balance between continuously diminishing natural resource and ever increasing demands the cultivation has been resorted. Naturally occurring Palmarosa is of 2 types i.e Motia and sofia, of which variety Motia of commercial importance.

Plamarosa is an important source for the production of geraniol which is an important compound not only for the perfumers but also for the flavourists to impart the rose flavour to their formulations.

As noted earlier with the rise in turpentine prices it is of utmost importance to search for a high yielding variety with high geraniol content to reach the benchmark rate of 10 USD / Kg.

3.) Long -term Crop :

a. **Duration** : min. 25 Years

b. **Species** : **Eucalyptus**

1. **Eucalyptus citrodora:** Citrodora plant has tasted commercial success in only a few pockets that too in clusters of southern states of India predominantly Kerala, Tamil Naidu & Karnataka. The cultivation of citrodora is practically nil in the northern and central region which boasts of extremely fertile land owing to the suitable conditions for growth of majority of the aromatic plants.

Eucalyptus citrodora is an extremely important plant as its oil on fractionating yields an important perfumery compound – Hydroxy citronella, Citronellol and citral to some extent. The large scale cultivation of eucalyptus is a feasible solution on controlling the competitive market with competitive price offering of close to 10 USD/ Kg.

2. **Eucalyptus hybrid** is a multi – purpose tree yielding good pulp – wood, fuelwood and charcoal as result of which large scale plantations were raised in different state of India to meet the demand of pulpwood & fuelwood but not much attention has been paid to this species in respect to its oil. The distillation of oil is also highly economical as 95% of oil recovery occurs within 2.5 hrs. of distillation, thus making entire process energy saving and a greener way to process the oils.

Conclusion:

Thus by the above listed means India can play a pivotal role and be a torch bearer in producing the natural essential aromatic isolates having a greener sustainable base of production. The chemistry of essential oils fundamentally revolves around the basic building block of essential oils – the Terpenes, thus in order to achieve the significant success in green production of aroma chemicals, these wonder molecules must be studied in depth.