Modeling and simulation of *Mentha arvensis* L. essential oil extraction by water-steam distillation process

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Abstract - *Oil from Mentha arvensis L. and its components are extensively used in flavor, fragrance and pharmaceutical industries. Commonly known as corn mint, around 225 x 10^3 ha of land gets cultivated in the mint belt in the geographical area of the Indo-Gangetic plains with gradual extension in the past few years. Among the distillation processes available, the process of water-steam distillation serves major role in the essential oil isolation from Mentha arvensis L. crop. The aim of the work is to model the yield of essential oil isolation process from corn mint crop. Diffusion in solid model for mass transfer has been used, based on flake particle (flat geometry). Experimental yield data of oil mass extracted as function of isolation time was used for comparison with the model used in the simulation. Experimental monitoring of yield data was carried out on a bench scale set-up as well as pilot scale field distillation unit, and was used for validation of the model.*

Key Words: **DISTILLATION, ESSENTIAL OIL, *Mentha arvensis* L., MATHEMATICAL MODEL, EXTRACTION YIELD, DIFFUSION COEFFICIENT, CLEVENGER, PILOT SCALE, FDU.**

1. INTRODUCTION

The essential oil of *Mentha arvensis* L. commonly known as menthol mint or corn mint is isolated by steam distilling freshly harvested or partially dried flowering or vegetative shoot [1]. The corn mint essential oil, *l*-menthol crystallized from the essential oil, de-mentholated essential oil and other mono-terpenes fractionated from de-mentholated oil are some of the important commercial products of this field crop. The food, pharmaceutical and cosmetic industries use the products of corn mint crop essential oil in large quantities. India, China, Brazil, Japan, France and USA are the major producers of corn mint essential oil [2]. Yield of essential oil through extraction process become important as oil is present in plant in low concentration. This makes process engineering important in extraction operation.

Distillation techniques used to isolate essential oil from medicinal and aromatic plants are classified into three categories on the basis of difference in operation as well as geometric configurations of the equipments used. These three distillation techniques are hydro-distillation, water-steam distillation and steam distillation. In hydro-distillation, the biomass is completely immersed in boiling water. In water-steam distillation, the biomass is supported on a grid and below this support water is used in the same vessel for producing steam for the extraction process. Thus, the boiling water does not overheat or burn the biomass, and the water hydrolysis of the oil components does not take place as possible in case of hydro-distillation. Hence, a distinct advantage is achieved in water-steam distillation process. In steam distillation, steam is generated separately in a boiler and passed through the biomass of the distillation still. Steam distillation requires efficient operation and maintenance. Water-steam distillation is the preferred choice for corn mint oil extraction, adopted and commercially employed by majority of farmers and distillers in the field as field distillation unit (FDU).

1.1 Utility of mathematical models

Lower recoveries in field distillations have been reported because of the following two major reasons: Incomplete recovery of the essential oil from the crop biomass and loss of dissolved essential oil in condensate or distillation water. Crop biomass of palmarosa was distilled in the field distillation unit, and the distillation efficiency ranged from 64% to 65% in comparison to Clevenger distillation [3]. Thus, an efficient field distillation operation is quite important in terms of good recovery of essential oil present in crop. Since the essential oils are present in very low amount in oil bearing crop, knowledge of the oil yield and modeling of extraction process become important for the technological and economical analysis.

Mathematical models are useful in development of scale-up procedures from laboratory to pilot and industrial scale. Such models are also used to generalize the experimental results and enable to fit some experimental data for process simulation. To select an appropriate mathematical model for process simulation, knowledge and information on essential oil distribution in plant materials and experimental results on production kinetics can be used [4]. It has been stated that the rate of vaporization of oil during steam distillation from a plant material is not influenced by relative volatility of oil components but by their solubility in water in vapor phase, that is steam. A first-order kinetic model was used to simulate pilot scale steam distillation units for essential oil extraction yield from lemon grass [5].

Essential oil extraction from different herbs on the basis of mechanism of mass transfer, follow falling rate (diffusion controlled) regime. Here an unsteady situation prevails throughout and the solute concentration at the exit falls progressively as the extraction proceeds. Extraction of natural material with relatively low amount of material to be extracted, show such type of behavior. An appropriate model based on production kinetics contributes to the fundamental understanding of the extraction process and serves for its better control and higher efficiency. The mathematical modeling of essential oil extraction is an inevitable step to project commercial plants with good operational parameters, since we are dealing with natural plant feed. This feed is really different and difficult to handle in comparison to a chemical feed of fixed specifications.

1.2 Oil extraction through mint herbs

Extraction of solute from natural product like essential oil carrying herbage is a mass transfer process involving release of solutes from porous or cellular matrices into a solvent phase. The process of water-steam distillation as well as hydro-distillation and steam distillation are environmental friendly producing high quality oil and relatively safe to operate. These processes are used, for example to extract cornmint oil with high commercial value menthol component from *Mentha arvensis* L. crop. It is very difficult to completely extract the fresh mint herbs by field distillation. Wilting and drying of the plant material is being done because during this preprocess, the cell membranes gradually break down, and the liquids up to certain extent become free to penetrate from cell to cell.

Essential oil storage in glandular trichomes on the leaf surface is a feature of the family Lamiaceae and has been examined for several plants belonging to that family [6]. This characteristic of oil distribution helps in understanding preprocessing phenomena of the mint herbs as well as mass transfer and diffusion behavior. Mint species have majority of oil born on its surface. During steam distillation of fresh unwilted mint all leaf surfaces become flooded by moisture from the plant cells that collapse in the presence of steam. The cut herb left for drying loses cell moisture and creates the absorptive surface on which all transference of heat from the steam to the oil depends. The oil yield in case of dried crop is higher, as in the dried crop mass transfer resistance is reduced. Surface of mint species are absorptive up to certain extent and partial drying increases this absorptive surface.

1.3 Oil distribution characteristics in Lamiaceae family herbs

It has been reported that the majority of essential oil is localized in exogenous deposits on the leaves and there are few exogenous and endogenous sites in the stem. Algerian *Mentha spicata* L. essential oil yield evolution during hydro-distillation has been investigated as a function of time [7]. Hydro-distillation of essential oils was studied using a model and two types of particles have been described. Ground particles with initial homogeneous solute distribution, and are formed by grinding seed or root. This is spherical particle with the core of intact cells surrounded by region of broken cells. Second type of particles are formed from herbs having essential oil deposited in glandular trichomes on the surface of their leaves and other flat and thin parts as in the herbs of family Lamiaceae. This particle is a flake (flat shape) having glandular trichomes on its upper surface [8].

Yield of citronella (*Cymbopogon winterianus*) essential oil by steam distillation was studied and mathematical modeling was performed using a model based on diffusion mechanism related to mass transfer [9]. Same approach has been used later and essential oil recovery has been predicted of rosemary (*Rosmarinus officinalis* L.), basil (*Ocimimum basilicum* L.), and lavender (*Lavandula dentate* L.) by steam distillation [10]. Mathematical models are used to simulate a process to know about extraction process behavior. Present study is aimed to investigate the production kinetics and qualitative characteristics of corn mint oil yield experimental data obtained in the laboratory as well as pilot scale level. The experimental kinetics data obtained for the process of water-steam distillation has been applied for comparison with the diffusion model based on mass transfer. Validity of the model has been analyzed for its use in the simulation of extraction of essential oil from corn mint crop of family Lamiaceae. The model is based on one-dimensional unsteady-state diffusion through flake (flat) particle geometry.

2. Materials and methods

2.1 Plant material

Experiments were carried out during the vegetation periods of the crop planted in subtropical humid climatic conditions of northern India in the field of Fragrance and Flavor Development Centre, Kanpur. The crop was planted with standard agricultural practice and the plantation is done from mid of February to mid of March. Using transplantation method, the germinated pieces of suckers grown in nursery are transplanted in the experimental farm. For experiments the planted crop was used after it had completed almost 90 days of its growth.

The over-ground shoots were harvested around 5 to 8 cm above ground level. During harvesting of the crop for experiments, storage of fresh crop and during ambient drying of the crop, same procedures were followed to maintain uniformity in handling, storage and treatment (preprocessing). For simultaneous moisture analysis, a part of the collected material was used. The moisture content of the crop was estimated by azeotropic method (Dean Stark method), which is used to estimate the amount of moisture present in the natural plant material. The average moisture content of harvested crop substrate was evaluated. Also, the average value of the leaf thickness was estimated to be used in the mathematical modeling. For studying the behavior and associated yield of the dry state of the crop, it was subjected to shade drying under ambient condition ensuring that the crop did not turn brittle and the extent of drying does not bring loss in oil content of the crop, which could affect the oil yield.

2.2 Isolation of essential oil

Distillation was carried out in laboratory in a still designed to operate under conditions meeting the requirements of water-steam distillation for *Mentha arvensis* L. crop. The capacity of this unit under external heating (rheostat controlled electrically heated) was 0.006 m^3, and the still could be randomly filled by metal pall ring packing up to the desired level which is higher to the level of water charged for steam generation. This arrangement provides a platform for the packed vegetable biomass and prevents it from getting immersed in water. Water could be used up to required capacity with sufficient gap between plant material and water under boiling stage during process. Thus, overheating and thermal degradation of the plant material is avoided as possible in case of hydro-distillation. Only saturated steam comes in contact with crop charged in the vessel. Boiling water was in the bottom of the vessel and the crop well supported was nicely packed in the upper portion of the vessel.

The outlet of the vessel was connected to a water-cooled condenser which had a separator at its downstream in which oil and distillate water got separated. The set-up was similar in operation to the water-steam field distillation unit. The aim of any essential oil distillation unit is to isolate as large as possible percentage of the essential oil present in the aromatic herbage with the oil yield in a state of acceptable purity.

2.3 Mathematical modeling

The mass transfer of essential oil through oil bearing plant particle during water-steam distillation occurs as an unsteady-state diffusion process. For a batch process where no chemical reaction is involved, it can be described by Fick's second law of one-dimensional unsteady-state diffusion:

$$\frac{\partial C_A}{\partial t} = D\frac{\partial^2 C_A}{\partial y^2} \qquad \text{----------------------------------} \quad (1)$$

C_A is the average concentration of the essential oil in the plant particles at time t, y is the distance along the direction of diffusion and D is the effective diffusion coefficient. Here we are able to predict that how diffusion causes the concentration field to change with time. While obtaining the solution of equation (1), following assumptions are made:

i. The value of diffusion coefficient, D remains constant.
ii. The soluble constituent is having initial uniform concentration in the particles which are to be processed.
iii. The concentration of essential oil on the external surfaces of the plant particles at any moment during the extraction process is zero.
iv. There is no resistance to diffusion in the fluid that is surrounding the solid particles.

The last two assumptions become valid with the steam carrying out all oil instantaneously from the external surfaces of the plant particles and the fluid is continuously getting replaced during the extraction process. Also, there is no resistance to the mass transport of essential oil from the external surfaces of the plant particles. It is important to note that the diffusion resistance within the solid is the stage controlling process [11]. Equation (1) can be solved by integration with the appropriate initial and boundary conditions for simple geometrical cases of flat shape, cylinder or sphere [12]. Figure 1 is showing flat shape geometry.

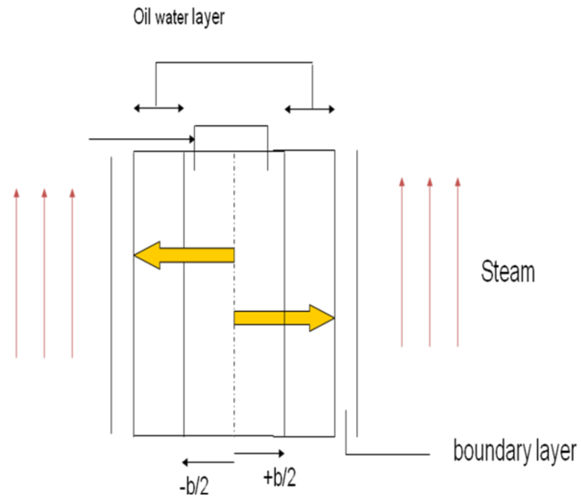

Fig -1: Flat shape particle geometry surrounded by fluid

As shown in figure 1, for one dimensional rectangular geometry for a flat plate (flake) with the diffusion taking place only toward and from the flat parallel faces, with b as thickness of flat geometry and, $(0 \le y \le b)$, we have ;
With initial condition of $C_A = C_{A0}$ for t = 0 and boundary conditions of,

$C_A = 0$ for y = 0 and $C_A = 0$ for y = b,

the solution to equation (1) is given by the following equation:

$$1 - \frac{m_t}{m_\infty} = 1 - E(t) = A \sum_{n=0}^{\infty} e^{-\left(\frac{(2n+1)^2 \pi^2 Dt / b^2}{(2n+1)^2}\right)} \qquad \text{-----}(2)$$

Where, A = $\frac{8}{\pi^2}$ = Constant, and with,

E (t) = Degree extraction of oil at time t = $\frac{m_t}{m_\infty}$

Total amount of oil extracted after time t = m_t
Maximum amount of oil extracted in infinite time = m_∞
For different essential oil bearing plants, Clevenger apparatus is being used for determination of maximum yield of essential oil that can be recovered or isolated. Clevenger distillation determines oil content of the crop due to continuous redistillation or cohobation of condensate (distillate) water and more controlled distillation of aromatic and medicinal crop biomass as regards to time [3,13]. The essential oil content determined by Clevenger method under standard conditions, for the fresh crop was 0.83 ± 0.01 %. To estimate the oil content in the crop, the accurate yield is available from the Clevenger distillation of the crop selected from the same lot and of the same state. This has been taken as the value of m_∞. The equation (2) can be expressed as:

$$1 - \frac{m_t}{m_\infty} = \frac{8}{\pi^2}\left[e^{-\frac{\pi^2 Dt}{b^2}} + \frac{1}{9}e^{-\frac{9\pi^2 Dt}{b^2}} + \frac{1}{25}e^{-\frac{25\pi^2 Dt}{b^2}} + \ldots\ldots\ldots\right]$$

The above expression is sum of exponential decays, and at long time the later (more rapidly decaying) terms are of less significance and the first exponential term (n=0) in equation (2) becomes dominating and the equation (3) assumes the following form,

$$1 - E(t) = \frac{8}{\pi^2}e^{-\frac{\pi^2 Dt}{b^2}} = (0.811)\,e^{-kt} \quad\text{-----------------(4)}$$

Here k is the kinetic constant that includes the value of effective diffusion coefficient.
Finally equation (4) can be expressed as:

$$ln\left[\frac{1}{1-E(t)}\right] = 0.209 + kt \quad\text{------------------(5)}$$

Thus, in the diffusion model, to obtain parameter D, equation (5) that represents a straight line and yield data of the experiments have been used.

3. Results and discussion

Table (1) shows the cumulative oil yield in relation to time during the extraction process on water-steam distillation laboratory set-up. The kinetic data of oil extraction providing experimental yield on weight basis, Y(w/w) and the degree extraction, E(t) are the quantities used in the mathematical simulation from experimental data. Obtaining the value of degree extraction of oil at time t has been described earlier. The values have been shown in Table (2).

Table -1: Experimental data of essential oil cumulative yield from water-steam distillation laboratory set-up

Time (s)	Oil mass, m_t(g)
0	0
1800	1.936
3600	3.256
5400	4.224
7200	4.752
9000	5.016
10800	5.28
12600	5.368
14400	5.398

At the bench-scale level amount of crop used as feed for the runs was taken as 700 g and the yield curves were obtained on the basis of the oil mass that was isolated in relation to the sample quantity used in the distillation process on wet basis. The yield curves were obtained for the pilot scale runs, and here the amount of crop used was to the level of 48 kg. Here also the yield curves have been obtained on the basis of the oil mass that was isolated in relation to the feed quantity used in the process on wet basis. The harvesting and preprocessing of the crop was carried out as described earlier in sub-section 2.1, and has been used as feed for essential oil extraction process.

The plot of of ln [1/1-E(t)] versus extraction time of oil from *Mentha arvensis* L. crop on water-steam distillation laboratory set-up has been shown in chart (plot) 1, providing the values of the slope and intercept. Subsequently linear regression of the data was carried out and the value of diffusion coefficient was worked out. Same procedure was adopted for oil extraction carried out on water-steam distillation pilot scale unit.

Table -2: Yield data used in mathematical simulation as a function of time

Time(s)	Yield(w/w)	E(t)
0	0	0
1800	0.00276	0.333
3600	0.00465	0.560
5400	0.00603	0.727
7200	0.00678	0.817
9000	0.00716	0.863
10800	0.00754	0.908
12600	0.00766	0.923
14400	0.00771	0.929

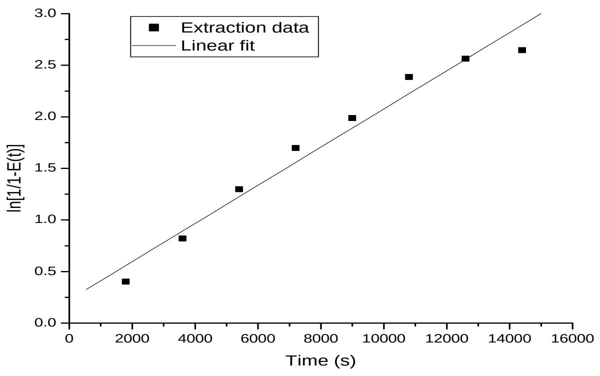

Chart -1: Plot of ln [1/1-E(t)] vs. Extraction time for lab set-up

The comparison among the laboratory experimental data and the computed values from the mathematical model of water-steam distillation yield with time is shown in chart 2. Extraction yield curve with time for pilot scale experimental data and mathematical model is shown in chart 3. In the present study, diffusion in solids model has been applied for the mathematical analysis of experimental kinetics data obtained from isolation of oil from water-steam distillation. Diffusivity, D value obtained for the lab run was 1.027×10^{-11} m^2/s. This parameter was obtained using equation (5) representing a straight line and experimental yield data. Linear regression analysis and the value of correlation coefficient suggest excellent linear reliability. Correlation coefficient value of 0.98 was obtained. Diffusivity, D value obtained for the pilot scale run was 1.0287×10^{-11} m^2/s. The analysis of the results of both the cases as shown in the plots project that the mathematical model based on diffusion serves to fit quite well the experimental data. The reliability and confidence of the procedure is upgraded when pilot scale experimental data was dealt with.

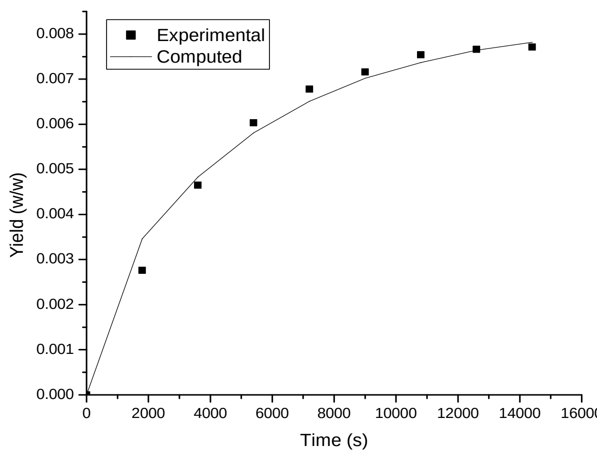

Chart -2: Water-steam distillation yield curve vs time for lab experimental data and mathematical model

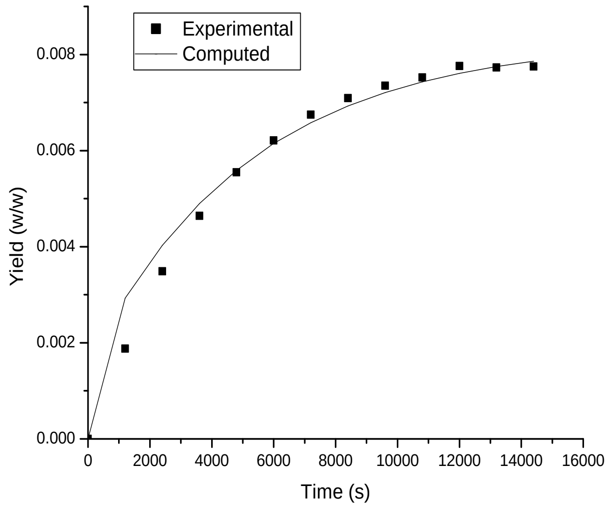

Chart -3: Water-steam distillation yield curve vs time for pilot scale experimental data and mathematical model

4. CONCLUSIONS

The present research was carried out emphasizing the utility of water-steam distillation process and crop as a raw material was utilized in best feed form. Lab findings were compared and verified with pilot scale results. The experimental results of *Mentha arvensis* L. oil isolation yield agree very well with the flat particle based unsteady state diffusion model. The values determined for the diffusion coefficient when compared with the available literature data correspond in terms of order of magnitude. Thus the model can be applied to predict the time required to obtain a given isolation yield and would provide useful information for the commercial process. This would lead towards a proper operation and management of a commercial unit which is in most of the cases is a water-steam field distillation unit.

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