Modelling the yield of Coriandrum sativum

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***Abstract*—The study of yield from Coriander seeds (*Coriandrum sativum*) and its modelling was conducted. The theoretical models applied for the yield modelling was Desorption model, Hot Ball Diffusion model, Brunner model and Esquivel Model. The experimental data was collected from Zoran Zekovic's (2017) experiment on Supercritical fluid extraction of coriander seeds. The significance of this experimental result is the method of extraction via supercritical fluid extraction is becoming a trend in recent methods of extraction. The results obtained was then fitted into the models mentioned above, to determine which model would predict the best for yield from Coriander seeds. Model fitting was done by applying Microsoft Excel's data tool, Goal seek. It was determined that the Brunner model which was based on Fick's law, was giving the best fit when compared to the extraction results conducted.**

Keywords*— *Coriander seeds, yield modelling, Brunner model, process optimization.

I. INTRODUCTION

Coriander is a plant found annually in the family Apiaceae and commonly, the leaves and seeds are widely used as a condiment in the food industry. It is being used to add flavor to various commercial foods such as teas, meat products and pickles (V. Illés, 2000). In addition to that, they have also been recognized as their role in medicinal properties. Based on studies conducted, the seeds have been used to overcome gastrointestinal problems, rheumatism, joint pains, with the recent studies also demonstrating the effects on carbohydrate metabolism which causes hypoglycemic action (H. Wangensteen, 2004). The seeds and leaves both possesses certain type of antimicrobial activity to fight against several pathogen bacteria and yeasts (J.C. Matasyoh, 2009). Besides that, for the coriander seeds (CS), they contain up to 1% of essential oil (EO) (M. Bajpai, 2005) such which the main compound is monoterpenoid linalool (>50%), and geraniol, limonene and camphor are present in significant quantity (Z. Zekovi´c, 2011). Furthermore, the coriander seeds also contain vegetal oil containing high concentration of monounsaturated fatty acids, especially the concentration petroselinic acid (H. Mhemdi, 2011).

For obtaining the best result in terms of yield, there are a few variables and methods in which can be applied. In terms of laboratorial variables, there are a few in which the yield obtained is affected for example the temperature, pressure, solvent flowrate and also mean particle diameter. With a set variable, the next issue regarding yield obtained is the extended variable such as infinite time or varying the temperature, pressure, solvent flowrate and particle diameter. This can be overcome through models, as models can further extrapolate the data obtained to achieve the objective such as the maximum yield capable or the trend of the yield. However, before modeling can be done, a set of experimental results is needed to be able to be fit into the selected model. For a yield from a plant, there are several methods of extraction.

The most common method of extraction used is steam distillation due to its low cost method of extraction, however it may cause chemical changes to the extract by oxidation of certain compounds (G. Anitescu, 1997). Organic solvent extraction is moderate in terms of capital and operating cost (Houcine Mhemdi R. E., 2010). On the other hand, there are concerns regarding the solvent residues in oleoresin products. There are new regulations regarding emissions of volatile organic solvents in the air, thus further refining is required restrains the use of this technology (Owen J. Catchpole, 1996). The most recent technology that is increasing in importance in the production of oils and other substances from natural products is the supercritical fluid extraction. The supercritical fluid extraction technique has the highest capital cost among the three techniques with moderate operating costs (Houcine Mhemdi E. R., 2011).

The purpose of utilizing a mathematical model is to allow us to generalize the experimental results obtained, which then can be applied to different process conditions (different temperature, pressure extraction flowrate) and to other materials than those already studied. Additionally, modelling are valuable in the development of scale up procedures from a laboratory scale to a pilot scale and to an industrial scale. There are three different approaches that have been suggested for the mathematical modelling of the supercritical fluid extraction of oils, which are empirical model, models based on heat transfer analogy, and differential mass balance integration. The empirical model approach can be suitable when the information of the mass transfer mechanisms and the equilibrium relationships are missing. However, these models are little more than an interpolation of the experimental results. In models based on heat transfer analogy case, the extraction is treated as a heat transfer phenomenon. Each single solid particle is considered as a hot ball cooling in a uniform medium. In material balance model, the model have been widely used to describe the behavior of fixed beds during solid-liquid operations like adsorption/desorption, chemical reaction and extraction.

II. METHODOLOGY

A. *Mathematical modelling of Coriandrum sativum*

The experimental data for the yield was obtained from the experiment conducted by Zoran (2016) in which supercritical fluid extraction process of coriander seeds. Supercritical fluid extraction was performed at different set of process parameters: pressure (100, 150 and 200 bar), temperature (40, 55 and 70 ◦C) and CO2 flow rate (0.2, 0.3 and 0.4 kg/h).

i. Diffusion model

The diffusion model enables us to define all the important aspects of the process such as the mass transfer resistances, the phase equilibrium and the flow pattern – by substituting relevant relationships into the mass balance equations (Sovová, 2012). On the other hand, this kinetic model does not include describing extraction flow-rate, but solely relies on time. Therefore, by doubling volumetric supercritical carbon dioxide flow-rate would give little effect on extraction efficiency per unit time, if the efficiency of extraction is controlled by the kinetics of the initial desorption step and the other extraction parameters remain constant (Zhen Huang X.-h. S.-j., 2012). The mathematical representation of the model is as shown below

$$\frac{m_t}{m_0} = 1 - A_d \exp(k_d t) \tag{1}$$

Where mt is the time dependence of the mass of the extracted solute (g), m0 is the mass of solute to be extracted and present in the parent matrix (g), Ad is a dimensionless model coefficient, kd is the desorption rate constant (s−1) and t is the extraction time (s).

The yield percent in the mathematical representation above is mt/mo, therefore in calculations, the mt/mo is written as yield %. With desorption rate constant obtained from the experiment with a range of 0.0068 to 0.0451, the unknown is the dimensionless model coefficient, Ad. For this, Goal Seek data tool is applied in order to determine the value, with the original experiment running as the control or the base line of the model. The approximate value for the model coefficient is approximately 1, therefore for this, the value is set to 1 by changing the goal seek value of dimensionless model coefficient. The value of yield percent, Y will then change accordingly as the value for dimensionless model coefficient is iterated. For the given range of desorption rate, the dimensionless model coefficient obtained was 2.4802. With all the values now available, the values are then fitted into the model with variation in terms of the time. The yield extraction time for the models are tested with times of 80, 160, 240 minutes, which in the same as the experiment conducted by Zekovic (2016).

ii. Hot Ball Diffusion model

In the Hot Ball Diffusion model, the supercritical fluid extraction process may be treated analogously as a heat transfer phenomenon by considering the solid particles as hot balls cooling down in a uniform surrounding. The extracted particles are then assumed to be spherical in shape with initially uniformly distributed solute. Thus, Bartle et al. in 1990 proposed a Hot Ball Diffusion (HBD) model for describing supercritical fluid extraction processes (Keith D. Bartle A. A., 1990).

The supercritical fluid extraction process may be treated correspondingly as a heat transfer phenomenon by assuming that the solid particles as hot balls cooling down in a uniform surrounding (Zhen Huang X.-h. S.-j., 2012). They have deeply discussed the effect of matrix shape, size variation, solute distribution and solubility limitations on the hot ball model for real systems (Keith D. Bartle T. B., 1992). Unlike the BIC situations where some of the solute is readily accessible to the solvent on particle surface (Sovová, H., 1994), the hot ball model is suggested for a matrix which contains small quantities of extractable materials such that the extraction is not limited by solubility.

$$\frac{m_t}{m_o} = \frac{6}{\pi^2}\left(\frac{D_e t}{R^2}\right)^{\frac{1}{2}} \tag{2}$$

Where, m_t is the time dependence of the mass of the extracted solute (g), m0 is the mass of solute to be extracted and present in the parent matrix (g), De is the effective diffusion coefficient in a solid substrate (m^2/s), R is the radius of spherical solid particles (m), and t is the extraction time (s).

For the Hot Ball Diffusion model, similar with the Diffusion model, the yield percent in the mathematical representation above is mt/mo, therefore in calculations, the mt/mo is written as yield %. The effective diffusion coefficient in a solid substrate of Coriander is obtained in Catchpole (1996) experiment, which gives a value of 5.1x10-12 m2/s. The radius of spherical solid particles is obtained from Reverchon (2001) which was also applied by Zekovic (2016), which was 1.56x10-3 m. The yield extraction time for the models are tested with times of 80, 160, 240 minutes.

iii. Brunner model

The model equation was originally obtained from Brunner's Equation (Zekovic, 2016) in which it represents a specific solution for the Fick's law. Fick's second law of diffusion, is represented as a linear equation and the diffusion of each of the chemical species will occur independently. With the properties mentioned above, it would make the transport of mass or extraction yield, relatively simple and easy to simulate numerically.

For fitting a diffusion model, the general idea is that all the diffusion coefficients are equal and are also independent of temperature, pressure (Tiziana Fornari, 2014). With this simplification, it will ensure the mass transport equations in the modelled will have linearity.

$$Y = x_o(1 - e^{-kt}) \tag{3}$$

The mathematical representation of the Brunner model is as shown above, where Y is the extraction yield (%), x0 is the initial content of the solute in the solid phase (g/g), t is the extraction time (min), k is the rate constant (min−1). The x0 is usually obtained by the Soxhlet extraction with suitable organic solvent. However, this equation only has one adjustable parameter which is the rate constant, while x0 is constant. The equation above is modified for a mathematical modelling as shown below.

$$Y = Y_\infty(1 - e^{-kt}) \tag{4}$$

In this mathematical representation, the Y∞ is the total extraction yield, which can be obtained for infinite extraction time. This infinite extraction time is different for each experimental run, which is governed by the parameters (Zekovic, 2016). For the experiment conducted by Zekovic (2016), the Y∞ for the given parameters were in the range of 0.63 to 6.98, the rate constant values of 0.007 to 0.0451 min−1. The yield extraction time for the models are tested with times of 80, 160, 240 minutes.

iv. Esquivel model

The research conducted by Esquivel was based on a single sphere model. In single sphere model originally by Bartle (1990), it was assumed that solute is extracted from a bed of particles which was composed of porous and inert spheres with all the spheres having the same size and all the particles in the bed are fed at the same stage of extraction. The compounds which is to be extracted, is described as being able to move through the particles by a process `similar to diffusion' (Keith D. Bartle A. A., 1990).

Table 1: Model fitting for pressure of 100 bar, 55 Celsius for 80, 160 and 240 minutes.

			Experimental	Brunner model	Esquivel model	Desorption model	Hot ball diffusion model
P [bar]	T [°C]	t [min]	Y [%]	Y Brunner [%]	Y Esquivel [%]	Y Desorption [%]	Y Hot ball [%]
200	55	80	4.900	5.160	7.120	7.939	0.465
200	55	160	7.000	6.980	9.240	3.280	0.255
200	55	240	7.160	7.720	10.860	6.883	0.465
AARD				0.280	2.720	2.345	5.959

As the process is described to be `similar to diffusion' in which it means that the solute leaves the particles, was not discussed by Bartle (1990). For a solute that is very soluble, the method in which it is extracted is through pore diffusion only. However, for a less soluble component, the intraparticle mass transfer which involves the pore fluid and undissolved solute may occur. Esquivel (1999) has proposed an empirical model containing one adjustable parameters as represented by the following equation, where me is the mass of extract (g), x0 is the initial content of the solute in the solid phase (g/g), F is the mass of solid material (g), t is the extraction time (min), and b is adjustable parameter (min).

$$m_e = x_0 F \left(\frac{t}{b + t} \right) \tag{5}$$

This equation was then modified with the addition of one adjustable parameter, and is shown in the mathematical representation below, where Y is the total extraction yield (%), while k2 and Y∞ are the adjustable parameters.

$$Y = Y_{\infty} \left(\frac{t}{k_2 + t} \right) \tag{6}$$

III. RESULTS AND DISCUSSION

In figures 1, 2, 3, 4 and 5 shows the relationship between the yield percentages with respect to time. In terms of comparison between the yield obtained through experiment conducted by Zekovic (2016) with the four models that have been selected, it can be seen that the most consistent and with the lowest value of average absolute relative deviation is the model by Brunner. The Brunner model is, as mentioned in the previous section, based on the Fick's second law of diffusion. Here, the diffusion is represented as a linear equation and the diffusion of each of the chemical species will occur independently. The second lowest value of AARD was shown by the Esquivel model and the highest AARD value was shown by the Desorption model. The Desorption model has failed to prevail in the instance of showing the proper yield extraction of Coriander seeds. From comparison of the theoretical information of the Brunner model and the Desorption model, it can be said that the extraction of Coriander seeds is governed by the rate at which it is slowest, i.e. desorption step. Therefore, with the results of modelling, it can be said that the Brunner model gives the best fit in terms of its discrepancy of the actual experiment and the modelling.

In terms of the actual yield of Coriander seeds, the highest yield is shown with the process condition of 200 bar and 55 Celsius and the lowest yield is with 100 bar and 55 Celsius. From here, it can be seen the effect of pressure upon the yield of the Coriander seed. For the experiment conducted by Zekovic (2016), the pressure in which supercritical extraction of Coriander seed has been conducted are 100, 150 and 200 bar. With the variable of temperature, it can be seen that higher pressure gives a higher value in terms of yield. According to Tiziana (2014), for supercritical extraction of plants, pressure has been known as to give a significant impact on the yield. The increase of pressure will cause the increase of carbon dioxide density, in turn leads to an increase of dissolving power by the carbon dioxide.

Based on the value of AARD values calculated from the Brunner model, Esquivel model, Desorption model and Hot Ball Diffusion model, it can be seen that on average, the Brunner model shows the lowest value with 0.280, Esquivel model with 2.720, Desorption model with 2.345 and Hot Ball Diffusion model with 5.959 for 200 bar and 55 Celsius. The Hot Ball Diffusion model with 5.959 shows that with the conditions at 200 bar and 55 Celsius, it gives the least suitable correlation for the modelling of yield of Coriander seed. However, the Brunner model, which is based on Fick's law, was able to provide the best performance in terms of correlation. As it shows the lowest AARD value, it can be said that the Brunner model can be used to predict other process conditions.

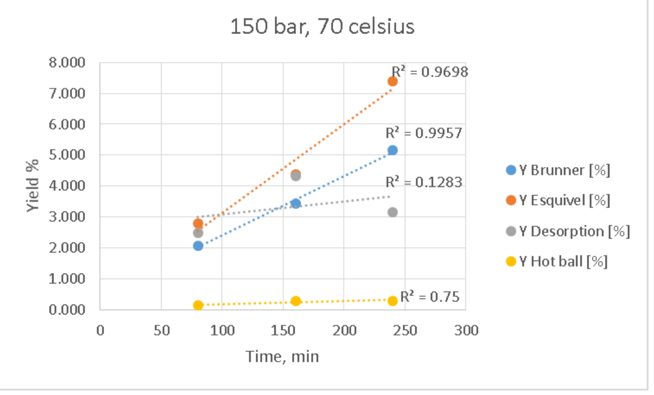

Figure 1: Yield of Coriander seeds for 150 bar, 70 celsius.

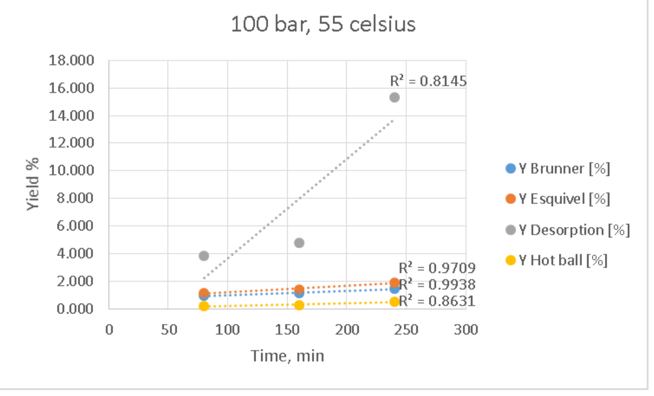

Figure 2: Yield of Coriander seeds for 100 bar, 55 celsius.

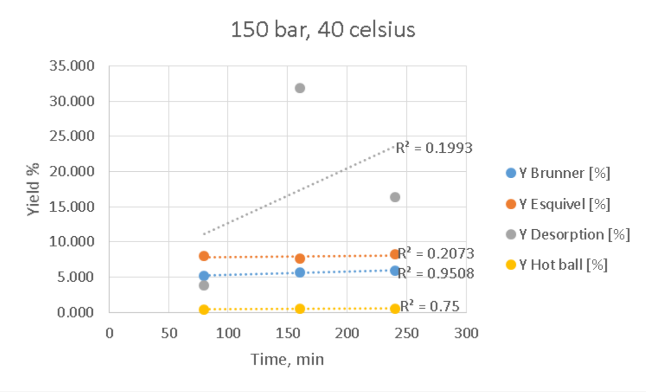

Figure 3: Yield of Coriander seeds for 150 bar, 40 celsius.

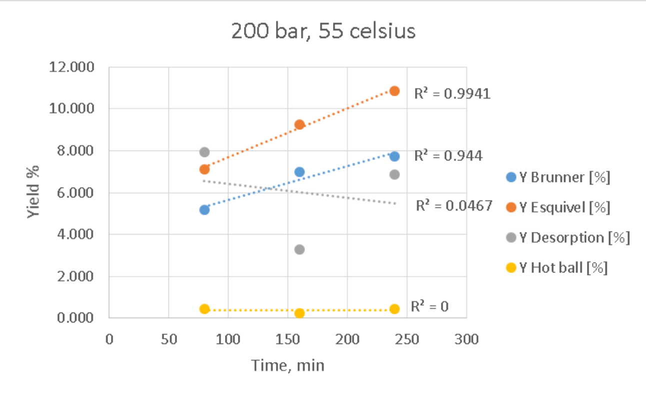

Figure 4: Yield of Coriander seeds for 200 bar, 55 celsius.

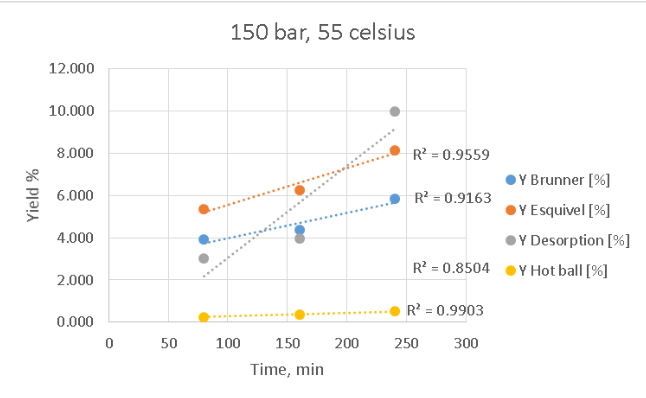

Figure 4: Yield of Coriander seeds for 150 bar, 55 celsius.

IV. CONCLUSION

For the yield of Coriander seeds, the important point for extraction of Coriander seeds is the control of the pressure. As shown in the previous section, the pressure has a more pronounced effect, causing increase of yield percent of Coriander seed by increasing carbon dioxide density. Temperature exhibited different effect on both carbon dioxide density and vapour pressure of the solute, while carbon dioxide flow caused significant increase of yield percent only at lower pressure. Based on the modelling conducted on the yield of coriander seeds, the model in which gives the best fit or is with least amount of deviation from the experimental result is the Brunner model, whereby it applies the concept of Fick's law. As Fick's law is based on diffusion, when modelling diffusion, it is often a good idea to begin with the assumption that all diffusion coefficients are equal and independent of temperature, pressure, etc. This simplification ensures the linearity of the mass transport equations in the modelled area and often allows simpler correlations to known analytical limits.

Although advances have been made for the simulation of extraction processes for plant seeds namely Coriander seeds by means of supercritical carbon dioxide extraction technology, more effort and development is required in scaling up and also the design for commercial applications. The models that were examined thoroughly have been generally and physically important to describe the extraction process. The models with analytical solutions can be applied readily, however they have disadvantages as they can be simple. Due to the complicated nature of the plant seeds, the interactions between the solute and solid may not be negligible.

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