Mathematical modeling of supercritical CO_2 extraction of valuable compounds from *Eucheuma Cottonii* and *Gracilaria Sp*

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Abstract. Extraction by using supercritical CO_2 has been extensively developed to extract materials that are easily decomposed at high temperatures. Therefore, in this study extraction of valuable compounds (such as: carotenoids and fatty acids) from macroalgae of Eucheuma cottonii and Gracilaria sp was carried out experimentally with supercritical CO_2 and mathematical model of Broken and Intact Cells (BIC) and Chrastil model. The result with BIC model is compared with the experimental result that has been done. Extraction was conducted at various pressures of 15, 20, and 25 MPa, temperature of 40, 60, and 80 ^oC, CO_2 flow rate of 6 mL/min, and ethanol concentrations for cosolvent of 5 %, 7.5%, and 10% CO_2 flow rate. The content of extract was analyzed by using a Spectrophotometer UV - Vis and HPLC. The total yield of extract on *Eucheuma cottonii* was about 0.01623-0.03752 gr extract/gr sample at operating conditions 15 MPa pressure, temperature 60 ^oC, and ethanol flow rate of 10%. The total yield of the extract on *Gracilaria sp* was 0.1982-0.4237 gr extract/gr samples, at operating conditions 15 MPa pressure, 60 ^oC temperature, and ethanol flow rate 7.5% CO_2 flow rate. The solubility of *Eucheuma cottonii* are greater than *Gracilaria Sp* with constant of Chrastil k, a, and b that are: 2,52; 0,911; and -27,66 at operating conditions. Broken and Intact Cells model could also describe well for extraction yield. The best fitting parameters in BIC model depends on condition at extraction process, such as : 0.45 – 0.46 for f, 0.5 - 0.75 for X_c, and 0.15 - 0.4 for K value..

1. Introduction

Macroalgae is well known not only as a valuable biofuels source, but also for various other compounds such as carotenoid, caragenant, lipid acid, and phenolic. since the biomass is be able to synthesize lipids, carbohydrates and proteins[1]. Macroalgae is a naturally product that has been applied by some countries. Macroalgae has aplied as suplementary food, medicine, cosmetic, animal feed, and organic fertilizer by chinese and japan since 1670. Algae has some nutrient contents, thats are: proteins, amino acids, minerals, ashes, vitamin A, vitamin C and fats. Some types of algae are include *Eucheuma Cottoni* and *Gracilaria Sp*. *Eucheuma cottoni* are known as red algae (Rhodophyceae) has founded under the sea. *Eucheuma cottonii* and *Gracilaria Sp* also contains carotenoids and fatty acids[2].

Carotenoids (β-carotene) is serves as a preventative of heart and cancer disease as well as strength the immune of system. This research is about the supercritical fluid extraction of lipids from macroalgae, a new development in recent years whose have purpose to replace conventional solvent extraction. Supercritical fluids are substances that have a critical temperature and pressure. This work is about the supercritical fluid extraction of lipids from macroalgae, a new technique developed in recent years whose purpose is to replace conventional solvent extraction, that has a greater environmental impact mainly due to the use of toxic substances.[3]. The solvent strength of this fluid depends on density. Pressure was increased with increasing of density and solubility was enhanced with enhancing of pressure. Therefore, operating pressure and temperature can be varied to optimize mass-transfer properties like density, diffusivity, viscosity, and, especially solubility. Carbon dioxide is extremely appropriate as a supercritical fluid since its critical conditions are at quite lower pressure : 7.38 Mpa, and temperature : 31.35 °C, [4].

Supercritical CO_2 extraction of lipids from macroalgae exploits the high solubility of fatty acids in supercritical CO_2 and high selectivity for non polar and low polar

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Nomenclature

a model's constant (vR^2/D_eL)
a_p interfacial area per unit volume of bed (m^{-1})
b model's constant (y_s/x_0)
d_p model's constant (m)
E dimensionless extraction yield (F/Nxi)
f initial fraction solute in broken cell in particle
F extract (kg)
G model's constant ($k_sa_p/(1-\varepsilon)$)
k_f film mass transfer coefficient in fluid(m/s)
k_s film mass transfer coefficient in solid (m/s)
K partition coefficient
$\overline{K}$ partition coefficient in dimensionless (Kx_{10}/y_0)
L bed length (m)
N solid charge in extractor (kg)
r radial coordinate
r_c critical radius of core (m)
R particle radius (m)
S solvent flowrate (kg/s)
t time (s)
v interstitial fluid velocity (m/s)
x concentration of solid phase (kg solute/kg insoluble solid)
x_c transition concentration (kg solute/kg insoluble solid)
x_i solute fraction in untreated solute (kg solute/kg insoluble solid)
x_0 initial solute fraction in particle (kg solute/kg insoluble solid)
x_1 solid phase concentration with broken cells (kg solute/kg insoluble solid)
x_{10} solid phase initial concentration with broken cells (kg solute/kg insoluble solid)
x_2 solid phase concentration with intact cells (kg solute/kg insoluble solid)
x_{20} solid phase initial concentration with intact cells (kg solute/kg insoluble solid)
X dimensionless concentration of solid phase (x/x_0)
X_c dimensionless concentration transition (x_c/x_{10})
X_1 dimensionless concentration broken cells (x_1/x_{10})
X_2 dimensionless concentration intact cells (x_2/x_{10})

Greek letters
ε bed voidage
θ dimensionless time (vt/L)
ρ_f density of fluids (kg/m^3)
ρ_s density of insoluble solid (kg/m^3)
τ dimensionless time (D_et/R_2)
ψ_e dimensionless external mass transfer ($\varepsilon v/k_fa_pL$)
ψ_i dimensionless internal mass transfer ($(1-\varepsilon)v/k_sa_pL$)

compounds. Furthermore, a co-solvent (such as methanol, ethanol, water), can improve the solubility of polar compounds as well [5].

The research are compares both original extraction data for two macroalgae strains (*Eucheuma cottonii* and *Gracilaria Sp*) with a simple approach to modeling the supercritical CO_2 extraction of lipids by a broken and intact cells model and Chrastil model.

2. Materials and method

2.1. Materials

Red algae *Eucheuma cottonii* and *Gracilaria sp* found on Coastal Coast in Pamekasan, Madura. Indonesia. Carbon dioxide (CO_2) liquid with a purity of 99.7% purchased at PT. Samator and ethanol 97% as co-solvent was purchased at UD.Chemical Main Source (SUK).

2.2 Method

Macroalgae *Eucheuma cottonii* and *Gracilaria sp* which have been taken from Madura beach are washed with fresh water which is aim to remove dirt and salt content that still attached to the macroalgae.

The dried macroalgae is then ground to size reduction until the size is approximately 20-35 mesh. It aims to enlarge the area of contact of algae extraction with solvent. At the bottom (inlet) and top (outlet) extractor added glassbead as much as 2.5 gram each. The addition of glassbead aims to prevent channeling. After that, install the extractor in a series of supercritical extraction equipment [6].

Furthermore, the extraction process is modeling for Broken and Intact cell (BIC) model using MATLAB R2013a application with numerical solution by Crank Nicholson method. Experimental data were compared to model analyze.

3. Mathematical Modeling

3.1. Broken and intact cells model

Modeling of the process was established based on mass transfer balances to estimate renewal of extracted compounds: β -karotene and fatty acids. The model was developed about on extraction in the batch system extractor with inside diameter of 21 mm, length of 130 mm and volume of 43 mL. [7].

The model that describes the extraction process is important to optimize the parameters that control and to fix the efficiency. During the extraction process, the oil was move from the macroalgae cells to the solvent quantity, so that the models are focused on the description of mass transfer from a solid matrix to a supercritical fluid. The parameters are the mass transfer coefficients. The model of broken and intact cells was developed by Sovová [8].

Broken and Intact Cells model was chosen because it is illustrates particularly well the macroalgae structure after the pre-treatment. Although it was built at first to describe the supercritical fluid extraction of vegetable oil from plants, it will be shown that it works as well with the extraction of oil from macroalgae[8].

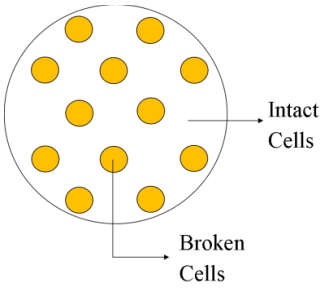

Fig. 1. Illustration of particle for Broken and Intact Cells Models.

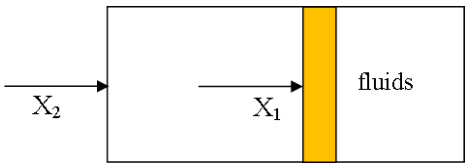

Fig. 2. Simplified representation of solute transfer from the particle to the solvent (fluids).

Therefore, as shown in Figure 1, two regions can be distinguished in the particle: the region of broken cells near the surface with easy accessible solute, and another region in the core as intact cells. The simplified representation of solute transfer from the particle: X_1 as broken cells dan X_2 as intact cells, to the solvent (fluids) can be described in Figure 2 .These condition lead to divide the extraction process in two periods. In the first extraction period, the free solute inside the intact cells (X_2) through the side of broken cells (X_1) goes easily from the particle to the solvent (fluids).

3.1.1 Parameter models

The Sovová model is characterized by equations for the mass balances: the phase equilibrium and the mass transfer that allow to calculate the extraction curve[8]. The equations for the extraction curve are fitted to experimental data to calculate and optimize the parameters X_c, f and K.

The way to solve the mass balance equations are introduce the dimensionless parameters and different equations are formulated for extraction periods, in the cases of plug flow. These equations, published by Sovová in 2005, represent a new general model that extends the group of models based on broken and intact cells [8].

3.1.2 Mass balance equations

The mass balance equations are written for the solute in three phases [8], those are : the fluid phase in equation 1, the solid phase with broken cells equation 2, and the solid phase with intact cells in equation 3, For the mass balance in the fluid phase the accumulation part and the convective part have to be considered :

$$\rho f \varepsilon \left(\frac{\partial y}{\partial t} + \upsilon \frac{\partial y}{\partial z} \right) = js \qquad (1)$$

where: ρf is the solvent density, ε is the porosity, y is the solute concentration in the fluid phase, t is the extraction time, υ is the interstitial velocity, z is the axial coordinate, js is the flux from broken cells to solvent.

In the solid phase with broken cells there is no convective term and the flux from intact cells to broken cells is included, that in the previous equation was supposed to be equal to zero :

$$f \rho_s (1-\varepsilon) \frac{\partial x1}{\partial t} = jr - js \qquad (2)$$

where: f is the grinding efficiency, ρ_s is the solid density, $x1$ is the solute concentration in broken cells, jr is the flux from intact cells to broken cells, and the others were already defined previously.

Finally, in the solid phase from intact to broken cells only the flux in the solid phase affects the accumulation of solute over time :

$$(1-f) \rho_s (1-\varepsilon) \frac{\partial x2}{\partial t} = -jr \qquad (3)$$

where: $x2$ is the solute concentration of intact cells and all the other variables are already defined. To solve the differential equations 1, 2, and 3, the initial concentrations are used as boundary conditions:

$$y|_{t=0} = y_0 = y*; \quad y|_{z=0} = 0;$$

$$x_1|_{t=0} = x_{10}; \quad x_2|_{t=0} = x_{20} = x_i; \left.\frac{dy}{dz}\right|_{z=L} = 0 \qquad (4)$$

where: y_0 is the initial solute concentration in the fluid phase while $x_1;\ 0$ and $x_2;\ 0$ are the initial solute concentrations in broken and intact cells, respectively.

A solute concentration x_c is then defined, that indicates the capacity of the matrix for interaction with the solute. Above this concentration, solubility is equal to phase equilibrium, while below xt it depends on a partition coefficient:

$$y*(x_1) = y_s; \quad for\ x_1 > x_c$$

$$y*(x_1) = Kx_1; for\ x_1 \le x_c$$

$$where\ Kx_c < y_s \qquad (5)$$

where: $y*(x_1)$ is the equilibrium fluid phase concentration, y_s is the thermodynamic solubility of the solute in the solvent and K is the partition coefficient.

The way to solve the mass balance equations, fluxes js and jr have to be defined, being aware that for jf the discontinuity of the phase equilibrium has to be

considered. Therefore, the flux from broken cells to the solvent is defined as:

$$js = kfa_p\rho f(y* - y) \quad (6)$$

$$jr = k_s\, a_p\rho_s(x_2 - x_1) \quad (7)$$

The yield of oil extracted, F, collected during the extraction process is calculated as:

$$F = S\int_0^t y\mid_{z=L} dt \quad (8)$$

where: S is the solvent flow rate and L is the length of the extraction bed. Which are some have changed the relationship of equilibrium suggested by Perrut et al [9].

3.1.3 Dimensionless model equations

The model equation are modify into a dimensionless using the dimensionless variable :

$$Z = \frac{z}{L};\ \theta = \frac{vt}{L};\ X_c = \frac{x_c}{x_{10}};\ X_2 = \frac{x_1}{x_{10}};$$

$$Y^* = \frac{y^*}{y_0};\ Y = \frac{y}{y_0};\ X_1 = \frac{x_1}{x_{10}} \quad (9)$$

Dimensionless model equations with initial and boundary conditions according to these notations ,and equation 1 can be written as :

$$\frac{\partial Y}{\partial \theta} + \frac{\partial Y}{\partial Z} = \frac{1}{\Psi_e}(Y^* - Y) \quad (10)$$

The overall dimensionless mass-transport coefficient in equation 2,3 and 4 can be expressed as a function in equation 11, 12, and 13.

$$\frac{\partial X_1}{\partial \theta} = \frac{1}{\Psi_{if}}(X_2 - X_1) - \frac{\Phi}{\Psi_e}(Y^* - Y) \quad (11)$$

$$\frac{\partial X_2}{\partial \theta} = -\frac{1}{\Psi_{i(1-f)}}(X_2 - X_1) \quad (12)$$

$$E = \frac{F}{N_{X_i}} = \frac{\Phi f}{1+\Phi}\int_0^\theta Y|_{Z=1}\, d\theta \quad (13)$$

4. Results and discussion

In this experiment was conducted the variation of operating conditions, specifically: temperature, pressure, and ethanol flow rate. The first experiments were carried out at constant pressure and temperature to find the most suitable extraction time and the CO_2 flow rate was kept constant in all the experiments [10]. The extraction time depends mainly on 240 minutes. Afterwards, the role of ethanol was investigated, tempting the different percentages those are: 5; 7.5; and 10%, with CO_2 flow rate of 6 ml/min.. In this research, the results of pressure, temperature, and supercritical CO_2 flow rate of two macro algae on extraction yield were examined, and the experimental and model results were compared [11].

Table 1 and table 2 show the experimental data that were compared with the model of broken and intact cells. Analysis will examine in the following section.

Table 1. *Eucheuma Cottoni,* 15 MPA, 40°

Time (min)	Yield (gr extract/ gr sample)	%recover b-carotene	%recover fatty acid
30	0.1240	0.0562	0.0455
60	0.1428	0.06477	0.05189
90	0.1531	0.06944	0.05635
120	0.1833	0.08311	0.05783
180	0.1937	0.08782	0.06275
240	0.2007	0.09099	0.0656

Table 2. *Gracilaria Sp,* 15 MPA, 40°

Time (min)	Yield (gr extract/ gr sample)	%recover b-carotene	%recover fatty acid
30	0.2123	0.0301	0.0392
60	0.3720	0.0527	0.0756
90	0.3763	0.0533	0.07664
120	0.3875	0.0549	0.07991
180	0.4191	0.0594	0.0871
240	0.4353	0.0617	0.0913

Table 3. Initial concentration in BIC Model.

P (MPa)	T (°C)	y_0 [-]	x_0 [-]
15	40	0.021	0.19
20	60	0.04	0.3
25	80	0.052	0.35

4.1 Effect of Temperature

Broken and Intact Cells (BIC) model were compared into the experimental data. The initial concentration is important for known the values of concentration profile as function in extractor height for BIC model.

The values of concentration profile as function in extractor height for BIC model has shown in Figure 3. The BIC Models has some initial fraction for fitting parameters, those are: *f* as ground particle, dimensionless

transition concentration as X_c, and partition coefficient as K.

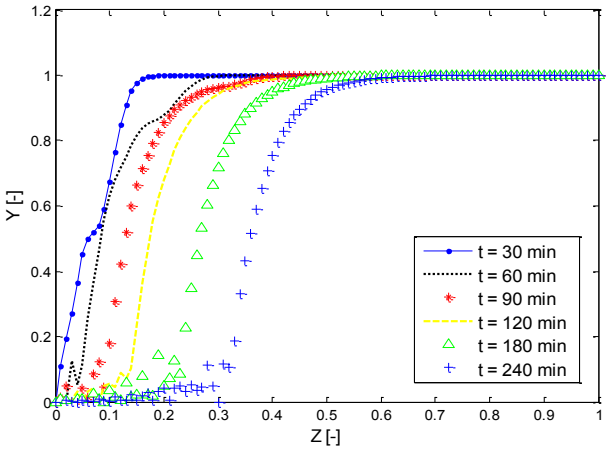

Fig. 3. The values of concentration profile as function for extractor from BIC model.

Figure 3 shows the value of solute concentration (Y) in the fluid phase decrease with increasing of extraction time. In the beginning, solute was certainly dispersed in the fluid phase of extractor. Solute that contained in the particle was placed in the bottom of extractor and was rapidly removed from particle, even particle place at the top of extractor. The solute in the intact cells was simply dispersed into the broken cells and over dispersed solute in the cells of particle. In the BIC model, equilibrium was simply achieved according in the Figure 3.

Table 4. The values of fitting parameters in BIC model.

Condition	***f*** **[-]**	X_c **[-]**	***K*** **[-]**
P : 15 mpa	0.45	0.5	0.15
P : 20 mpa	0.46	0.6	0.2
P : 25 mpa	0.45	0.7	0.2
T : 40^{o}C	0.46	0.7	0.3
T : 60^{o}C	0.46	0.75	0.25
T : 80^{o}C	0.46	0.75	0.2
Solvent-Flowrate :5%	0.45	0.5	0.4
Solvent-Flowrate :7.5%	0.45	0.5	0.4
Solvent-Flowrate : 10%	0.45	0.5	0.4

The effect of temperature on extraction yield with comparison to BIC Model from macroalgae *Eucheuma cottonii* and *Gracilaria Sp*, at : 15 MPa, and CO_2 flowrate 6 ml/min are shown in Figure 4 and 5. Those figures shows that extraction yield increased with increasing of temperature. In the extraction process, the operating temperature is varied by 40, 60, and 80 ^{o}C at supercritical fluid extraction affects into the solvent of density and vapor pressure of the solute to be extracted.

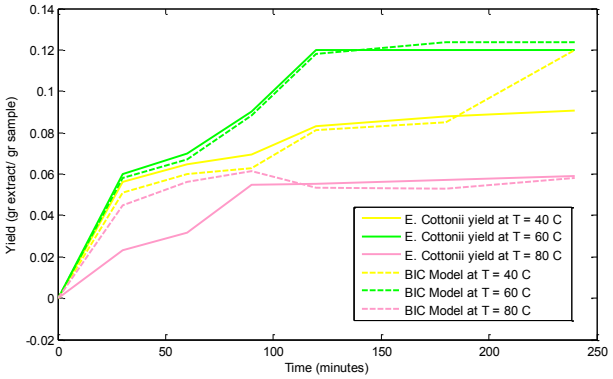

Fig. 4. The effect of temperature on extraction yield with comparison to BIC Model.
(*E. Cottonii*, 15 MPa, CO_2 flowrate 6 ml/min)

As shown in Figure 4, at 30 to 80 minutes the yield of extract at 60 and 80 ^{o}C was smaller than the yield of temperature 40 ^{o}C, due to the decreased CO_2 density along with the increased in temperature at pressure: 15 MPa.

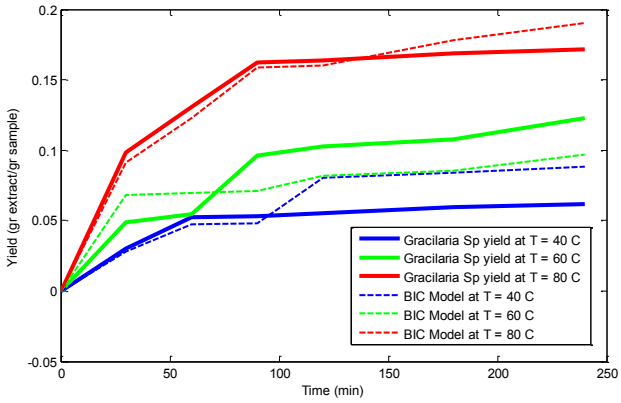

Fig. 5. The effect of temperature on extraction yield with comparison to BIC Model.
(*Gracilaria Sp*, 15 MPa, CO_2 flowrate 6 ml/min)**.**

The different from Figure 5, in time 30 to 90 minutes the yield of extracts at 60 and 80 ^{o}C were higer than the temperature of 40 ^{o}C due to increased CO_2 density along with the increase in temperature at low pressure: 15 MPa. However, at 240 minutes the yield of extract at 60 and 80 oC was increased slowly so that the accumulation was higher than the extract at 40 ^{o}C. Those are causes the vapor pressure of the solute increased and allows the components to diffuse into the solvent. So that the solubility of the solute in solvent was increased, and the total extract produced increases. The total extract at a temperature of 40 ^{o}C is more lower than the temperature of 60 and 80 ^{o}C because at temperature of 40 ^{o}C the influence of solvent density are more dominant[12].

The BIC model could show the experimental data and the comparison of BIC Model had good compatibility with experimental data, but the BIC model could not show the experimental data well at temperature 40 and 60 °C at figure 4 and 5. This might be due to the use of more than one fitting parameters in BIC model. It is important to make the optimum fitting parameter. In addition, the initial concentration of solute in solid (x_0) should also based on maximum yield from experimental data [13].

4.2 Effect of Pressure

The effect of pressure on the extraction process with comparison to BIC Model has been studied at constant temperature of 60 ° C and constant CO_2 flow rate of 6 ml/min with a 5% co-solvent (ethanol) flow rate. To study the effect of pressure in the extraction process, the operating pressure is varied by 15, 20, and 25 MPa. The appropriating extraction yield data for *Eucheuma cottonii* and *Gracilaria Sp* are informed in Figure 6 and 7.

Figure 6 and 7 shows the effect of pressure on the total extract obtained. It can be seen that the increase in pressure is directly proportional to the increase of extract obtained. The most of *Eucheuma cottonii* extracts were obtained at 25 Mpa pressure with weight of 0.00237 gr extract/gr sample.

The addition of extract in Figure 6, at 25 MPa from 30 to 120 minutes has a significant increase but tends to be constant at 120 to 240. This indicates that at the time of extraction for 240 minutes most of the extract has been taken.

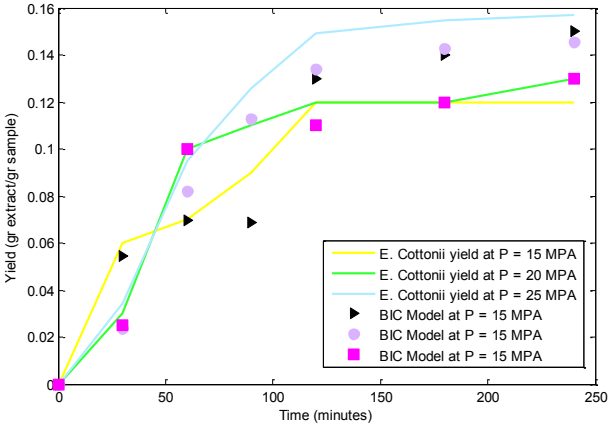

Fig. 6. The effect of pressure on extraction yield with comparison to BIC Model.
(*E. Cottonii*, 60°, CO_2 flowrate 6 ml/min)

Figure 7 has shown the data for *Gracilaria Sp*, that has a middle similar trend to *Eucheuma cottonii*. The total extract that can increase with increasing pressure due to increasing pressure leads to increased of supercritical fluid density, so that the strength of SC-CO_2 as solvent to dissolve the solute also increased.

The contrast yield from *Gracilaria Sp* and *Eucheuma cottonii* caused by the molecular structure of algae *Gracilaria Sp* in the form of flat proved by SEM analysis. So, for the lipid increased difficult to penetrate at high condition shown in the figure 10 :

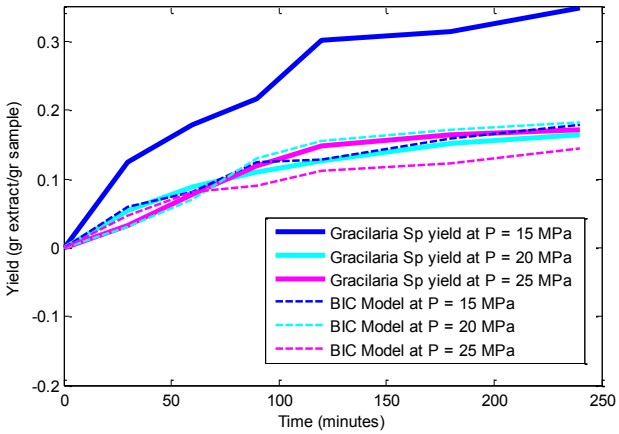

Fig. 7. The effect of pressure on extraction yield with comparison to BIC Model.
(*Gracilaria Sp*, 60°, CO_2 flowrate 6 ml/min)

4.3 Effect of Co-Solvent Flowrate

Figure 8 and 9 shows the effect of co-solvent (ethanol) flowrate on extraction yield with comparison to BIC Model from macroalgae *Eucheuma cottonii* and *Gracilaria sp* were investigated by varying the volume of ethanol that streamed by 5%, 7.5%, and 10%. The addition of ethanol as a co-solvent is needed to increase the solvent power. So that, the extract can be taken maximal.

As shown in figure 8 and 9, extraction yield was increased with increasing of co-solvent flowrate. The higher of co-solvent flowrate, the total yield was increased. The addition of ethanol as a co-solvent flowrate is need to affect the solubility of the extract.

Solvent serves to improve the efficiency of extraction and may affect the properties of supercritical CO_2 by adding ethanol as a co-solvent to help develop biomass pores, by adding supercritical CO_2 interactions with solute matrix cells [14]. BIC Model calculation is explain the satisfactory described the experimental data has shown in figure 8 and 9.

4.4 Solubility and rate extraction

In this study, the extraction rate is increases with increasing of pressure. This is by reason of the CO_2 density increases along with the increasing in operating pressure. Increase in CO_2 density shows an increase in the amount of CO_2 per unit volume that causes more CO_2 molecules to dissolve β-carotene and linoleic acid. The solubility of linoleic acid is better than β-carotene because the amount of linoleic acid in *Eucheuma cottonii* and *Gracilaria sp* is higher than that of β-carotene. Solubility of the experimental results is then correlated with the chrastil equation which results are shown by the table 6 and 7 below:

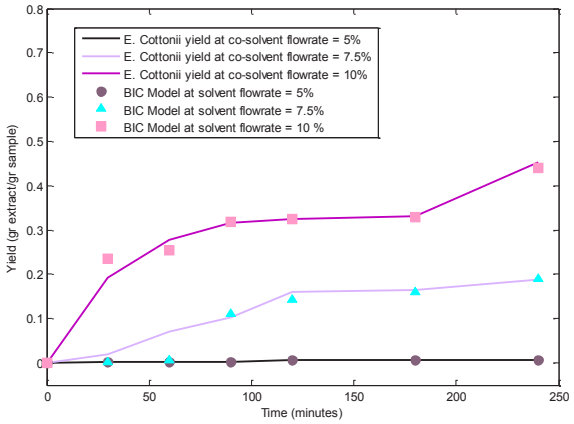

Fig. 8. The effect of co-solvent flowrate on extraction yield with comparison to BIC Model.
(*E. Cottonii*, 60°, 15 MPa)

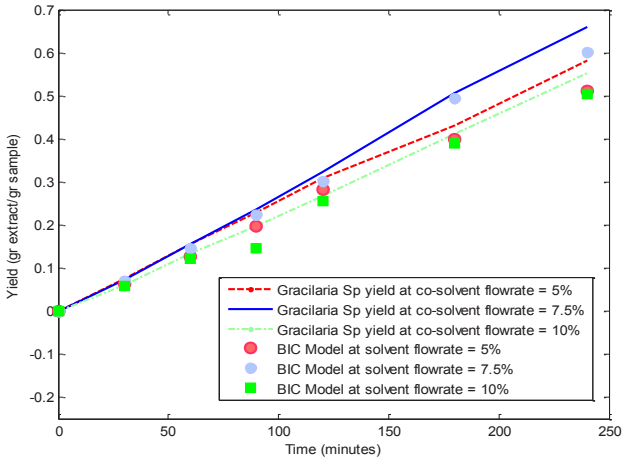

Fig. 9. The effect of co-solvent flowrate on extraction yield with comparison to BIC Model.
(*Gracilaria Sp*, 60°, 15 MPa)

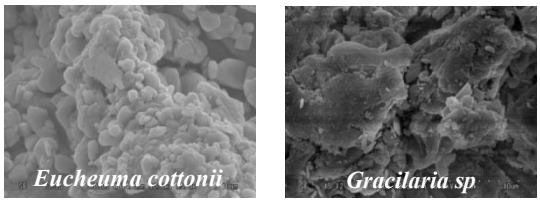

Fig. 10. *Eucheuma cottoni* and *Gracilaria sp* structure of SEM-Analyze.

Table 5. Constant of Chrastil of *Eucheuma cottonii* and *Gracilaria sp* at constant temperature and variation pressure

Macroalgae	Solubility	Constant		
		k	a	b
Eucheuma cottonii	β-carotene	2,52	0,911	-27,66
	linoleic acid	1,82	0,93	-19,84
Gracilaria sp	β-carotene	1,808	-0,066	-22,046
	linoleic acid	-0,758	1,01	-2,44

Table 6. Solubility of *Eucheuma cottonii* at temperature constant

T (K)	P(MPa)	Solubility of Experimental (gr/L)	
		β-karoten	Linoleat
333	15	0,00001	0,00028
	20	1,57E-05	0,000395
	25	1,93E-05	0,000435
T (K)	**P(MPa)**	**Solubility of Chrastil (gr/L)**	
		β - karoten	**Linoleat**
333	15	1,03E-05	0,000282
	20	1,58E-05	0,000384
	25	1,93E-05	0,000443

Table 7. Solubility of *Gracilaria Sp* at temperature constant

T (K)	P (MPa)	Solubility of Experimental (gr/L)	
		B-karoten	Linoleat
333	15	0,000028	0,000665
	20	0,000042	0,000616
	25	0,000044	0,000536
T (K)	**P (MPa)**	**Solubility of Chrastil (gr/L)**	
		B-karoten	**Linoleat**
333	15	2,86E-05	0,000675
	20	3,95E-05	0,000589
	25	4,59E-05	0,00053

5. Conclussion

Oil from macroalgae: *Eucheuma cottonii* and *Gracilaria sp,* were extracted by using SC-CO_2 and ethanol as a co-solvent to consider the effects of temperature, pressure, and ethanol flowrate. Extraction of yield was increased with increasing of pressure and temperature, but straightly increased with addition of ethanol as a solvent. In addition, the experimental data were compared with Broken and Intact Cells (BIC) model in the fluid and solid phase condition. From the comparison of experimental and model calculation, BIC model could describe well for extraction yield. The best fitting parameters in BIC model depends on condition at extraction process. The solubility value of linoleic acid is better than β-carotene because the amount of linoleic acid in *Eucheuma cottonii* and

Gracilaria sp is higher than that of β-carotene correlated with the Chrastil equation.

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