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#### SCIENTIFIC PAPER

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# THE ANALYSIS OF DIFFERENT PROCESSES OF EXTRACTION: YIELD OF EXTRACTS OB-TAINED FROM ALOE VERA (*Aloe barbadensis* Miller) AND SWEET BAY (*Laurus nobilis* L.) AND THE EXERGY ANALYSIS OF APPLIED PROCESSES\*

The present study was aimed to investigate and compare the efficiency of different methods for the isolation extract from a plant material. Extracts from dried leaves of Aloe vera (A. barbadensis Mill.) and Sweet Bay (Laurus nobilis L.) were obtained applying the following techniques: supercritical carbon dioxide (SC CO<sub>2</sub>) extraction at 30 MPa and 100 °C, a combined ultrasonic extraction and pre-treatment using SC CO<sub>2</sub> (US-SCCO<sub>2</sub>), and a conventional ultrasonic extraction (US) with 96% ethanol. US-SCCO<sub>2</sub> resulted in much higher yields of extracts of aloe and bay compared to SC CO<sub>2</sub> extraction. Determined extract's yield was used for calculating the maximum useful work and exergy loss as a measure of irreversibility of the extraction process. Calculated maximum useful work per 1 kg of the extract was ranged from 0.7 to 226 kJ while estimated values of the exergy loss were from 48 to 416 kJ per 1 kg of the extract. The maximum useful work and exergy loss have the largest value for SCE much more than for other processes of extraction (US and US-SCCO<sub>2</sub>). The pre-treatment of the plant material with SC CO<sub>2</sub> before an ultrasound-assisted extraction or the decrease of a particle size used for ultrasound-assisted extraction of Aloe vera has led to the decrease of maximum useful work and exergy loss. Unlike, pre-treatment with SC CO<sub>2</sub> followed by ultrasound-assisted extraction increased the exergy loss when bay was used as the plant material.

Key words: supercritical extraction; ultrasonic extraction; Aloe barbadensis Miller; Laurus nobilis; exergy analysis.

The essential oils and oleoresins isolated from herbs and spices have been used as food additives, flavours, fragrances, colours or pharmaceuticals. The available extraction techniques for their isolation such as hydro- or steam distillation, organic solvent extraction, and near-critical (liquid or supercritical) extraction have certain advantages and disadvantages considering the operating cost, capital cost, yield, and quality of extract. Hydrodistillation is the most practiced and cheapest extraction method but it is limited to volatiles or essential oil production, only. The organic solvent extraction is intermediate in capital and operating costs but it is usually in contrast with requirements defined by standards and the presence of solvent residues in the final extracts and emissions of volatile organic solvent in the air. The extraction with dense gases (supercritical extraction) is characterized by a high capital cost but moderate operating costs. However, no solvent residues remain in the product after a supercritical extraction, nor are there any chemical changes initiated in the extracts due to applying such a processing technique, which gives an extract of outstanding quality [1]. Combined technologies such as high-pressure processing, pulsed electric fields, dense gases and ultrasound offer the potential for improving the existing separation processes as well as for developing new extraction options [2]. Therefore, the conventional sol-

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vent extraction of active subctances from plant material might be improved by ultrasound power due to mass transfer intensification, cells disrupture and improved penetration of the solvent through the vegetable tissue [3]. Mass transfer of specific compounds through the solid phase is faster as a consequence of swelling of the plant material during its exposure to SC  $CO_2$  [4,5]. Due to rapid decompression the plant tissue rupture was observed which is then followed by easily release of active principles [4].

The extracts of Aloe leaves can be isolated by a conventional solvent extraction with methanol [6], US extraction with ethanol and hexane [7,8] and SC CO<sub>2</sub> extraction [7]. The conventional solvent extraction performed using hexane, water, ethanol [9], methanol [10,11] acetone, tetrahydrofuran, isopropanol [12], as well as SC CO<sub>2</sub> extraction [13-15] used for isolation of antioxidant extracts from bay have also been reported in literature. Among herbs, Aloe Vera (Aloe barbadensis Mill.), well-known for its anti-inflammatory, anti-bacterial, anti-viral, anti-fugal, anti-cancer and immunemodulatory properties has been intensively studied for its antioxidant activity [7-14]. The Sweet Bay (Laurus nobilis L.) has been used as a flavour in culinary and food industry and studied for anti-bacterial, anti-fungal, antidiabetes and anti-inflammatory effects [10] and recently has also been screened for its antioxidant activity [11-13].

The economics for a given extraction process depends on the choice of the extraction method which is affected by many factors such as solubility, solute yield, solvent to feed ratio, mass transfer, equipment size, material handling, energy consumption, etc. [16]. To the best of our knowledge, the energy requirements of the extraction processes for the isolation of bioactive compounds from herbaceous material has been poorly investigated and discussed in the literature [4,5,16,17].

The present work presents new data on energy requirements for different methods of the extraction of bioactive principles from plant material by applying exergy analysis. Bejan et al. [18] outlined the fundamentals of the methods of exergy analysis and entropy generation minimization (or thermodynamic optimization-the minimization of exergy destruction) [18]. Exergy represents the quantitatively "useful" energy, or the ability to do or receive work-the work content-of the great variety of streams (mass, heat, work) that flow through the system. Another benefit is that by accounting for all the exergy streams of the system it is possible to determine the extent to which the system destroys exergy. The destroyed exergy is proportional to the generated entropy [18]. The exergy method provides insight into the quality of the energy and quantifies the useful work that may be done by a certain quantity of energy and can be helpful in improving the energy efficiency of the extraction processes especially on the industrial scale [16-18].

The present study was aimed to investigate and compare the efficiency of different methods for isolation of antioxidant extracts from aloe (*A. barbadensis* Mill.) and bay leaves (*Laurus nobilis* L.) with respect to extract's yield, as well as maximum useful work and exergy loss as a measure of the process irreversibility on a laboratory scale. Hence, a supercritical carbon dioxide extraction (SCE), an ultrasonic extraction from previously treated herbaceous matrix with supercritical fluid (US-SCCO<sub>2</sub>), and a conventional ultrasonic extraction (US) have been investigated and discussed.

## **EXERGY ANALYSIS**

The change of exergy or the change of maximum theoretical useful work of applied extraction techniques was used in this study for calculating the loss of the energy efficiency. The exergy balance for the open steady-flow system state (Fig. 1) can be written as [16]:

$$Ex_{\rm in} + Ex_Q = Ex_{\rm out} + W + I \tag{1}$$

where  $Ex_{in}$  and  $Ex_{out}$  are exergy rates on inlet and outlet of the given system (Eqs. (2) and (3), respectively):

$$Ex_{\rm in} = \sum m e_x({\rm in}) \tag{2}$$

$$Ex_{\rm out} = \sum m e_x({\rm out})$$
(3)

The exergy of the stream ( $e_x$ ) consider the steady-flow system, where the given state is represented by the specific enthalpy, *h*, chemical exergy,  $e_{ch}$ , entropy, *s*, kinetic energy,  $v_0^2/2$ , and gravitational potential energy,  $gZ_0$ , as given by Eq. (4):

$$e_{x} = (h - T_{0}s) - (h_{0} - T_{0}s_{0}) + e_{ch} + v_{0}^{2}/2 + gZ_{0}$$
(4)

The  $e_x$  is expressed in kJ/kg, and is evaluated relative to the environment ( $T_0$ , $p_0$ ) [17]. The environmental temperature and pressure were 293.15 K and 0.1 MPa, respectively. In Eq. (4), term ( $h-T_0s$ ) represents the flow availability of the stream. The  $e_x$ represents the difference between the flow availability at the indicated state and the flow availability of the same stream at the environmental state. In the present work, the contributions of the chemical exergy ( $e_{ch}$ ) as well as kinetic and potential energies ( $v_0^2/2$  and  $gZ_0$ ) are neglected.

The exergy content of heat transfer is given by Eq. (5) [17]:

$$E_{Q} = \sum_{j} \left[ \dot{Q}_{j} \left( 1 - \frac{T_{0}}{T_{j}} \right) \right]$$
(5)

The destroyed exergy (irreversibility of process, lost power) for the open system at stationary conditions (Eq. (6)) can be calculated from Eq. (1) and it is proportional to generated entropy due to phase transformations. Hereby,  $Q_j$  is the heat exchange in the *j*-th heat exchanger,  $T_j$  is the temperature of the reservoir in *j*-th heat exchange and  $W_k$  is external work done in *k*-th exchange with the surroundings.

$$\dot{W}_{\text{lost}} = \mathcal{T}_0 \dot{S}_{\text{gen}} = \sum m e_x(\text{in}) - \sum m e_{\text{ex}}(\text{ou}t) + \sum_j \dot{Q}_j (1 - \frac{\mathcal{T}_0}{\mathcal{T}_j}) - \sum_k \dot{W}_k$$
(6)

Exergy represents the working potential of the system at a given state in a specified environment. The maximum useful work ( $W_{max}$ ) or reversible work is given as exergy change and represents the maximum work generated ( $\Delta E > 0$ ) or the minimum work required ( $\Delta E < 0$ ) for the given transition of the system from one to another state.

$$\dot{W}_{\max} = E x_{in} - E x_{out} = -\Delta E$$
 (7)

The thermodynamic properties of supercritical and liquid carbon dioxide used in calculations of exergy are given in Table 1.

Dividing Eqs. (6) and (7) with *m*, the maximum useful work ( $W_{max}$ ) and exergy loss (/) per kg of CO<sub>2</sub> for the supercritical CO<sub>2</sub> extraction (SCE) process presented in Fig. 1 can be obtained (Eqs. (8) and (9)). Therewith,  $Q_{23}$  and  $Q_{34}$  are heat released by cooling in the cryostate (kJ/kg) and heat delivered to the extractor by an electrical heater (kJ/kg).  $W_{12}$  is work done during the compression of the CO<sub>2</sub> from gas (atmospheric conditions) to liquid in a tank (Table 1), while  $W_{34}$  is the commpression work of a pump (kJ/kg).

$$I = [h_{1} - h_{4} - To(s_{1} - s_{4})] + [Q_{23}(1 - \frac{T_{0}}{T_{cr}}) + Q_{34}(1 - \frac{T_{0}}{T})] - (W_{12} - W_{34})$$
(8)

$$W_{\max} = -\Delta E = h_1 - h_4 - T_0(s_1 - s_4)$$
(9)

where

$$Q_{23} = \Delta h_{23} = h_2 - h_3 \tag{10}$$

	Atmosphere	Tank	Pump	SCE (30 MPa)	SCE (10 MPa)		
Quantity	State						
	1	2	3	4	4'		
<i>Т</i> (К)	298.15	298.15	268.15 K	373.15	313.15		
<i>р</i> (MPa)	0.1	6	6	30	10		
<i>h</i> (kJ/kg)	1000	910	682	883	807		
<i>s</i> (kJ/kg K)	5.97	5	4.25	4.75	4.62		
ν(m <sup>3</sup> /kg)	0.5	0.0053	0.00103	0.0015	0.0016		



Figure 1. Flowsheet of a supercritical CO<sub>2</sub> extraction process (SCE): T, CO<sub>2</sub> storage tank; C, cryostat; P, high pressure liquid pump; H, heater; E, extractor vessel.

$$Q_{34} = \Delta h_{34} - V \Delta p_{34} \tag{11}$$

$$W_{12} = p_1(v_2 - v_1) \tag{12}$$

$$W_{3} = p_{3}(v_{4} - v_{3})$$
 (13)

The change of exergy and the maximum useful work for the ultrasound-assisted or ultrasonic extraction can be calculated from Eqs. (14) and (15):

$$I_{EV} = \Delta_{vap} h^{\theta} - T_0 \Delta_{vap} s^{\theta} + mc_{\rho} (T_b - T_0)$$
(14)

$$W_{\max,EV} = \Delta_{vap} h^{\theta} - T_0 \Delta_{vap} s^{\theta}$$
(15)

The  $\Delta_{vap} h^{\theta}$  and  $\Delta_{vap} s^{\theta}$  are standard enthalpy and standard entropy of ethanol evaporisation.

 $\Delta_{vap} h^{\theta} = 837 \frac{kJ}{kg}$   $\Delta_{vap} s^{\theta} = 2.381 \frac{kJ}{kgK}$   $c_{\rho} = 2.44 \frac{kJ}{kgK}$   $I = I_{SCE} + I_{EV}$ (16)

$$W_{\rm max} = W_{\rm max,SCE} + W_{\rm max,EV}$$
(17)

## **EXPERIMENTAL**

## Chemicals and materials

Commercial carbon dioxide (99 mass% purity, Messer Tehnogas, Belgrade, Serbia) was used for supercritical extractions. Ethanol (96% purity, Kemika, Zagreb, Croatia) was used for ultrasound-assisted extractions.

#### Plant material

Dried leaves and Sweet Bay (Montenegro) were obtained from the local market. Whole fresh leaves of

five-year old Aloe Vera (Serbia) were dried in the air at constant temperature. Dried leaves of plant material were ground and sieved. Fraction 0.315-0.5 mm was used for experimental studies. In order to investigate the ultrasonic extraction from finely ground plant material, a fraction of ground Aloe Vera which passed through the 0.315 mm sieve was used as well and this fraction is referred to as aloe powder.

#### Supercritical extraction

Extractions with SC CO<sub>2</sub> were performed in Autoclave Engineers SCE Screening System with a 150 cm<sup>3</sup> extraction cell previously described [19]. Lighter compounds from Aloe Vera and Bay leaves were extracted at mild conditions (10 MPa and 313.15 K) and fractions containing a larger quantity antioxidants were isolated at 30 MPa and 373.15 K [6,7,16]. 38.6 g of dried leaves of aloe and 30.3 g dried leaves of bay were used for extractions with SC CO<sub>2</sub>. The mass flow rate of the CO<sub>2</sub> was 0.15 kg/h in all experiments.

## Ultrasonic-assisted extraction

For the ultrasonic-assisted extraction experiments, an open rectangular ultrasonic cleaner bath (Bandelin Sonorex RK 52, BANDELON electronic, 35 kHz, 60 W) with a useful volume of 1.8 L (internal dimensions:  $(150\times140\times100)$  mm was used to carry out the extractions. The experimental conditions were selected based on studies on the ultrasonic extraction found in literature [3,7]. The samples of 5 g of ground plant material ( $d_p$  = 0.315-0.500 mm with an average diameter of 0.400 mm) were added into 200 ml of 96% ethanol in a 250 ml flask and subjected to the ultrasonic bath, filled with water and sonicated for 30 min. Subsequently, the solution was filtrated and ethanol was evapo-



Figure 2. The procedure for isolation of the extracts of Aloe barbadensis Mill. and Laurus nobilis L. by US and US-SCCO2.

rated by a rotary vacuum evaporator at 355.15 K. Powdered aloe vera leaves ( $d_p < 0.315$  mm) was used for the ultrasound extraction to study the particle size influence on the extract's yield as well.

In order to investigate the effect of a pre-treatment of the plant material on the extract's yield, which might be obtained by the ultrasonic extraction, 4.5 g of ground bay leaves or 5 g of ground Aloe leaves were subjected to SC  $CO_2$  at 10 MPa and 313.15 K for an hour and subsequently plant materials were led to rapid decompression. Thereupon, the ultrasonic extraction with ethanol followed using the above defined procedure.

#### **RESULTS AND DISCUSSION**

## Total yields of extracts

Yields of extracts obtained by US, US-SCCO<sub>2</sub> and SC CO<sub>2</sub> extractions are presented in Table 2. The yields (mass%) of Aloe and Bay extracts obtained by SCE at 10 MPa and 313.15 K after spending 2.6 kg<sub>CO2</sub>/kg<sub>plant material</sub> (Aloe) and 10 kg<sub>CO2</sub>/kg<sub>plant material</sub> (Bay), were 0.13 and 1.18%, respectively. Yields of Aloe and Bay extracts (mass%) obtained by SCE after the pressure and temperature were increased (30 MPa and 373.15 K) versus SC CO<sub>2</sub> consumption are given in Fig. 3. The operational parameters for SCE had been chosen with respect to previously accomplished optimization of SCE of antioxidant fraction from Lamiaceae herbs [20].

The observed yields of the extracts isolated from bay and Aloe leaves were compared to previously reported in the literature (Table 2).

The yield of Aloe supercritical extract obtained at 30 MPa and 373.15 K (1.4 mass%) was similar as previously reported [7], whereby the maximum yield of 1.47 mass% was isolated at 35 MPa, 323.15 K with methanol as co-solvent (Table 2). Unlike, the yield of bay supercritical extract reported in this study was higher than previously reported [12,14,15] under similar conditions (Table 2).

Ultrasound assisted extraction was carried out under experimental conditions that had been based on the reports from open literature [3,7,8]. Ethanol was a solvent of choice for it has been reported to be stable under sonication (96-50%) [3]. The application of ultrasound to improve the efficiency of the solvent extraction has been already highlighted in open literature [3,21]. Ultrasonic disruptions of the cell walls thus take some time (≈30 min) after which the release of the cell content is much more rapid. Cavitation induced by sonication is the process in which bubbles with a negative pressure are formed near cell walls, grow, oscillate, and may split and implode. The collapse of cavitation bubbles near cell walls is expected to produce a cell disruption together with a good penetration of the solvent into the cell through an ultrasonic jet [3,21].

The yields of the extracts of aloe and bay obtained by US were much higher compared to SCE (Table 2). Analogies of these observations have been



Figure 3. Yields (mass%) of extracts from Aloe Vera (■) and from Sweet Bay (O) versus SC CO<sub>2</sub> consumption obtained at 30 MPa and 373.15 K.

previously reported [7]. There is no available date on the yield of the US bay leaves with ethanol as a solvent except the data obtained by the solvent extraction with ethanol [9] where a higher yield was observed compared to the yield detected in this study (Table 2). It could be explained by different origin of the plant. As for the Aloe extracts, longer time of sonication could also lead to higher yields [7] as well.

A considerably lower yield of the extract obtained by SCE compared to US is the result of different selectivity of ethanol in comparison to SC CO<sub>2</sub>. However, the isolation of a desirable group of compounds from aloe and bay leaves using the supercritical extraction can be achieved by tuning pressure, temperature and by adding some modifier or co-solvent [7,13-15].

The yield of the extracts isolated by US could be influenced by pre-treatment with SC  $CO_2$  and by changing the particle size of the vegetable material (Table 2). Rapid decompression after exposure of plant material to SC  $CO_2$  caused a disruption of the vegetable tissue and the content of secretory structures started being readily available for the ultrasonic extraction. Namely, the resistance for mass transfer was reduced and the ultrasonic extraction was significantly accelerated. Pre-treatment of the vegetable material with SC  $CO_2$  prior US led to the increase of the extract's yield for 133 (Aloe) and 20% (Bay) (Table 2). It has been shown that a pre-treatment with SC  $CO_2$  has more influence on the yield of the aloe extract obtained by ultrasonic extraction than a change of particle size influence (Table 2).

## The exergy analysis

The values for maximal useful work ( $W_{max}$ ) and exergy loss (/) in kJ per kg of CO<sub>2</sub> and the mass of isolated extracts were used for the calculation of maximum useful work and exergy loss in in kJ per kg of the extract ( $W_{max,e}$  and  $I_e$ ). The calculated values of maximum useful work and loss of exergy per 1 kg of the extract for the SC CO<sub>2</sub>, US and US-SCCO<sub>2</sub> extraction processes were presented in Table 3. The obtained values were much higher for the SCE than for US and US-SCCO<sub>2</sub> and especially for SCE of aloe leaves.

If  $W_{max}$  is negative ( $\Delta E > 0$ ) it represents the maximum work generated and if it is a positive value ( $\Delta E < 0$ ) then it is the minimum work required for the given system transition from one to another state. According to performed calculation, the SCE is realized with a larger change of useful work and loss of exergy per 1 kg of the extract. The exergy dissipation in the SCE at laboratory scale which is observed in this study can be explained by the fact that CO<sub>2</sub> is released into atmosphere. However, the SC CO<sub>2</sub> is commonly recycled in

Table 2.	Yields of the aloe and	bay extracts obt	ained by different	methods: investigation	performed in this stud	ly and literature review
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Plant material/origin	Method	Conditions/solvent density	Total Yield, mass%	Reference
A. barbadensis Mill., air-dried leaves (Serbia)	SCE	30 MPa / 373.15 K, 662 kg/m <sup>3</sup>	1.53	This study
	US	30 min, 96 % ethanol, room temperature	6	
	US-SCCO <sub>2</sub>	30 min, 96 % ethanol, room temperature	14	
A. barbadensis Mill., powdered air-dried leaves (Serbia)	US	30 min, 96 % ethanol, room temperature	8	
<i>A. barbadensis</i> Mill., lyophilised aloatic epidermis (Jiangsu Province, China)	SCE	35-45 MPa, 305.15-323.15 K, 0-20% Methanol, 900-1000 kg/m <sup>3</sup>	0.15-0.46 (0% methanol); 0.13-0.41 (10% methanol); 0.09-1.5 (20% methanol)	[7]
	US	60 min, ethanol and hexane, room temperature	17.3 (Ethanol) 1.53 (hexane)	
<i>A. barbadensis</i> Mill., lyophilised leaf pulp (Jiangsu Province, China)	US	60 min, ethanol and eexane, room temperature	23.6 (Ethanol) 0.7 (Hexane)	[7]
L. nobilis L., dried leaves	SCE	30 MPa/373.15 K, 662 kg/m <sup>3</sup>	4.18	This study
(Montenegro)	US	30 min, 96% ethanol, room temperature	10	
	US-SCCO <sub>2</sub>	30 min, 96% ethanol, room temperature	12	
<i>L. nobilis</i> L., dried leaves (Ardiç region of Çesme, Turkey)	Method not defined	<i>n</i> -Hexane, ethanol, water	15.3; 20.2; 10.1	[9]
<i>L. nobilis</i> L., dried leaves (Madrid, Spain)	SCE	10-40 MPa/313.15 K, 622-956 kg/m <sup>3</sup> , 60 min	0.32-1.45	[12]
L. nobilis L., dried leaves (Turkey)	SCE	8-15 MPa/313.15-323.15 K, 40 min	1.13-1.34	[14]
<i>L. nobilis</i> L., dried leaves (Murcia, Spain)	SCE	25 MPa/333.15 K, 777kg/m <sup>3</sup> , 60 min	0.67	[15]

Sample	<i>d</i> <sub>p</sub> / mm	Method	Total yield, mass%	<i>W</i> <sub>max</sub> / kJ kg⁻¹	// kJ/kg	$W_{\rm max,e} \times 10^{-3}$ / kJ kg <sup>-1</sup>	extract /e×10 <sup>-3</sup> / kJ kg <sup>-1</sup> extract
Aloe Vera	0.400 <sup>a</sup>	SCE	1.53	-246.7	454.5	-226	416
		US-SCCO <sub>2</sub>	14	-82	434.7	-0.7	75
		US	6	127.1	148.4	68	80
	<315	US	8	127.1	148.4	51	60
Bay	0.400 <sup>a</sup>	SCE	4.18	-246.7	454.5	-98	180
		US-SCCO <sub>2</sub>	12	-82	434.7	-0.9	129
		US	10	127.1	148.4	41	48

Table 3. Calculation of maximum useful work (W<sub>max,e</sub>) and exergy loss (I<sub>e</sub>) per 1 kg of extract isolated by different extraction techniques

<sup>a</sup>Determined as average value for fractions with 0.315-0.500 mm diameter

the pilot-plant and industrial units for SCE, so that much less exergy dissipation occurs during extraction process. Sievers *et al.* [17] who used the exergy method to determine and compare energy requriments for SCE of hops (on industrial scale) with a conventional solid/liquid extraction suggested that the conventional solid/liquid extraction is energetically superior to the supercritical fluid extraction. In the same study [17], the authors suggested that much lower energy costs of the SCE process can be achieved by heat recovery at the expense of the additional equipment.

In this study, the process of US-SCCO<sub>2</sub> generates a much smaller amount of useful work per 1 kg of the extract in comparison to SCE, whereby the exergy loss was moderate (Aloe) to high (Bay). Pre-treatment of the plant material with SC CO<sub>2</sub> and the particle size decrease have led to the decrease of the maximum useful work and exergy loss per 1 kg of the extract in the case of the ultrasonic extraction of aloe leaves. Unlike, the exergy loss per kg of the extract for the ultrasonic extraction of the bay leaves increased with introducing the pre-treatment with SC CO<sub>2</sub>. The minimum required work and exergy loss per kg of the extract were moderate for conventional US extractions.

The estimated values of the maximum useful work and exergy loss depended principally on the extraction method as well as on the type of the plant material.

## CONCLUSION

In this paper, yields of extracts of Aloe Vera and Sweet Bay obtained by SCE as well as US and US--SCCO<sub>2</sub> with ethanol have been compared. This study reveals that the yield of ethanolic extracts obtained by US (6 mass% for Aloe and 10 mass% for Bay) was much higher than the yield obtained by SCE (1.4 mass% for aloe and 3.0 mass% for bay). Pre-treatment of vegetable material with supercritical CO<sub>2</sub> for one followed by rapid decompression prior to ultrasonic-assisted extraction has resulted in the increase of the yield for 133 and 20% for Aloe and Bay compared to the yields obtained by the ultrasonic-assisted extraction alone. This study also showed that the yield of the extracts obtained by US depended on the particle size of ground leaves but it was smaller than that achieved from the plant materials pre-treated by SC CO<sub>2</sub>. Namely, the yield of the ethanol extract of Aloe Vera powder obtained by conventional US (8%) was higher than the one obtained from the sample which comprised 0.400 mm particles (6%). However, the yield is still considerably lower than the yield of the extract from the sample that had been previously subjected to SC CO<sub>2</sub> pre-treatment (14%).

The present study indicated that energy requirements for the extraction of phytochemicals depend both on the extraction method and type of plant material. The maximum useful work and energy loss (per kg of the extract) principally depend both on the extraction method and used plant material as raw material. The maximum change of useful work and loss of energy per 1 kg of the extract were calculated in the case of SCE compared to US and US-SCCO2. A high exergy loss during SCE at laboratory scale occurs due to CO2 release into the atmosphere. The exergy loss during the ultrasound-assisted extraction can be lowered by pre--treatment of the plant material with supercritical CO2 and, in the case of Aloe Vera, by the decrease of a particle size. On contrary, in the case of the extraction of US bay the exergy loss is greater when a pre-treatment is applied.

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## Nomenclature

- *E*<sub>x</sub> Exergy rate (W)
- *e*<sub>x</sub> Exergy of stream (kJ/kg)
- $E_Q$  Heat-transfer exergy (W)
- h Specific enthalpy (kJ/kg)
- / Exergy loss (kJ/kg)
- *m* Mass flow rate (kg/h)
- *p* Pressure (MPa)

- $c_p Q$ Heat capacity (kJ/kg K)
- heat transfer rate (W)
- Q Heat transfer (kJ/kg)
- ${\cal S}_{
  m gen}$ Entropy generation rate (W/K)
- Specific entropy (kJ/kg K) s
- Т Temperature (K)
- Specific volume (m<sup>3</sup>/kg) v
- V Extractor volume (m<sup>3</sup>)
- Ŵ External work rate exchange with the surroundings (W)
- W<sub>max</sub> Maximum useful work rate (W)
- $W_{lost}$ Lost power (W)
- $W_{\rm max}$ Maximum useful work (kJ/kg).

## Subscripts

- Inlet in
- out Outlet
- 0 Ambient state
- ch Chemical
- Per kg of extract е
- EV Evaporation
- SCE Supercritical extraction
- Maximum. max

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