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Determination of Hansen solubility parameters for sugarcane oil. Use of ethanol in sugarcane wax refining

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SUMMARY: Currently, the refining of sugarcane wax is carried out with 95% v/v ethanol as solvent. This process has a high rate of ethanol consumption thus, the main objective of this work was to corroborate the feasibility of 95% v/v ethanol as a solvent in the refining of sugarcane wax. The suitability of its performance over other organic solvents was evaluated through the relative energy difference (RED) determined from Hansen solubility parameters (HSPs) of sugarcane oil, which were calculated using HSPiP software. HSPs turned out to be δ_D = 16.24 MPa^{½}, δ_P = 3.21 MPa^{½} and δ_H = 10.34 MPa^{½}, similar to those reported for pine resin and castor oil. The best solvent was 1-decanol. 95% v/v ethanol turned out to be a bad solvent. Absolute ethanol had a RED value of 0.993, which made it a better candidate since it could reduce consumption rates, and constituted an eco-friendly solvent produced in Cuba for the refining process.

KEYWORDS*: Ethanol; Hansen solubility parameters; Sugarcane oil; Sugarcane press mud*

RESUMEN: ***Determinación de los parámetros de solubilidad de Hansen para el aceite de caña de azúcar. Uso del etanol para la refinación de la cera de caña de azúcar.*** La refinación de la cera cruda de caña se realiza con etanol a 95% v/v, incurriendo en altos índices de consumo, por lo que el objetivo principal de este trabajo es determinar si el etanol a 95% v/v es un solvente adecuado. Su uso respecto a otros solventes orgánicos es evaluado por la diferencia de energía relativa (RED) determinada a partir de los parámetros de solubilidad de Hansen (HSPs), se calcularon usando el programa HSPiP. Los HSPs fueron δD = 16.24 MPa^{½}, δP = 3.21 MPa^{½} and δH = 10.34 MPa ½, siendo similares a los reportados para la resina de pino y el aceite de ricino. El mejor solvente fue 1-decanol, el etanol del 95% v/v fue un mal solvente; el etanol absoluto con un RED= 0.993 es un mejor candidato, ya que podría reducir las tasas de consumo, manteniendo un solvente ecológico y producido en Cuba para el proceso de refinación.

PALABRAS CLAVE*: Aceite de caña de azúcar; Cachaza; Etanol; Parámetros de solubilidad de Hansen*

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1. INTRODUCTION

The press mud, obtained during the purification of sugarcane juice, is mainly used as an organic fertilizer in sugarcane fields, as well as in biogas production. The mud contains sugarcane wax at 3% w/w of the cake (ICIDCA, 2000). During the second half of the last century in Cuba the American Sugar Co. Swenson (1947) developed and introduced a technology for the production of sugarcane wax by extraction with heptane, which was further exported to the United States for refining. During the 90s a wax refining technology was developed, and a wax refining plant was built in Cuba due to the interest in refined wax (WR) as raw material for the production of some pharmaceutical products.

Sugarcane wax has a dry base average composition of 68.53% wax, 28.61% oil and 2.47% impurities, also called resins. The sugarcane wax refining technology consists of a solvent extraction process with 95% v/v ethanol. The refining process begins by bringing the sugarcane wax into contact with cold 95% v/v ethanol for eight hours in a stirring tank. Then the dispersed solid is centrifuged and the heavy phase, rich in refined wax, is subsequently extracted with hot ethanol in an extractor-decanter centrifuge; the refined wax is cooled and separated in a disk centrifugal bowl. After that, the refined wax is dried and packaged for later commercialization. This technology uses 95% v/v ethanol as solvent because it is a renewable solvent of national production. There are several reports about the use of ethanol for vegetable oil extraction, but there is no evidence about how useful it is compared to other solvents.

The extraction of vegetable oils with ethanol is not an exclusive feature of sugarcane wax refining, since literature reports several works about the solubility degree of this solvent with several vegetable oils. During the first half of the last century, Taylor *et al.,* (1936) investigated the solubility of 14 different vegetable oils in ethanol, including corn, olive, peanut, peach, soybean and sunflower oils, among others. This study showed that they have different solubility degrees according to their composition and that they vary from 1 to 10 kg of oil per 100 kg of ethanol at 90% w/w and between 5 to 15 kg of oil for 100 kg of absolute ethanol. Measurements were made at 25 ˚C. The results showed the influence of small amounts of water on the solubility of vegetable oils in this solvent. In their studies Kaparthi *et al.,* (1955) concluded that even in the case of absolute ethanol, this solvent is not a useful solvent for vegetable oils, such as sunflower, peanut and cottonseed because concentrations higher than 10 kg of oil per 100 kg of ethanol at temperatures lower than 30 ˚C are not achieved, although at 70 ˚C the sunflower, peanut and cottonseed oils are soluble.

Rao *et al.,* (1955) carried out research in the extraction of vegetable oils from cotton, peanut, sesame and soybean seeds using ethanol of various alcoholic degrees and under several temperature conditions. For all the oils, they determined solubility curves and showed that there was a linear relationship between the "critical temperature", defined as the temperature at which the alcohol solution reached saturation for the oil studied, and the alcohol concentration used.

Given the importance of ethanol in Brazil, Freitas *et al*., (2010) showed the advantages of the use of ethanol instead of hexane for the extraction of coffee and sunflower oil, owing to the ecological nature of ethanol. With its use for the extraction of coffee and sunflower oil, they obtained results of 11.4 and 18.6%, respectively, during their extraction of seeds, although these results are lower than those obtained with hexane. A similar study was developed by Rodrigues *et al*., (2010) for soybean oil and concluded that the use of ethanol for this process is feasible; while Rodrigues *et al*., (2010) evaluated it in the extraction of rice oil. Both studies used experimental designs for their respective purposes and concluded that temperature and the alcoholic degree were the main independent variables, which agreed with the results reported in previous works on the use of ethanol as a vegetable oil solvent.

The solubility of canola, maize, jatropha and maracauba oils in ethanol at temperatures of 25-60.15 ˚C was investigated by Da Silva *et al.*, (2010); while Shariati *et al.*, (2013) determined the solubility curves of sunflower oil in ethanol.

There are only a few studies in which Hansen's solubility theory was used as a tool to determine the HSPs of vegetable oils to know which would be the most suitable solvent for these oils. Batista *et al.*, (2015) determined the HSPs of used frying oil, coconut oil, palm oil and biodiesel. They confirmed that used frying oil and biodiesel–diesel blends were feasible alternatives that could be used as additives for diesel fuel.

A study by De la Peña-Gil *et al*., (2016) to develop a specific method to determine the HSPs of complex vegetable oils used group contribution methods with two approaches: the first assumed that the contributions of the 3 forces could be subdivided into larger functional groups (i.e. fatty acids and fatty acid methyl esters), which are additives; while the second approach assumed that vegetable oils are composed of simple triglycerides mixtures in the same mass fractions as fatty acids. They concluded that the HSPs calculated for vegetable oils with the second assumption provided similar values to the HSPs obtained from the HSPiP software.

During studies developed by The Cuban Research Institute of Sugarcane Derivatives (ICIDCA) in the 90s about sugarcane oil extraction from sugarcane wax with ethanol at 18-20 ˚C, only 17.9% efficiency was achieved with ethanol at 93% v/v and 42.9% with absolute ethanol. Therefore, the use of absolute alcohol in the refining process of sugarcane wax was suggested, but investigating the possibility of using other more efficient solvents for this purpose were recommended, topics which are investigated in this work.

In the current refined wax plant, low efficiencies and high 95% v/v ethanol consumption rates are reported during sugarcane oil extraction. The objective of this work was to verify whether ethanol 95% v/v is a suitable solvent for the sugarcane wax refining process using Hansen's solubility theory, as well as to determine other solvents that can be suitable for this process.

2. MATERIALS AND METHODS

2.1. Oil purification

Sugarcane oil obtained from the sugarcane wax refining factory annexed to the Majibacoa sugar mill in Las Tunas province, Cuba, was used for this study. HPLC grade acetone at 25 ˚C was used for the purification process, according to factory laboratory standards. This impure oil obtained in the factory, with an average dry base composition of 78.9% oil, 15.78% wax and other impurities, was subsequently dissolved in acetone at 25 ˚C with an acetone-oil ratio of 4:1 and filtrated under vacuum with a Buchner funnel and fast filtration paper to be purified. Acetone with oil was evaporated in a vacuum rotary evaporator and then the oil was dried in an oven at 100 ˚C. The oil obtained was subjected to a second purification step.

2.2. Hansen Solubility Parameters determination (HSPs)

2.2.1. Fundamental

HSPs determination is a useful tool for solvent selection in the extraction of natural chemical products because it expresses the affinity degree between a solute and any solvent based on the Hansen theory, which stipulates that "likes attract likes". There are two important groups of methods for HSPs determination, experimental and theoretical methods, but only experimental methods are evaluated in this work for the HSPs determination of sugarcane oil.

The basic equation governing the assignment of Hansen parameters establishes that the total cohesion energy between two molecules, E, must be the sum of the individual energies: non-polar interactions or atomic dispersion (ED), molecular di-polar interactions (EP) and hydrogen-bonding interactions (EH) (Hansen C.M. 2007), so**:**

$$E = ED + EP + EH \quad (1)$$

Dividing this by the molar volume gives the square of the Hildebrand solubility parameter as the sum of the squares of the Hansen D, P, and H components: dispersion (δ_D), polar (δ_P), and hydrogen bonding (δ_H).

$$\frac{E}{V} = \frac{ED}{V} + \frac{EP}{V} + \frac{EH}{V} \quad (2)$$

$$\delta_T^2 = \delta_D^2 + \delta_P^2 + \delta_H^2 \quad (3)$$

The Hansen parameters of different solutes and solvents may be plotted in a tridimensional plot x,y,z (δ_D,δ_P ,δ_H). The closer the solute-solvent pair is in the three-dimensional space, the more soluble they are. The distance between the solvent (a) and solute (b) is usually called R_a and can be determined by the following expression:

$$R_a = [4*(\delta_{Da} - \delta_{Db})^2 + (\delta_{Pa} - \delta_{Pb})^2 + (\delta_{Ha} - \delta_{Hb})^2]^{1/2} \quad (4)$$

Experimental evaluation of a solute with various solvents, generally between 40-50 different solvents, and its classification into "good" or "bad" solvents by visual inspection, helps us to determine the HSPs of the solute (solute's coordinates within Hansen space).

Considering that the "good solvents" surround the solute forming a hypothetical sphere, called "Hansen's Sphere", good solvents can also be found on the surface of the Hansen sphere, so for them Ra is equal to the radius of the sphere (R_0). By defining the Ra/R_0 ratio as the relative energy difference (RED), the good solvents will obtain RED values less than 1 and the bad solvents higher. Both the radius of the sphere and the center (HSPs) are determined by the use of appropriate multi-response optimization algorithms. (Abbott and Yamamoto, 2015; Díaz and Hernández, 2020).

$$RED = \frac{R_a}{R_o} \quad (5)$$

2.2.2. Hansen solubility parameters determination through classic Hansen method

The determination of Hansen's parameters was executed with 48 different analytical degree solvents as shown in Table 1. Solvent-oil samples in a 9:1 ratio were placed in duplicate test tubes and shaken for 24 hours at 30 ^{0}C and then allowed to rest 72 h for a visual inspection of the presence of phase separation (Batista *et al.*, 2015).

Visual inspection was performed by each author separately and individual ratings were compared. The samples were divided into three groups: soluble (without phase separation), not soluble (phase separation) and doubtful. The doubtful group included the samples in which their evaluation differed for each author and also those classified directly as such. Due to the nature of the oil used, the solution tended to darken and it was sometimes difficult to visually determine whether or not there was phase separation. Therefore, tests classified as "doubtful" were observed under the microscope or a drop of sample was placed in a filter paper; if a black spot was formed at the sample application point, then it was classified as not soluble, on the other hand, if the sample formed a ring of uniform color, it was soluble according to the established procedure (Redelius, 2004).

Samples in which the solvent solubilized the solute received a score of 1 and samples in which the solvents did not solubilize the solute the score were labelled 0. Both the HSPiP software using the genetic algorithm and the improved Microsoft Excel workbook from the authors were used for data processing to define the HSPs for sugarcane oil (Abbott and Yamamoto, 2015; Díaz and Hernández, 2020).

2.2.3. Fit improvement of Hansen solubility parameters

The reliability of the parameters was mainly based on the fact that the solvents used in the study would cover the largest possible area of the three-dimensional space in such a way that the edge of the sphere and its center could be correctly defined.

To check the quality of fit, the values called "Core" by HSPiP software were used. This option showed how much the solute´s HSPs could vary in different directions without too high a penalty. Clearly the larger the "Core" values, the less the Sphere was defined, so some additional solvents may be needed to redefine it.

One way to improve the fit is to use the "Sphere Radius Chk option" in HSPiP software. It goes through a list of green solvents that can be edited and finds any that are near the boundary of the Sphere (i.e. they have a RED of 0.9 to 1.1). It then checks each of those solvents for closeness to solvents in your test list. If they are close, then you already have enough data in that area. But if no solvent is nearby then it is likely that this test solvent would provide useful new information to improve the quality of the fit.

The suggested solvents by the software to achieve a better fit were: 2-nitropopane, 1-bromonaphthalene, 1,3-butanediol, butyronitrile and chlorobenzene. Since they were not available the "Solvent Optimizer" option was used. This option calculates solvent mixtures capable of achieving similar characteristics to recommended solvents. The mixtures were named Somix, tested, classified and scored according to the procedure described above. To determine the HSPs of sugar cane oil, a total of 53 solvents were tested, including mixtures.

2.3. Intrinsic viscosity measurements method

One of the more promising methods to evaluate polymer HSPs for limited data is by using intrinsic viscosity (Hansen, 2007).

In this technique, intrinsic viscosities determined with different solvents are normalized by dividing each one by the highest intrinsic viscosity value. These normalized data (≤ 1) are then used in a weighted averaging technique, according to the following equations, to determine the HSPs of the solute (Hansen, 2007).

TABLE 1. **Good and bad solvents for sugarcane oils to determine the Hansen solubility parameters**

No[a].	Solvent	Dispersion component (δ_D) $MPa^{1/2}$	Polar component (δ_P) $MPa^{1/2}$	Hydrogen bonding component (δ_H) $MPa^{1/2}$	Score[h]	Relative Energy Difference (RED)	Molecular volume (MVol) cm^3/mol
197	1-Decanol	16.0	4.7	10.5	1	0.146	191.8
542	1-Octanol	16.0	5.0	11.2	1	0.189	158.2
375	Ethylene Glycol Monobutyl Ether	16.0	5.1	12.3	1	0.256	131.8
306	1,4-Dioxane	17.5	1.8	9.0	1	0.295	85.7
930	1-Hexanol	15.9	5.8	12.5	1	0.319	125.2
617	Tetrahydrofuran (Thf)	16.8	5.7	8.0	1	0.334	81.9
429	Isoamyl Acetate	15.3	3.1	7.0	1	0.359	150.2
328	Ethyl Acetate	15.8	5.3	7.2	1	0.362	98.6
182	Cyclohexanol	17.4	4.1	13.5	1	0.371	105.7
545	Oleic Acid	16.0	2.8	6.2	1	0.392	319.7
552	1-Pentanol	15.9	5.9	13.9	1	0.418	108.6
732	2-Methyl-2-Butanol	15.3	6.1	13.3	1	0.422	109.6
93	2-Butanol	15.8	5.7	14.5	1	0.457	92.0
524	Methylene Dichloride (Dichloromethane)	17.0	7.3	7.1	1	0.505	64.4
156	Chloroform	17.8	3.1	5.7	1	0.520	80.5
92	1-Butanol	16.0	5.7	15.8	1	0.558	92.0
649	Trichloroethylene	18.0	3.1	5.3	1	0.572	90.1
58	Benzyl Alcohol	18.4	6.3	13.7	1	0.581	103.8
431	Isobutyl Alcohol	15.1	5.7	15.9	1	0.604	92.9
5	Acetic Acid	14.5	8.0	13.5	1	0.624	57.6
570	2-Propanol	15.8	6.1	16.4	1	0.628	76.9
255	Diethyl Ether	14.5	2.9	4.6	1	0.628	104.7
254	Diethyl Carbonate	15.1	6.3	3.5	1	0.732	121.7
569	1-Propanol	16.0	6.8	17.4	1	0.736	75.1
7	Acetone	15.5	10.4	7.0	1	0.751	73.8
698	o-Xylene	17.8	1.0	3.1	1	0.762	121.1
999	So Mix[b]	18.7	3.8	3.7	1	0.770	86.0
367	Ethylene Dichloride	18.0	7.4	4.1	1	0.772	79.4
398	Formic Acid[g]	14.6	10.0	14.0	0	0.779	37.9
999	So Mix[c]	18.5	4.2	2.8	1	0.823	103.0
598	Pyridine	19.0	8.8	5.9	1	0.838	80.9
187	Cyclopentane	16.4	0.0	1.8	1	0.851	94.6
637	Toluene	18.0	1.4	2.0	1	0.859	106.6
52	Benzene	18.4	0.0	2.0	1	0.924	89.5
11	Acetophenone	18.8	9.0	4.0	1	0.929	117.4
325	Ethanol	15.8	8.8	19.4	1	0.992	58.6
181	Cyclohexane	16.8	0.0	0.2	1	0.996	108.9
122	Carbon Tetrachloride (0 Dipole Moment)	17.8	0.0	0.6	1	0.998	97.1
999	So Mix[d]	15.3	12.4	5.1	1	1.000	98.0
999	So Mix[e]	16.2	12.1	4.3	1	1.000	76.0
297	Dimethyl Formamide (Dmf)	17.4	13.7	11.3	0	1.002	77.4
540	Octane	15.5	0.0	0.0	0	1.019	163.4
409	Heptane	15.3	0.0	0.0	0	1.024	147.0
417	Hexane	14.9	0.0	0.0	0	1.040	131.4
999	So Mix[f]	16.5	8.1	20.9	0	1.081	82.0
670	2,2,4-Trimethylpentane	14.1	0.0	0.0	0	1.086	165.5
437	Isopentane	13.8	0.0	0.0	0	1.107	117.1
303	Dimethyl Sulfoxide (Dmso)	18.4	16.4	10.2	0	1.289	71.3

No[a].	Solvent	Dispersion component (δ_D) MPa$^{1/2}$	Polar component (δ_P) MPa$^{1/2}$	Hydrogen bonding component (δ_H) MPa$^{1/2}$	Score[h]	Relative Energy Difference (RED)	Molecular volume (MVol) cm^3/mol
456	Methanol	14.7	12.3	22.3	0	1.425	40.6
10	Acetonitrile	15.3	18.0	6.1	0	1.442	52.9
368	Ethylene Glycol	17.0	11.0	26.0	0	1.631	55.9
406	Glycerol	17.4	11.3	27.2	0	1.750	73.4
696	Water	15.5	16.0	42.3	0	3.203	18.0

[a] Solvent identification number in the HPSiP program.
[b] Solvent mixture (57% v/v benzene, 43% v/v pyridine) representing 1-Bromonaphthalene
[c] Solvent mixture (acetophenone 43% v/v, benzene 35% v/v, toluene 22% v/v) representing Chlorobenzene
[d] Solvent mixture (acetonitrile 54% v/v, diethyl carbonate 39% v/v, oleic acid 7% v/v) representing Butyronitrile
[e] Solvent mixture (acetonitrile 60% v/v, cyclohexane 25% v/v, acetophenone 15% v/v) representing 2-Nitropropane
[f] Solvent mixture (glycerol 50% v/v, isobutyl alcohol 40% v/v, 1,4 Dioxane 10% v/v) representing 1,3 Butanediol
[g] Bad solvent within the Hansen sphere
[h] Score 1: good solvents
Score 0: bad solvents

$$\delta_{D2} = \sum(\delta_{Di} * [\eta]_i) / \sum[\eta]_i \quad (6)$$

$$\delta_{P2} = \sum(\delta_{Pi} * [\eta]_i) / \sum[\eta]_i \quad (7)$$

$$\delta_{H2} = \sum(\delta_{Hi} * [\eta]_i) / \sum[\eta]_i \quad (8)$$

The members on the left side of each equation represents dispersion, polar and hydrogen bonding forces respectively; the subscript 2 represents the solute. On the right side of each equation is, as appropriate, weighted averaging of the component of the force of attraction according to normalized intrinsic viscosity ($[\eta]_i$); the subscript i represents the solvent.

2.3.1. Determination of Hansen solubility parameters using the intrinsic viscosity method

To determine the HSPs using the intrinsic viscosity method, 7 solvents were chosen with the criterion of expanding the exploration zone for the calculation of the HSPs of sugarcane oil. Among them were: isopropanol, 1,4 Dioxane, Ethyl acetate, 1 Decanol, 1 Octanol, 2- Methyl -2- Butanol and o-Xylene.

To calculate the intrinsic viscosity, sugarcane oil solutions were prepared for each solvent chosen from 10; 15; 20; 25; 30 kg / m^3. A ubbelohde viscometer was used to measure the relative viscosity (η_{re}) for each concentration. Each measurement was performed in triplicate while maintaining a temperature of 25 ^{0}C (Stanciu I, 2009).

A linear regression of the inherent viscosity was adjusted against the concentrations, where the intercept is the value of the intrinsic viscosity:

$$\eta_{inh} = \frac{\ln \eta_r}{c} \quad (9)$$

Where η_r is the reduced viscosity which was calculated by:

$$\eta_r = \eta_{re} - 1 \quad (10)$$

With the HSPs values of the solvents studied and those of the normalized intrinsic viscosity, the HSPs of the solute was estimated.

3. RESULTS AND DISCUSSION

3.1. Hansen solubility parameter determination

The HSPs obtained for sugarcane oil using HSPiP software were δ_D = 16.56 MPa$^{1/2}$, δ_P = 2.78 MPa$^{1/2}$ and δ_H = 10.54 MPa$^{1/2}$. Of all solvents analyzed, 14 were alcohols, among which 12 were aliphatic with two aromatics. For this particular case, methanol was the only one that had a RED greater than 1; other alcohols were good solvents for sugarcane wax oil. 1-decanol was the best of all the solvents analyzed. Usually, according to the international chemical safety sheet, it is used in the manufacture

of plasticizers, lubricants, surfactants and as solvent, but its use in this application requires a technical-economic feasibility analysis.

When running the HSPiP program, the HSPs of the sugarcane oil varied their values, thus slightly moving the center of the Hansen sphere in three-dimensional space according to an indicator of the program, mentioned above as the "Core". At times. when the program was run, the absolute ethanol did not fit inside the sphere, leaving it outside with a RED of 1,009, which is incorrect, since it had been classified as a good solvent. In addition, other solvents that were classified as bad remained within the sphere, including Dimethyl Formamide (Dmf), formic acid, among others, depending on where the algorithm had defined the center of the sphere.

The HSPs presented at the beginning of this section were the best fit that was achieved, with 97.9% fit, in which all the solvents classified as good were within the sphere and only formic acid, which turned out to be classified as a bad solvent was wrongly situated inside.

Of course, accuracy depends on the reliability of the data used, which is indicated by the fit of the Hansen sphere "Core" Values. According to Abbott (2013), if errors were made during sample evaluation, many solvents that do not dissolve the solute would fall inside the sphere or many that dissolve the solute would be outside. Figure 2 shows that only one solvent that does not dissolve the solute is within the sphere, which validates the reliability of the input data.

3.1.1. Fit improvement in Hansen solubility parameters

For the first fitting, the "Core" was 1.30, 1.60, 1.35. In the program it is defined that if, for the parameter analyzed, the core is greater than 1, it is possible that the adjustment was inaccurate. This tells us that the amount of solvents analyzed was not sufficient to guarantee a result with high reliability.

Table 1 shows the classification of solvents as Good and Bad. Recalculating the HSPs provided: δ_D = 16.24 $MPa^{½}$; δ_P = 3.21 $MPa^{½}$; and δ_H = 10.34 $MPa^{½}$ with a "Core" of 1.00, 0.50, 0.85, respectively. This indicates a more reliable result, although the parameter δ_D could still be investigated. The results obtained from the use of the GRG nonlinear optimization method of Microsoft Excel Workbook were 16.38, 3.10 and 10.25 for δ_D, δ_P and δ_H, respectively, not quite different from the use of HSPiP software.

Absolute ethanol was located at the limit of the Hansen solubility sphere with a RED = 0,993. this means that any mixture of ethanol-water that is used for the extraction of this oil would not be good. Absolute ethanol is produced in Cuba and is an environmentally friendly solvent capable of decreasing the plant's consumption rates and increasing extraction efficiency. If used, the technology would not change much, making it a possible substitute for 95% v / v ethanol currently used.

Table 2 compares different types of vegetable oils according to their HSPs and it is observed that absolute ethanol is only reported as a good solvent for sugar cane oil, being the only one with a RED less than 1. In order to know why this oil has a larger δ_H, an infrared spectroscopy was performed to identify its main structural groups.

Figure 1a shows the infrared spectrum of crude wax oil, which was very similar to the infrared spectrum of castor oil and pine resin (Figures 1b and 1c, respectively) (Institute of Chemistry University of Tartu, 2019). A wide band of low intensity between 3200-3650, bands between 1540-1850, 2200-3000 and signals in 1200-1420 suggest the presence carboxylic groups. This result allows us to corroborate a possibility that δ_H is influenced by the presence of carboxylic groups.

Figure 2 shows the plotted Hansen sphere using 3-D axes for sugarcane oil and solvents as shown in Table 1. Blue spheres represent good solvents and red cubes represent bad solvents. The unfilled cube with the red edges (formic acid) indicate a bad solvent that fell inside the Hansen sphere. It could be because the program needs more information for a better fit, such as the evaluation of more solvents. When running the program for different times, the HSPs values of the sugarcane oil did not vary much and reached an adjustment of 98.1%.

According to RED values, sugarcane oil is soluble in 39 of the solvents tested. For Batista *et al.*, (2015) the best solvents for the vegetable oils analyzed were n-butyl acetate, ethyl acetate and o-xylene. In the case of ethyl acetate and o-xylene, which were tested in the present study, they were good solvents, but they were not among the best. Contrary to the results obtained by Batista *et al.*, (2015), who exposed 1-decanol as a poor solvent, in the current work 1-decanol was the best solvent

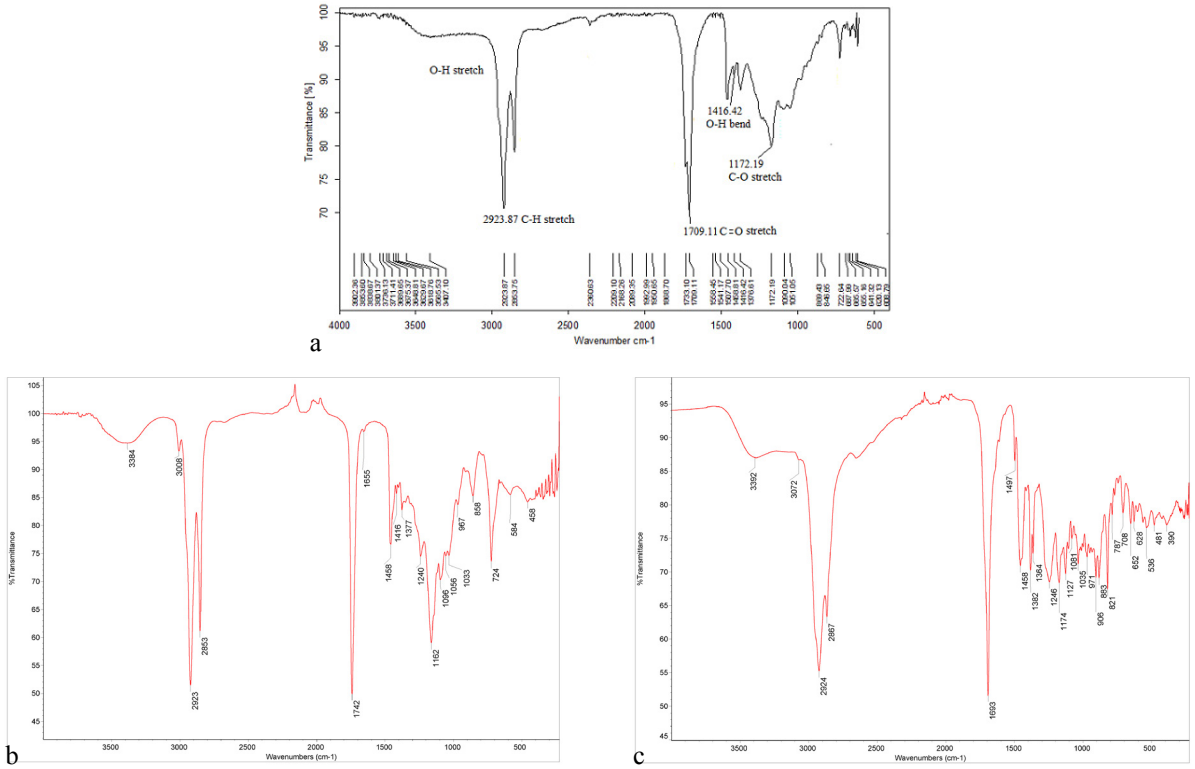
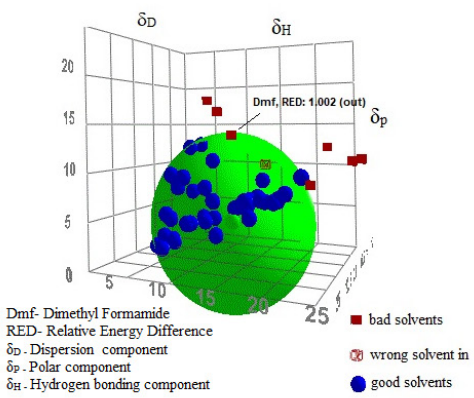


FIGURE 1.- Infrared spectra of different oils. (a) Raw sugarcane wax; (b) castor seed oil and (c) pine resin. (b) and (c) source: Institute of Chemistry University of Tartu

TABLE 2. **Parameters of different types of vegetable oils found in the literature**

Solute	Dispersion component (δ_D) MPa$^{1/2}$	Polar component (δ_P) MPa$^{1/2}$	Hydrogen bonding component (δ_H) MPa$^{1/2}$	Distance between solute-ethanol (R_a)	Hansen sphere radius (R_0)	Relative Energy Difference (RED)	References
Sugarcane oil	16.24	3.21	10.34	10.72	10.80	0.993	This work
used frying oil	15.35	3.77	6.87	13.52	9.57	1.413	Batista *et al.*, 2015
Coconut oil	14.95	4.63	6.98	13.22	9.80	1.349	Batista *et al.,* 2015
Palm oil	17.54	3.34	4.08	16.62	7.48	2.222	Batista *et al*., 2015
Soybean oil	16.50	2.00	2.70	18.08	NR	NR	De la Peña *et al.,* 2016
Canola oil	16.50	2.10	2.60	18.14	NR	NR	De la Peña *et al.,* 2016
Coconut oil	16.20	2.50	2.80	17.77	NR	NR	De la Peña *et al*., 2016
Cocoa butter	16.20	2.10	2.20	18.47	NR	NR	De la Peña *et al*., 2016
Soybean oil (tgas + glycerol)	16.80	1.90	9.60	12.15	NR	NR	De la Peña *et al*., 2016
Canola oil (tgas + glycerol)	16.80	1.90	9.60	12.15	NR	NR	De la Peña *et al*., 2016
Coconut oil (tgas + glycerol)	16.40	2.30	11.40	10.37	NR	NR	De la Peña *et al.,* 2016
Cocoa butter (tgas + lycerol)	16.50	1.90	9.50	12.14	NR	NR	De la Peña *et al*., 2016
Pine oil	15.60	3.00	9.80	11.22	NR	NR	Hansen, 2007
Olive oil	15.90	1.20	5.40	15.93	12.00	1.328	Hansen, 2007
Castor oil	15.90	4.60	12.00	8.51	NR	NR	Hansen, 2007
Palm oil	17.70	3.50	3.70	17.00	4.70	3.617	Hansen, 2007
Linseed oil	14.17	3.65	3.65	16.89	NR	NR	Burke, 1984
Cottonseed oil	15.14	3.39	4.07	16.31	NR	NR	Burke, 1984

NR Not reported



Solvent	Score[g]	Solvent	Score[g]	Solvent	Score[g]	Solvent	Score[g]
1-Decanol	1	Dichloromethane	1	Ethylene Dichloride	1	Dimethyl Formamide	0
1-Octanol	1	Chloroform	1	Formic Acid[f]	0	Octane	0
Ethylene Glycol Monobutyl Ether	1	1-Butanol	1	So Mix[b]	1	Heptane	0
		Trichloroethylene	1	Pyridine	1	Hexane	0
1,4-Dioxane	1	Benzyl Alcohol	1	Cyclopentane	1	So Mix[a]	0
1-Hexanol	1	Isobutyl Alcohol	1	Toluene	1	2,2,4-Trimethylpentane	0
Tetrahydrofuran	1	Acetic Acid	1	Benzene	1	Isopentane	0
Isoamyl Acetate	1	2-Propanol	1	Acetophenone	1	Dimethyl Sulfoxide	0
Ethyl Acetate	1	Diethyl Ether	1	Ethanol	1	Methanol	0
Cyclohexanol	1	Diethyl Carbonate	1	Cyclohexane	1	Acetonitrile	0
Oleic Acid	1	1-Propanol	1	Carbon Tetrachloride (0 Dipole Moment)	1	Ethylene Glycol	0
1-Pentanol	1	Acetone	1			Glycerol	0
2-Methyl-2-Butanol	1	o-Xylene	1	So Mix[c]	1	Water	0
2-Butanol	1	So Mix[a]	1	So Mix[d]	1		

[a] Solvent mixture (57% v/v benzene, 43% v/v pyridine) representing 1-Bromonaphthalene
[b] Solvent mixture (acetophenone 43% v/v, benzene 35% v/v, toluene 22% v/v) representing Chlorobenzene
[c] Solvent mixture (acetonitrile 54% v/v, diethyl carbonate 39% v/v, oleic acid 7% v/v) representing Butyronitrile
[d] Solvent mixture (acetonitrile 60% v/v, cyclohexane 25% v/v, acetophenone 15% v/v) representing 2-Nitropropane
[e] Solvent mixture (glycerol 50% v/v, isobutyl alcohol 40% v/v, 1,4 Dioxane 10% v/v) representing 1,3 Butanediol
[f] Bad solvent within the Hansen sphere
[g] Score 1: good solvents
Score 0: bad solvents

FIGURE 2. Hansen spheres plotted using 3-D axes for the sugarcane oil and the solvents shown in Table 1

for crude wax oil, given its similar δ_H and δ_P values. This could be due to a different composition between the oils analyzed by Batista *et al.,* (2015) and the current work, which were expressed in Hansen's parameters.

A large amount of good solvents was consistent with the R_0 calculated by the HSPiP program which adjusted R_0 = 10.7. Solvents close to RED = 1, such as benzene, cyclohexane, N, N-dimethylformamide, ethanol, carbon tetrachloride, octane, acetophenone and the Somix used to improve HSPs of sugarcane oil, are those that improved the Hansen sphere by its influence to R_0 value.

3.2. Calculation of Hansen's solubility parameters using the intrinsic viscosity method

This method was used to verify the HSPs of the sugarcane oil obtained from the solvent testing method, since no information about them was found in the literature. The results are shown in Table 3. The HSPs calculated using the intrinsic viscosity method were: δ_D = 16.16 $MPa^{½}$; δ_P = 4.44 $MPa^{½}$; and δ_H = 10.40 $MPa^{½}$. The Results obtained by this method are compared with those reported by the HSPiP software in Table 4, where it may be observed that the values calculated by both methods are similar.

TABLE 3. **Intrinsic viscosity for each solvent**

Solvent	Intrinsic viscosity $[\eta]_i$, kg /m^3	Normalized intrinsic viscosity$[\eta]_i$
Isopropanol	0.0105 ± 0.0026	0.203
1.4 Dioxane	0.0107 ± 0.0018	0.211
Ethyl Acetate	0.0034 ± 0.0041	0.065
1 decanol	0.0494 ± 0.0008	0.974
1-Octanol	0.0018 ± 0.0005	0.036
2-Methyl-2-Butanol	0.0507 ± 0.0009	1.000
o-Xylene	0.0260 ± 0.0115	0.513

TABLE 4. **Comparison of HSPs values for sugarcane oil**

Method	Dispersion component (δ_D) $MPa^{1/2}$	Polar component (δ_P) $MPa^{1/2}$	Hydrogen bonding component (δ_H) $MPa^{1/2}$
Hansen	16.24	3.21	10.34
Intrinsic viscosity	16.16	4.44	10.40

In the intrinsic viscosity method, some inaccuracies in the results may arise due to the choice of solvents for the study, more in this case, where the HSPs of sugarcane oil were unknown; but the result obtained through the method of Intrinsic viscosity strengthens the one obtained using Hansen's Solubility Theory.

4. CONCLUSIONS

According to the crude wax oil, the HSPs obtained in this work indicated that absolute ethanol could be used as a solvent for its extraction. Although it is not the best solvent, it has the advantages of being of national production, environmentally-friendly with very low toxicity. The good solvents determined in this work must be evaluated from the economic point of view. Sugarcane oil HSPs resulting from the analysis are: δ_D = 16.24 $MPa^{1/2}$; δ_P = 3.21 $MPa^{1/2}$: δ_H = 10.34 $MPa^{1/2}$.

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