The Impact of Co-Solvents on the Extraction of Castor Oil from Castor Seeds

Zinhle Innocentia Mkhize[1], Peterson Thokozani Ngema[1], Suresh Ramsuroop[2]

Abstract**–**The study was conducted to evaluate the potential use of green co-solvents in the extraction of castor oil. The objective was to evaluate environmentally friendly co-solvents, the solubility of the castor oil in the co-solvents and propose an inexpensive extraction method. For this study, three co-solvents were used for the extraction of castor oil from castor seeds, which include d-limonene-ethanol, α-pinene-ethanol and p-cymene-ethanol at different ratios. A Soxhlet extractor was used for the extraction. The separation mixture was conducted using simple distillation. The thermodynamic data obtained from this study, can be used to size, design, and optimize extraction processes. The residual castor oil was investigated for physicochemical parameters to check the quality of the oil. It was found that, the addition of co-solvent increases the mixture density and the solubility of two immiscible liquid reactants, which can reduce the mass-transfer resistances between boundary layer of both reactants. Consequently, the mixture of p-cymene-ethanol solvent mixture produced the highest yield of 43.29% for the extraction time of two hours.

Keywords**–**Co-solvents; Castor Oil, Castor Seeds; Soxhlet Extractor

I. INTRODUCTION

The castor plant of the Euphorbiaceous family, formally known as Ricinus communis is a flowering plant that is of African nativity, it has been distributed to tropical, subtropical, and temperate regions around the globe through cultivation [1]–[3]. The castor plant has many variations when growing it can have a long stem or it will have a dwarf stem, depending on the area it is grown [2], [4]. The castor seeds contain an oil content of about 35% to 60 %, this is dependent on the variety of the seeds and the environment in which it was grown [5], [6]. The castor seeds oil content was reported to vary in yield according to the geographic area where they were grown, furthermore, the oil content of castor seeds was reported to be between 40 and 55% [7]. Castor oil extracted from castor seeds was reported to be a non-drying oil that is pale yellow in colour, viscous, non-edible and non-volatile [8], [9]. Castor seeds reportedly contain 80 to 90% of ricinoleic acid, which makes the viscosity to be 7 times higher than the other vegetable oils [7]. The water content in castor oil is reported to be higher than what is observed in other vegetable oils as the castor oil is said to be hygroscopic [10].

The castor seeds that contain special oil are the product of the castor plant. This plant varies in terms of its growth and appearance, which depends on geographic area. The castor different varieties differ in resemblance from one another as shown in Figure 1 [11]. For more details refer to the literature [9]. With the growing human population and industrialization, there has been a significant depletion of fossil fuel reserves and an increase in petroleum prices which has caused researchers to look for alternative fuel sources [1], [6], [12]–[19].

Castor oil is an excellent raw material in terms of price and quality, but especially this non-edible vegetable oil does not have any issues or compromise food security [20]. Recently, the use of castor oil has attracted attention for producing and optimizing biodiesel production, due to its high content of ricinoleic fatty acid and the possibility to esterify with only methanol, which assures low production costs [20], [21]. This study is focused on extracting castor oil using green solvents. A study of green of green solvents are reflected on publication [9], [19], [22]–[25]. The benefits of green solvents, several physicochemical properties, techniques for extraction of castor oil and Soxhlet extraction are detailed in literature [9], [19], [26]–[33].

In this study, the impact of co-solvents on the extraction of castor oil from castor seeds using potential green solvents obtained from [9] and [19], were investigated. The co-solvents were prepared from the selected green solvents: d-limonene; α-pinene; p-cymene; and ethanol. Ethanol was observed to produce a higher yield of castor oil even when the system was manipulated where the time of extraction was either increased or decreased, together with various temperature changes [9]. Therefore, it was selected as the primary solvent in the co-solvent mixture. The volume ratios of 1:2, 2:1 and 2:2 were measured for each solvent which would then be used as co-solvent mixtures. The experiments were conducted at atmospheric pressure and the temperature of 353.15 K at an extraction time of 2 hours. The castor oil yield was calculated using the weights or mass of crushed castor seeds before and after extraction. The separation of the solvent-oil mixture was carried out with a simple distillation, where co-solvents and castor oil were recovered, respectively. Further, the physical properties of the castor oil produced were measured to determine the stream purities and to check if any has reaction taken place during extraction.

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II. Experimental Procedure

A. *Materials*

Table 1 presents detailed information on the supplier and purities of the selected green solvents including hexane used in this investigation. Prior to utilising the green solvents, the DMA 4100 M refractometer from Anton Paar, which has an accuracy of ± 0.0002 nD was used to measure the density and refractive index. The measurements were conducted at 293.15 K and compared with literature values as presented in Table 2, this was used to validate that there is no contamination in the selected green solvents. Castor seeds were cleaned of debris and stones. Castor seeds were crashed using the mortar and pestle to deshell. The seeds were first deshelled by pressing the seeds until the covering popped open exposing the soft inside of the seeds as shown in Figures 2(a) to 2(d). The crushed deshelled seeds were then dried in an oven at 348.15 K for 18 hours to remove moisture. The size distribution was not taken into consideration because it was not an objective of this study. After 18 hours the crushed castor seeds were further air-dried for 48 hours at a temperature of 293.15 K before using them. An analytical mass balance (Ohaus Adventurer balance, model No. AV 114) which was calibrated by the supplier with the stated manufacturing uncertainty of ±0.0001 g in mass was used to measure the weight before and after the experiment.

B. Apparatus and Experimental method

The schematic diagram of the experimental setup, the Soxhlet apparatus used in this study and experimental procedure or method of Soxhlet extractor are detailed described and presented in the literature [9], [19]. The Physical properties measured using equipment specified in literature [9], [19].

Castor oil recovery: the amount of castor oil produced to the amount of dry castor seeds that were used can be defined as the yield, the yield is calculated by calculating the weight of dry castor seeds before the extraction and comparing the weight of castor seeds after extraction and drying has taken place. The yield (Y) was calculated using Equation 1 [9], [34]

$$\%Yield = \frac{y_1 - y_2}{y_1}(100) \quad (1)$$

where y_1 is the weight of the castor seeds before extraction (kg), and y_2 is the weight of the seeds weight (kg) after extraction. The process of separating the co-solvents-oil mixture collected in the round bottom flask was carried out using a simple distillation unit. For more details refer to publication [9], [19]. The recovered oil was analysed to determine purity and relevant properties. The liquid in the still was a pale-yellow extracted castor oil, which is the same as mentioned in the publication [8], [11].

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III. Results and Discussion

The selected green solvents were checked for purity before the experiment to ensure that there was no contaminant. The test system for hexane was conducted to validate the procedure and reproducibility of the existing data of hexane measured by [34]. The absolute average deviation was calculated in Equation 2 and the results are presented in Table 3.

$$AAD = \left|\frac{P_{lit} - P_{meas}}{P_{lit}}\right| \quad (2)$$

Co-solvents were prepared by adding to a primary solvent in small amounts to help increase the solubility of a poorly soluble substance (solvent). The addition of co-solvent increases the mixture density and the solubility of two immiscible liquid reactants (e.g., oil and methanol), which can reduce the mass-transfer resistances between the boundary layer of both reactants. The researcher [35], reported that the value of the solubility parameter of solvents may decrease and become closer to that of vegetable oil if proper temperature and pressure conditions are employed.

In this study the green solvents that were used (d-limonene, *p*-cymene, ethanol, and α-pinene) for the extraction of castor oil. The volume ratios of 1:2, 2:1, and 2:2 were measured for each solvent which would then be used as co-solvent mixtures. The authors [9] and [19] found that ethanol produces a higher yield of castor oil even when the time of extraction was either increased or decreased, together with various temperature changes. Therefore, it was selected as the primary solvent in the co-solvent mixture. The co-solvent mixtures were prepared as follows: p-cymene-ethanol; α-pinene-ethanol and d-limonene-ethanol at the specified volume at a constant temperature of 353.15 K and the extraction period of 2 hours. Table 4 presents castor oil yield obtained at various ratios at the specified conditions. The increase of ethanol does not have a significant effect on the castor oil yield, except for the mixture of d-limonene-ethanol which shows low yield. The mixture of *p*-cymene-ethanol solvent mixture produced the highest yield of 43.29%. Figure 5 to 7 presents the extracted castor oil yield at the specified condition. Castor oil extracted from caster seeds was viscous, pale yellow, non-drying and non-volatile drying oil, which is confirmed in the literature [8]. Table 5 presents the measured physical properties of produced castor oil at the temperature of 298.15 K after removing the solvents. The physical properties results show that it is pure castor oil obtained and there are no traces of any solvent. The measured data of castor oil were compared to the literature data [36], [40], [41]. The absolute error was calculated using Equation 3, it is an acceptable error.

$$Absolute\ error = |P_{lit} - P_{meas}| \quad (3)$$

IV. Conclusions

Selected co-solvents of green solvents, which include d-limonene, p-cymene, α-pinene and ethanol were evaluated at different ratios. Based on the study published by [9], [19], ethanol was chosen as the primary solvent because it was the one found to produce a high yield compared to others. The selected co-solvents were environmentally friendly, not harmful, and not expensive and the mixture gave the best yield of castor oil. It was found that the p-cymene-ethanol mixture provides the highest yield compared to other co-

solvent mixtures at the mentioned ratios. The castor oil was produced by separating co-solvents using simple distillation. The p-cymene-ethanol co-solvents show a positive impact on producing a higher yield of castor oil at the ratio of 1:2.

V. ACKNOWLEDGEMENTS

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TABLE I
THE SELECTED GREEN SOLVENTS USED IN THIS INVESTIGATION

Solvent	Chemical formula	Molecular weight (g/mol)	Purity (%)	Boiling points (°C)	Supplier
Limonene	$C_{10}H_{16}$	136.24	97	176.00	Merck
Ethanol	C_2H_5OH	46.07	99	78.37	Merck
p-Cymene	$C_{10}H_{14}$	134.21	99	177.00	Merck
α-Pinene	$C_{10}H_{16}$	134.21	98	156.00	Merck
Hexane	C_6H_{14}	86.81	99	69.10	Merck

TABLE II
PHYSICAL PROPERTIES OF THE SELECTED GREEN SOLVENT

Solvent	This study Refra-ctive index (nD)	Literature Refractive index (nD)	This study density (kg/m^3)	Literature density (kg/m^3)
Ethanol	1.3661	[a]1.3614	789.42	[a]789.47
Limonene	1.4723	[b]1.4701	838.41	[d]838.35
p-Cymene	1.4926	[c]1.4912	857.58	[c]857.38
α-Pinene	1.4626	[c]1.4631	858.63	[c]858.10

[a][37]; [b][38]; [c][39]; [d][40]

TABLE III
TEST SYSTEM USING HEXANE AS SOLVENT

Temperature (K)	Time (hours)	Literature (%) [42]	Measured (%)	AAD
329.15	2	31.99	31.36	0.019
333.15	3	33.44	33.67	0.007

TABLE IV
CASTOR OIL YIELD OBTAINED AT DIFFERENT RATIOS

Co-solvent	1:2	2:1	2:2
d-limonene-ethanol	34.80	33.06	33.96
α-pinene-ethanol	41.09	38.86	40.33
p-cymene-ethanol	43.29	42.63	42.98

TABLE V
MEASURED PROPERTIES OF CASTOR OIL PRODUCED

Parameter	Literature	This study	Units	Absolute Error
Refractive index	[a]1.4764	1.4761	nD	0.0003
Density	[b]958.00	958.12	kg/m^3	0.12
Viscosity	[a]9.307	9.390	Pa.s	0.08

[a][36,40];[b][41]

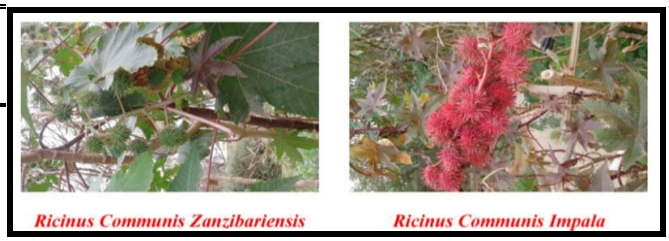

Fig. 1 Different types of castor plant [11]


Fig. 2(a) The castor seed before being processed


Fig. 2(b) Crushed castor seeds before extraction and drying


Fig. 2(c) Crushed castor seed after drying before extraction


Fig. 2(d) Crushed castor seed after solvent extraction and drying

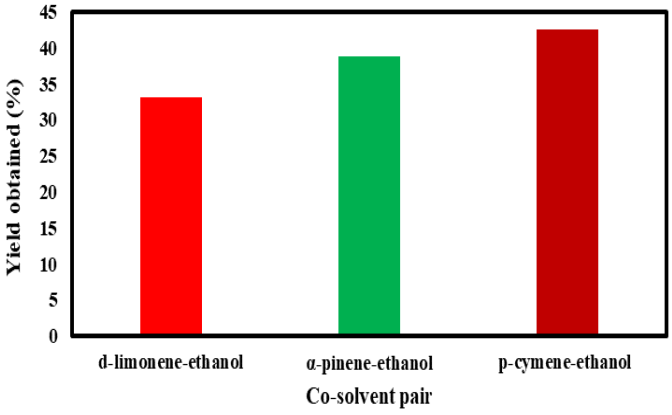

Fig. 5 Co-solvents mixtures at a volume ratio of 1:2

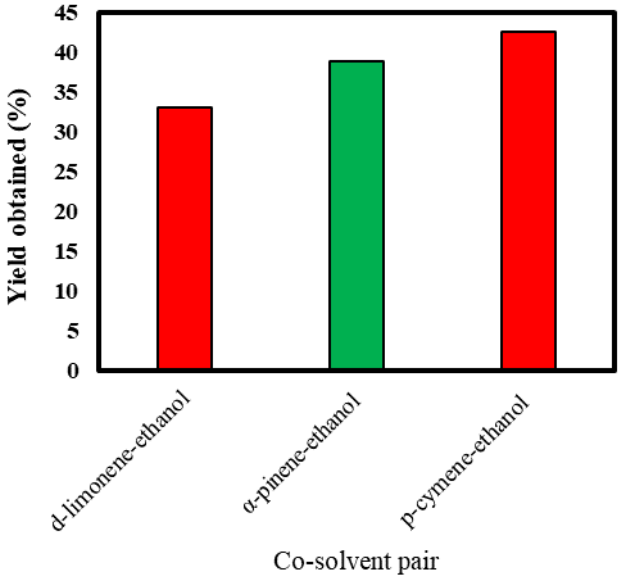

Fig. 6 Co-solvents mixtures at a volume ratio of 2:1

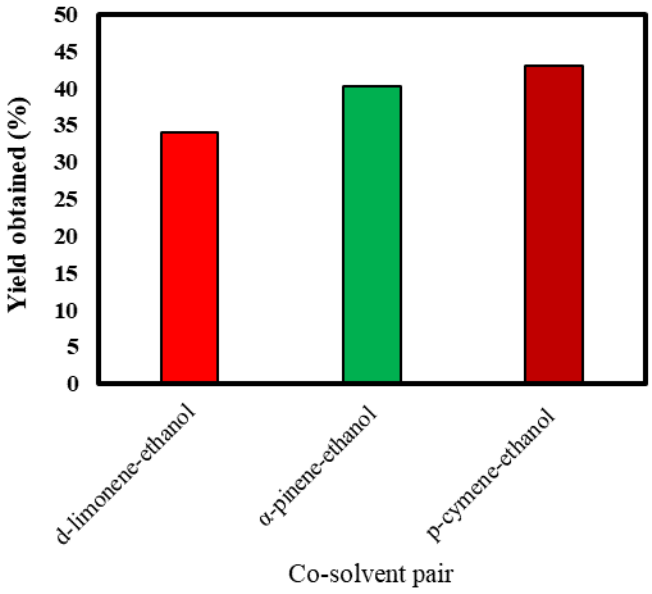

Fig. 7 Co-solvents mixtures at a volume ratio of 2:2

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