



SOLVENTS AND CO-SOLVENTS SELECTION FOR THE EXTRACTION OF CASTOR OIL FROM CASTOR SEEDS

By

**Zinhle Innocentia Mkhize
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Supervisor: Dr. P.T Ngema

Co-Supervisor: Prof. S Ramsuroop

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Technology**

As the Candidate's Supervisor/Co-supervisor I agree to the submission of this thesis.

15/01/23

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DECLARATION

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Date

DEDICATION

I would like to dedicate this work to my late mother and father who made it possible for me to pursue my dreams; your efforts and support made it possible for me to see this through. To my sister Phindile, you took over from mom and dad and gave me strength in when there seemed to be no light thank you. To my partner M.J. good to know you have my back.

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Abstract

There has been a notable demand increase in the manufacturing market globally for castor oil and the products derived from castor oil. Castor oil consists of almost 90% of ricinoleic fatty acid, and it is nearly a pure compound. Castor oil is renewable and naturally occurring. It is known to have multiple uses, and the derivatives are known to be used in the manufacturing of paints, soaps, and perfumes and used in the pharmaceutical industry. The chemical industrial extracts castor oil from castor seed using hexane as solvent. However, there are growing concerns around the use of petrochemical derived solvents, volatile organic compounds (VOC) emissions and use of non-renewable resources which impact the environment negatively.

This study is aimed to evaluate and find the best green solvent to extract castor oil with the highest yield and easiest recovery. Green solvents are derived from renewable resources and have minimal or no impact on the environment. The investigated green solvents were alpha-pinene, *p*-cymene, limonene, ethanol, and furfural, these solvents were also used as co-solvents. The Soxhlet extraction method was employed to investigate different green solvents. Hexane was used as a reference.

It was found that green solvent extraction capabilities or yield can be ranked as follows: furfural is 47.13%, ethanol is 45.37%, limonene is 39.15%, *p*-cymene is 39.15% and α -pinene is 38.11%. For the co-solvent mixtures, d-limonene-ethanol is 34.80%, α -pinene-ethanol is 41.09% and *p*-cymene-ethanol is 43.29%. Whilst furfural had the highest yield from the extraction, the furfural recovery process proved to be challenging. The oil and solvent mixture were separated by simple distillation, this process recovered the solvent used by separating the oil from the solvent. Ethanol was discovered to be the next best solvent for extraction as it had a yield of 45.37%, it was easily recovered after the extraction. The yield for ethanol was achieved in a period of 2 hours, whereas that of furfural was recorded at a period of 5 hours. Ethanol produced a satisfying yield at a shorter time frame than Furfural. Hexane recorded a percentage yield of 31.36% for a period of 3 hours and 30 minutes. Percentage yields of 33.4% and 31.99% were reported in literature, and they were reported to have been obtained in a period of 6 hours, this was explained to have been a result of extraction temperature, extraction time and polarity of the solvent among other factors.

The physical properties of the recovered solvents were measured and compared with that of pure solvents. The data for the best solvent was used to design a suitable extraction column. Finally, the economic feasibility was conducted for the extraction process. It was recommended that one use the data to upscale and design all other process equipment. One is recommended to investigate the challenges of recovering furfural solvent.

TABLE OF CONTENT

Abstract	v
LIST OF FIGURES	x
LIST OF TABLES	xii
CHAPTER 1	1
Introduction	1
CHAPTER 2	6
Literature Review	6
2.1 Introduction.....	6
2.1.1 Castor plant (<i>Ricinus communis</i>)	7
2.1.2 Genetics of plant.....	8
2.1.3 Description of castor plant.....	10
2.1.4 Castor plant breeding.....	11
2.1.5 Properties of castor seeds.....	12
2.1.6 Castor seeds agronomy.....	17
2.1.7 The benefits of castor oil.....	19
2.2 Traditional solvent.....	21
2.3 Green solvents.....	21
2.4 The extraction of castor oil.....	25
2.4.1 Traditional extraction.....	25
2.4.2 Solvent extraction.....	26
2.4.3 Conventional extraction.....	27
2.4.4 Soxhlet extraction.....	28
2.5 Parameter affect the extraction.....	30
2.6 Selected green solvents.....	32
2.7 Extraction of oil using n-hexane as solvent.....	39
2.8 Physical characterization.....	44
2.8.1 Yield.....	45
2.8.2 Refractive Index.....	45
2.9 Market demand for the castor oil.....	44

CHAPTER 3	48
Materials and Methods	48
3.1 The Soxhlet extractor.....	48
3.2 Experimental procedure.....	55
3.3 Operation procedure.....	56
3.4 The recovery of solvent and oil.....	57
3.5 Characterization of castor oil.....	58
3.6 Safety in the laboratory.....	61
CHAPTER 4	63
Results and Discussions	63
4.1 Introduction.....	63
4.2 Green solvents.....	64
4.3 Hexane test system.....	65
4.4 The effect of solvent type on the extraction of castor oil yield.....	66
4.4.1 The effect of time on the castor oil yield.....	68
4.4.2 The effect of temperature on the castor oil yield.....	76
4.5 Castor oil produced.....	85
4.6 Green solvents recovery after castor oil extracted.....	87
4.7 Moisture content of castor seeds.....	88
4.8 Production of castor oil using co-solvents.....	88
4.9 Scaling up the castor oil production to meet industry expectations.....	90
CHAPTER 5	91
Design of extraction column and economic study	91
5.1 Solid-liquid extraction column design.....	91
5.2 Preliminary economic study.....	92
CHAPTER 6	94
Conclusions and Recommendations	94
6.1 Conclusions.....	94
6.2 Recommendations.....	95
REFERENCES	96
APPENDIX A: Sample calculation	111

APPENDIX B: Sale estimation..... 113
APPENDIX C: Extraction column design..... 115

LIST OF FIGURES

Figure 2.1	Different types of castor plant.....	10
Figure 2.2	Biological image of the castor seed.....	13
Figure 2.3	Structure of the major component in castor seed ricinoleic acid and structure of castor oil.....	13
Figure 2.4	Toxic protein Ricinus found in castor seeds.....	14
Figure 2.5	Reaction points in the molecule of ricinoleic acid.....	15
Figure 2.6	Viscosity versus temperature.....	16
Figure 2.7	World production of castor seeds as at 2004.....	19
Figure 2.8	World production as at 2010.....	19
Figure 2.9	Schematic flow diagram of process of oil extraction using green solvents.....	27
Figure 2.10	Schematic diagram of the process of the solvent extraction	28
Figure 2.11	A diagram of the Soxhlet extractor.....	29
Figure 2.12	Effect of time on extraction.....	31
Figure 2.13	Depicting the effect of time on extraction.....	32
Figure 2.14	Chemical structure of d-limonene.....	33
Figure 2.15	Chemical structure of p-cymene.....	34
Figure 2.16	Chemical structure of ethanol.....	35
Figure 2.17	α -pinene chemical structure.....	37
Figure 2.18	Graph of performance of α -pinene to hexane.....	38
Figure 2.19	Physiochemical properties of various solvents and extracts.....	39
Figure 2.20	Furfural structure.....	40
Figure 2.21	A process flow of the refining of castor oil.....	43
Figure 2.22	A schematic representation of the refining process.....	44
Figure 2.23	A depiction of the uses of castor oil and the derivatives of castor oil in industry.....	46
Figure 2.24	Global castor oil and it's derivatives by application.....	47
Figure 3.1	An assembled Soxhlet extractor.....	50
Figure 3.2	The digital heating mantle.....	52

Figure 3.3	The cold-water bath/chiller.....	52
Figure 3.4	The distillation unit apparatus that was used to recover the solvent.....	53
Figure 3.5	The castor seed before being processed.....	55
Figure 3.6	Crushed castor seeds before extraction and drying.....	55
Figure 3.7	Crushed castor seed after drying before extraction.....	55
Figure 3.8	Crushed castor seed after solvent extraction and drying.....	55
Figure 3.9	Sample of oil extracted using α -pinene and d-limonene.....	57
Figure 3.10	Anton Paar DMA 4100 M refractometer with density meter.....	58
Figure 3.11	Anton Paar oscillation U-tube DSA 5000 M.....	60
Figure 4.1	A depiction of the castor oil yield obtained per solvent used.....	67
Figure 4.2	Graph depicting the castor oil yield obtained over time when d-limonene was used as solvent.....	69
Figure 4.3	Graph showing castor oil yield obtained using ethanol as the solvent.....	70
Figure 4.4	Graph of castor oil yield obtained when using α -pinene as the solvent....	71
Figure 4.5	Graph showing castor oil yield obtained when using <i>p</i> -cymene as the solvent.....	72
Figure 4.6	Graph showing castor oil yield obtained when using furfural as a solvent	73
Figure 4.7	Graph showing the effect of temperature on yield using ethanol as solvent.....	75
Figure 4.8	Graph showing the effect of temperature on the oil yield using furfural	76
Figure 4.9	Graph showing the effect of temperature on oil yield using d-limonene as solvent.....	77
Figure 4.10	Graph showing the effect of temperature on oil yield using <i>p</i> -cymene as solvent.....	78
Figure 4.11	Graph showing the effect of temperature on oil yield when α -pinene is used.....	79
Figure 4.12	Samples of extracted castor oil from green solvent.....	80
Figure 4.13	Co-solvents mixtures on yield of castor oil yield.....	84
Figure 5.1	Castor oil extraction process flow diagram.....	87

LIST OF TABLES

Table 2.1	Gene banks and number of accessions.....	9
Table 2.2	Physical properties of castor oil.....	16
Table 2.3	Fatty acid composition of castor oil.....	17
Table 3.1	Solvents used.....	54
Table 3.1	Measured refractive index of water.....	59
Table 3.2	Calibration of Anton Paar oscillation U-tube DSA 5000 M using double distilled water at 298 K.....	61
Table 4.1	Refractive index of green solvents.....	64
Table 4.2	Densities of green solvents used.....	65
Table 4.3	Castor oil yield obtained using hexane.....	66
Table 4.4	Castor oil yield per solvent used.....	67
Table 4.5	Optimum conditions for highest castor oil yield.....	80
Table 4.6	Physical properties of castor oil produced.....	82
Table 4.7	Castor oil produced.....	82
Table 4.8	Physical properties of the recovered green solvent.....	83
Table 4.9	Castor oil yield obtained per co-solvent mixture.....	85
Table C.1	Extraction unit design.....	111

CHAPTER 1

Introduction

An increase in population and industrialization processes over the past decades saw a permanent increase in the consumption of petroleum-based fuel (Banković-Ilić, Stamenković and Veljković 2012). This has led to fossil fuel reserves being depleted and petroleum prices have been on a rise. Non-edible oils have become the main raw material in the production of biofuels, medicine, lubricants, and paint coating among others (Patel *et al.* 2016). There is however competition for human consumption in the edible oils which makes it unideal to use edible oils for fuel (Gui, Lee and Bhatia 2008).

In the past years, the global production of vegetable oils has had constant growth. From year 2007, the annual vegetable oil production had increased by approximately 5%, the growth slowed down between the years 2012 and 2013. During the years 2016 and 2017, about 185.78 million metric tons of coconut, cottonseed, olive, palm, palm kernel, peanut, rapeseed, soybean, and sunflower seed oils were produced all over the world was a 6.28% raise (Statista 2022). With the growing interest in renewable energy sources; liquid bioenergy production from vegetable oils, is reported to be one of the possible options to reduce greenhouse gas (GHG) emissions (Bhuiya *et al.* 2016).

The castor plant of the Euphorbiaceous family known as *Ricinus communis*, has gained popularity amongst researchers because of the non-edible and renewable properties. It is a raw material in many industrial processes. *Ricinus communis* of the Euphorbiaceous family is a perineal oil crop seed that is grown in warm temperate regions (Koutroubas, Papakosta and Doitsinis 1999). *Ricinus communis* is an old, cultivated crop of the spurge family, which represents about 0.15% of the vegetable oil produced in the world (Severino *et al.* 2012; Yeboah *et al.* 2020). The castor plant is believed to be native to Africa, but through cultivation it has been distributed not only to tropical and subtropical regions but also many of the temperate countries of the globe. The castor plant can grow well at a fast rate, if situated in full sunlight and provided with ample fertilizer and water (Salihu, Gana and Apuyor 2014a).

Castor production worldwide is above 1.3 million tons per year. India being the major producer with a production of over 60%, China and Brazil produce 20% and 10% respectively (Belaid *et al.* 2011). West Indies and some regions of Africa produce small amounts of castor beans. India largely dominates the market as 80% of castor oil exported from there. The castor oil seed production of South Africa increased from 4000 tonnes since 1971 to 6476 tonnes in 2020 growing at an average annual rate of 1.14%, the price of castor oil was reported to have steadily on the rise since 2002 to 2003, from a price of \$946 per ton to \$2390 (Nekhavambe, Mukaya and Nkazi 2019). Mubofu (2016), predicted that the increase in the market would have reached \$1.18 billion by the year 2020.

Castor oil holds importance in its commercial value in the pharmaceutical, lubricant, paint, perfume, and coatings industry, therefore there is a need to extract larger quantities of castor oil. Conventionally castor oil has been extracted through mechanical means mainly hydraulic pressing, expeller pressing and solvent extraction. Solvent extraction has been adapted for economical and practical reasons as it is able to extract the oil that is left after pressing (Kumar *et al.* 2017). The castor oil extraction process not only produces castor oil but also a by-product which is high in ricin protein. The castor meal which can be used as an organic fertilizer or feed for animals though it needs to be treated to lower the ricin content before giving it to animals (Lima *et al.* 2011; de Andrade *et al.* 2019). There is a global demand of about 200 000 tons per year which is continually increasing, as oilseeds are important nutritional security for the global population (Perdomo *et al.* 2013).

Problem statement

The extraction process is the first step in separating the castor oil from castor seeds. The extraction process includes mechanical pressing, solvent extraction, distillation, and sublimation according to the extraction principle (Zhang, Lin and Ye 2018). The extraction of castor oil goes through the mechanical pressing, the oil that is left after the extraction is taken through the solvent extraction process. The solvent extraction process is carried out to extract oil that is left after the mechanical extraction of oil from castor seeds has been carried out. Conventionally solvent extraction is carried out using volatile organic compounds that are sourced from non-renewable resources. Hexane has been a solvent of choice for the extraction of most the oil seeds because of its ability to produce great yields of vegetable oil (castor oil). It has solubilizing abilities and low boiling

temperature(63–69 °C) (Liu and Mamidipally 2005). During the extraction and recovery processes, hexane is released into the environment and this forms ozone and photo chemicals (Hanmoungjai, Pyle and Niranjana 2000). Studies have revealed that hexane has an effect on neural system when inhaled by humans because of its solubility in neural lipids (Kumar *et al.* 2017). There is great concern for human health and the environment, therefore there is a need to substitute hexane without compromising the yield of oil. With the increasing concern of fossil fuel depletion and petroleum pricing rapidly rising, alternative fuel sources and environmentally friendly ways to obtain these fuel sources is needed. Consequently, a study of green solvents on the extraction of castor oil is something that will pave a way into finding potential alternatives to solvents that are cheaper and less harmful, while giving optimum castor oil yields.

Research aims and objectives

The aim of this research was to find a suitable green solvent or co-solvent for the extraction of castor oil to replace hexane.

The objectives were as follows:

- ✓ Evaluating the potential solvents that are environmentally friendly, not harmful, and not expensive and give the best yield of castor oil.
- ✓ To size or design an extraction column to produce castor oil.
- ✓ To evaluate an economical design for the extraction process to produce oil from the seeds.

The research questions

- ✓ Which green solvent and co-solvent mixture will give the best yield of castor oil, and will be recovered with ease?
- ✓ What process parameters (temperature, extraction time and solvent type) will favour the yield of oil, and what effect will it have on the quality of the oil?
- ✓ What process parameters will give optimal conditions for the yield?
- ✓ Are terpene-based solvents better at extracting castor oil than the alcohol-based solvents, will their boiling temperatures influence which solvent performs better?

The significance of the study

This study is conducted to extract castor oil using green solvents that are produced from natural biomass that are specifically terpenes and alcohol based, to see which solvent produces oil yield that is the same if not more in yield than the hexane. This is to ensure that hexane can be replaced as a solvent of choice for the extraction of vegetable oils. Most of the studies that have been carried there were more focused extraction using either limonene, hexane, or ethanol, no studies were found for the extraction of castor oil using furfural, p-cymene or alpha-pinene. Studies found were for other vegetable oils (e.g., Date-palm seed) this research seeks to broaden the study of extraction of castor oil using different types of terpenes at a range of temperatures to find the best solvent to extract castor oil from the castor seeds. This study seeks to open a path to finding solutions for the current crisis of energy and fuel shortage by finding a suitable solvent for castor oil extraction and address the effects on the environment that current organic solvents such formation of greenhouse gases and the ozone layer depletion.

Delineation of the study

The scope of this research was limited to the investigation of the effect of solvent type on the yield of oil castor seed oil, the effect of temperature on the yield of oil and the time of extraction on the yield of oil. There was no catalyst used, the size of the crushed castor seeds was not considered, and heating rate was also not considered.

Structure of the thesis

The research presented in this thesis was conducted at the Thermodynamics labs at Durban University of Technology at the Steve Biko campus, Durban in South Africa. The thesis was compiled such that it consists of seven chapters.

Chapter 1- This chapter presents the introduction which describes the conceptual basis of the study, the problem statement, the research aim, objectives, and questions or hypothesis. The significance and delineation of the study is also described in this section.

Chapter 2- In this chapter a comprehensive literature review on the history of energy and fuel sources, with the growing population, how it came about that vegetable oils be used as alternative fuels source. The conventional process of extraction of vegetable oils and the journey of finding potential greener alternatives to the solvents that had been used.

Chapter 3 – This chapter presents the materials, equipment and the methodology used to carry out the study.

Chapter 4 – This chapter present the results the effect of process parameters on the yield

Chapter 5- The chapter presents the design of the extraction column

Chapter 6 – Presents the preliminary economic study

Chapter 7 – Discusses the various conclusions that were made from the results presented in this thesis and recommendation on the improvements that can be made and future research work.

CHAPTER 2

Literature Review

This chapter presents a review of various literature that is the backbone of this study, the history of castor as raw material for industrial production of goods. The various ways of extracting castor oil from castor seeds and the challenges that were faced. It outlines the history of vegetable oil as an alternative fuels source and the challenges that have been faced and technologies that have been introduced to address the issue of shortage of energy, fuel and various methods that have used to improve on the yield.

2.1 Introduction

An important group of crop plants are the oilseeds, there are about 40 different oil seeds whose oil can be consumed but only a few are significant in the total world trade (Sharma, Gupta and Mondal 2012). Oil crops are planted harvested worldwide under varied agroclimatic situations and are vital commodities in the trade and commerce of many economies (Salihu, Gana and Apuyor 2014a). The global production of vegetable oil has steadily increased from approximately 90.5 million metric tons in 2000/2001 to 207.5 million metric tons in 2019/2020, these trends are expected to continue in future (Statista 2022). This increase in global production has been mainly due to rising demand for oilseed products, energy and fuel and shortage in supply (Sharma, Gupta and Mondal 2012; Gokdogan, Eryilmaz and Kadir Yesilyurt 2015).

The depletion of fossil fuel resources and the harmful effects they have on the environment are the two compelling motives that have researchers looking for alternative fuel sources (Halek, Delavari and Kavousi-rahim 2013). As much as there is a demand for alternative fuel sources, vegetable oils have been proven to be steadily providing this source of alternative fuel and energy. However, there is a competition for human consumption for the edible oils therefore non-edible renewable crops have to be used to source alternatives (Gui, Lee and Bhatia 2008).

Alternative fuel or energy derived from oilseeds and food waste, are the ones that are favoured most by researchers because of their ability to minimize air pollution and emission of greenhouse gases. These are also able to achieve reduction of dependency on fuel import, which results in reducing the overall energy cost (Halek, Delavari and Kavousi-rahim 2013). In this study the plant that has been chosen to produce vegetable oil, which is not edible, and will have minimal competition with human consumption is the castor plant which produces castor seeds that are used in the production of castor oil.

2.1.1 Castor plant (*Ricinus communis*)

Ricinus communis L. known as the castor plant is one of the major commercial non-edible oilseed crops that are grown in semi-arid and arid regions of India, China and Russia and it is reported to be drought tolerant. The castor plant is reported to have originated from Africa, though it has spread to other regions (Weiss 1971). Anjani (2012) reported that ancient Egyptian tombs dated back to 4000 BC contained castor seeds. Castor was primarily harvested by the ancient people for medical purposes. George translated The Ebers Papyrus, a 1552 BC-era medical book from ancient Egypt.

Castor oil was referred to as a purgative by Ebers in 1872. Egyptians reportedly employed castor oil for purging circa in 500 BC, according to Herodotus (Nekhavhambe, Mukaya and Nkazi 2019). During the Middle Ages, Arabs transported castor plants with enormous, fertile seeds to Southeast Asia and Africa. Castor was introduced by Europeans as a plantation crop in Caribbean Sea islands and on the American continent. In Central Asia, early growing of castor from Iran was introduced in 1921. In Madagascar, it was rumoured that seed from wild castor plants was collected for cultivation. Castor was first made available in Brazil in a study by (Weiss 2000; Salihu, Gana and Apuyor 2014b), it was reported that the castor plant is not only native to Africa being of Ethiopian origin it is also widely spread throughout the tropical, subtropical, and even warm temperate regions of the world. Anjani (2012) reported that castor was initially believed to have four centres of origin being (i) East Africa (Ethiopia), (ii) Northwest and Southwest Asia and Arabian Peninsula, (iii) India, and (iv) China. Ethiopia was the origin because of the high diversity. Moshkin (1986), reported that an ancient Egyptians collected wild castor seeds for medicinal use.

The castor plant is of the tropical spurge family (Euphorbiaceae), which is known in different parts of the world as castor bean; castor oil plant; ricin; higuerrilla; mamona; mamoeira or palma christi (Gokdogan, Eryilmaz and Kadir Yesilyurt 2015). In a study conducted by (Severino *et al.* 2012), it was reported that castor is not a legume and that researchers should avoid the use of the term “castor bean” which is frequently found in the literature of this crop. Castor oil extracted from castor seeds is nonedible and it has been used almost entirely for pharmaceutical and industrial applications.

Anjani (2012), reported that castor collections dated to many centuries ago, records in the history of castor collection and distribution can be traced to early taxonomists and botanists from former USSR between 1773 and 1976. All-Russia Research Institute of Oil Crops (VNIIMK), N.I. Vavilov Institute of Plant Industry (VIR) and Botanical Institute of the Academy of Science of the USSR (BIN) are reportedly the oldest institutes which began collecting castor genetic resources in 19th century

2.1.2 Genetics of castor plant

Germplasm conservation supports global efforts to ensure future food security by capturing natural and existing crop diversity and developing new crops for agriculture (Offord 2017). Global specimens collected and maintained at the research institutes were used to classify castor based on morphological and eco-geographical diversity. All-Russia Research Institute of Oil Crops (VNIIMK) and the N.I. Vavilov Institute of Plant Industry (VIR), introduced several samples of world collection during 1952 and 1976 to study (Moshkin 1986). Table 2-1 presents a report for the year 2011 extracted from the Food and Agriculture Organization on the State of the World’s Plant Genetic Resources for Food and Agriculture stated that 17,995 castor germplasm accessions were being held with various institutes in the world.

Table 2.1 Gene banks and number of accessions (Anjani 2012; Severino et al. 2012; Milani and Nobrega 2013)

Gene bank	Number of accessions
National Bureau of Plant genetics resources (NBPGR), India	4307
Institute of Crop Germplasm Resources, Chinese Academy of Agricultural Sciences (ICGR-CAAS), China	2111
United States Department of Agriculture - Agricultural Research Service, USA	1390
Centro Nacional de Pesquisa de Algodao (CNPQ), Brazil	1000
Vavilov Institute of Plant Industry (VIR), Russia	696
Institute of Biodiversity Conservation (IBC), Ethiopia	510
Others (52 institutes)	8699

Castor is reported to be classified as follows (Moshkin 1986; Milani and Nobrega 2013):

Super division: Spermatophyta - Seed plants

Division: Magnoliophyta - Flowering plants

Class: Magnoliopsida - Dicotyledons

Subclass: Rosidae

Order: Euphorbiales

Family: Euphorbiaceae - Spurge family

Genus: Ricinus L. – Ricinus

Species: Ricinus communis L. - Castor

It is reported that (Bremer *et al.* 2009), that castor must be classified as an Angiospermae, Eudicotyledone, Rosanae and Malpighiales.

2.1.3 Description of castor plant

The castor plant varies greatly in its growth and appearance, it varies in growth habit, colour of foliage, stems, seed size, colour, and oil content. The castor different varieties differ in resemblance from another. Castor may be large perennials often developing into small trees, others behave as short-lived dwarf annuals. The tree and short-internode types are commonly referred to as giant and dwarf castor types respectively (Weiss 1983; Salihu, Gana and Apuyor 2014a). The root of castor plants is determined by the location or geographic space it is in, if it is in a place with lot of rainfall then the growth is slowed down causing it to be dwarf but at conditions that are favourable (sunlight and semi-dry) the plants grow at a fast rate and they grow tall (Weiss 1983).

The stem of the castor plant is round, sometimes covered with red or green waxy bloom on the field the appearance is bluish. As the plant grows older the colour of the stem, it changes from green, red, purple to eventually being grey when the tree is matured (Salihu, Gana and Apuyor 2014a; Salihu, Gana and Apuyor 2014b). Figure 2.1 presents different types of castor plant. The leaves of the castor plant vary in size from 15 cm to 45 cm, the large usually dark glossy green. The leaf colour depends on levels of anthocyanin, therefore they vary from light green to varies from light green to dark red (Weiss 1983; Anjani 2012).



Figure 2.1 Different types of castor plant (Sbihi et al. 2018)

Castor is a flowering plant as it ages it produces flowers when in favourable climate conditions, it is reported to be cross-pollinated by the wind. The flowers are produced on the stem, in a form of a pyramidal raceme also known as spikes, terminally on main and lateral branches. The flowers may be monoecious (male and female), pistillate (female only) or interspersed (arranged intersperse) on the inflorescence (Shobha Rani *et al.* 2004). The flowering raceme produces fruit which harden when it is ripe, when broken it is where the castor seeds are located. The seed has a tiny and brittle seed coat enclosing a white kernel, the seeds may be white, dark brownish-red, brown, dark chocolate, red or black occurs as very attractive mottle on the covering. The seeds vary greatly in size, from a few approximately 250 mm long and in breadth from 5 to 16 mm (Salihu *et al.* 2013).

In the arial parts of *Ricinus communis* three terpenoids (naturally occurring, organic chemicals and tocopherol-related compound). The oils derived from the plant are composed of triglyceride molecules (technically called esters) which contain a 3-carbon alcohol (glycerol) and three 18-carbons (or 16-carbons) fatty acids. Among other vegetable oils, castor oil is most unique because it is the only commercial source of a hydroxylated fatty acid (ricinoleic acid). The oil contains around 90% of the fatty acid (Ogunniyi 2006). Castor oil normally contains a high concentration of ricinoleic acid, over 85%, which makes its viscosity 7 times higher than other vegetable oils (Babita *et al.* 2010; Gokdogan, Eryilmaz and Kadir Yesilyurt 2015).

The cultivation of castor comes with its own risk important as it is, it contains a toxic protein in it called ricin. The ricin toxin is found in abundance in the seed and in smaller amounts throughout the rest of the plant and it is reported to be deadly when broken seeds are ingested by animals (Salihu, Gana and Apuyor 2014b).

2.1.4 Castor plant breeding

The process of plant breeding is an application of genetic principles to produce plants that will be more useful to humans, these processes can be repeated for many generations with improvements. It is reported that current breeding programs around the world for castor are conducted to produce seeds that mature rapidly, plants architecture for mechanized harvest and are disease resistance. Also, for the reason of superior productivity of cultivars and seeds to produce a yield of at least of

48% to 50% oil content (Lavanya and Chandramohan 2003; Golakia *et al.* 2004; Ramana, Lavanya and Ratnasree 2005). Most breeding programs have searched genotypes with short height (less than 1.5 m), height of primary raceme between 20 and 40 cm, less than 150 days for harvesting, erect plant, and non-shattering fruits. In other regions, castor has been selected for increased tolerance to abiotic stresses such as drought, high temperature, salinity, exchangeable aluminium and reduction of toxicity of castor seeds (Milani and Nobrega 2013).

In India emphasis on the breeding program for high seed yield, increased seed oil content, and resistance to fusarium wilt, grey mould, leaf hoppers, and capsule borer (Lavanya *et al.*, 2006; Lavanya and Solanki, 2010). Hybridization involving single, double, or triple crosses is being used to combine the traits from different sources (Severino *et al.* 2012). The first commercial castor hybrid, GCH 3, was developed in India. This hybrid had seed yields 88% higher than the existing cultivars, medium maturity (140–210 d), and high oil content (46%). A total of 15 hybrids thereafter have been released in India many with resistance to fusarium wilt and high seed yield potential (Lavanya and Solanki, 2010).

2.1.5 Properties of castor seeds

In a study conducted by (Perea-Flores *et al.* 2011), it was reported that physical properties and the fine structure of castor seeds were studied under microscopic technique to find information necessary for industrial processing of the castor seeds. The true seed density was reported to be $1458 \pm 27 \text{ kg m}^{-3}$, bulk density was $538 \pm 11 \text{ kg m}^{-3}$, and thickness of seed coat was $281.97 \pm 13.21 \text{ }\mu\text{m}$. The lipid bodies in castor seed's endosperm were also bigger ($12.63 \pm 1.30 \text{ }\mu\text{m}$ in diameter) than other oilseeds such as peanut (*Arachis hypogaea* L). The chemical analysis conducted confirmed the seeds high contents of protein ($28.48 \pm 0.25\%$) and fat ($51 \pm 0.31\%$). The biological structure of the castor seed is presented in Figure 2.2. Figure 2.3 presents the chemical structure of the major component in castor seed ricinoleic acid and structure of castor oil.

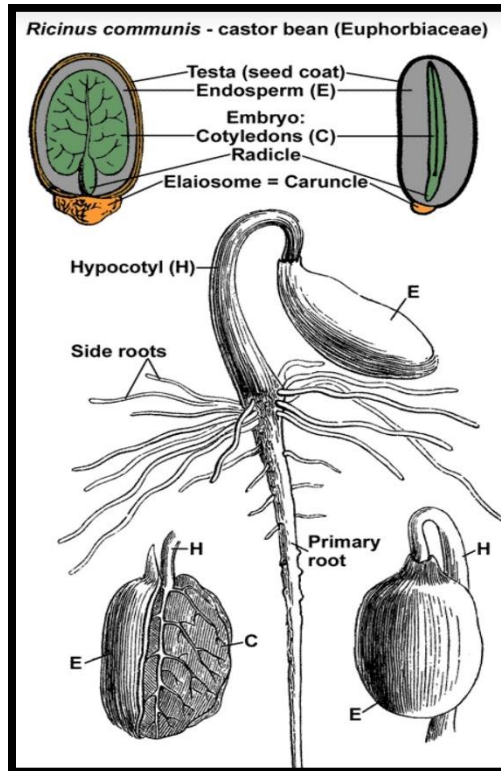


Figure 2.2 Biological image of the castor seed (Leubner 2007)

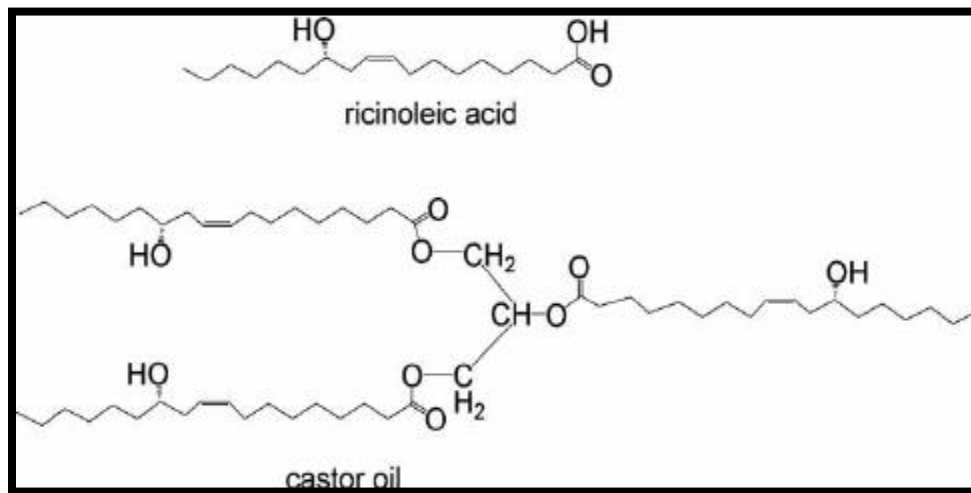


Figure 2.3 Structure of the major component in castor seed ricinoleic acid and structure of castor oil (Leubner 2007)

The values for geometric mean diameter were found to be 8.95 ± 0.05 mm. The castor seed was reported to contain an oil yield of 47-49% (Conceição *et al.* 2007). A study conducted by (Babita *et al.* 2010), reported that castor seeds contain 35-55% oil by weight.

Castor is one of the oldest cultivated crops however, it contributes to only 0.15% of the vegetable oil produced in the world. The oil from this crop is of importance to the global specialty chemical industry because it is the only commercial source of a hydroxylated fatty acid (Severino *et al.* 2012; Patel *et al.* 2016). In a study by (Patel *et al.* 2016), reported that castor oil produced from castor seeds, has long been of important commercial value primarily for the manufacturing of soaps, lubricants, and coatings among others. Castor oil is produced from pressing castor seeds of the plant of botanical name *Ricinus communis* is odourless, viscous, and non-drying. Figure 2.4 presents the structure of the *Ricinus* toxic protein biomarker Ricinine. Figure 2.5 presents the reaction points in the molecule of ricinoleic acid.

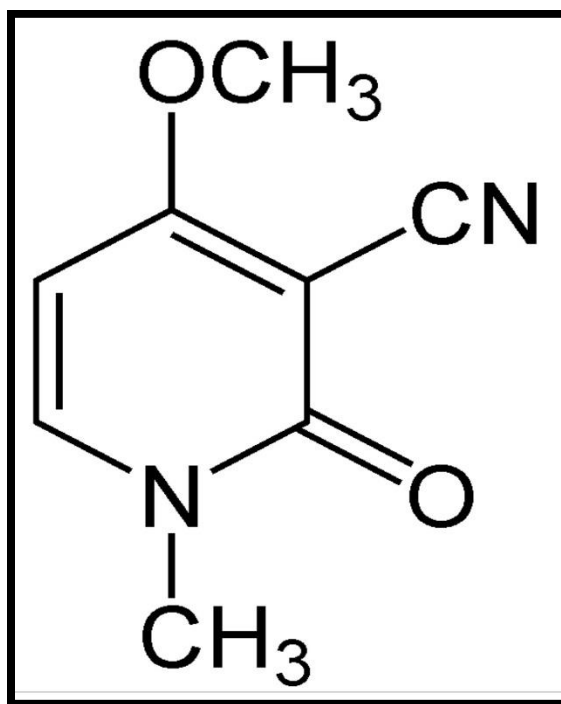


Figure 2.4 Toxic protein Ricinus found in castor seeds (Mutlu and Meier 2010)

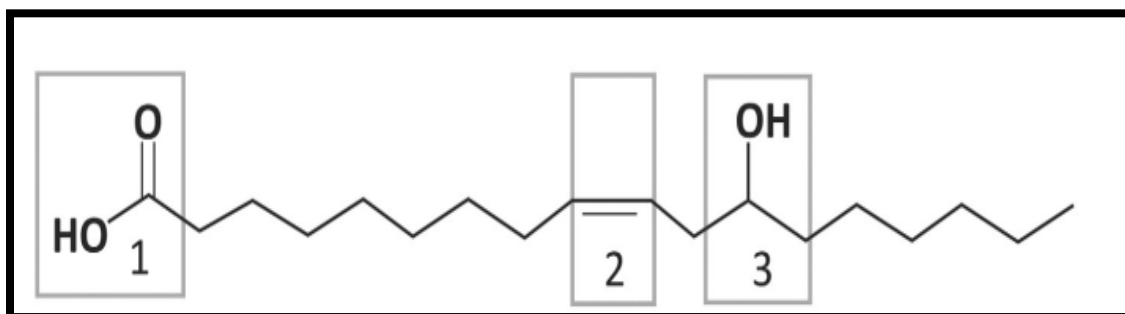


Figure 2.5 Reaction points in the molecule of ricinoleic acid (Mutlu and Meier 2010)

The castor oil industry expects low variability in the fatty acid profile of castor oil grown at either different locations or in different years (da Silva Ramos *et al.* 1984; Mutlu and Meier 2010).

The production of high purity derivatives is made possible by the high concentration of ricinoleic acid in castor seed allows. The hydroxyl group in ricinoleic acid is an uncommon and important point of chemical reaction that complements the double bond and the carboxyl group (Figure 2.3 and Figure 2.5), (Ogunniyi 2006). Castor oils high solubility in alcohol at room temperature is another important characteristic as it facilitates several chemical reactions (Silva *et al.* 2006).

A study by Halek, Delavari and Kavousi-rahim (2013) , reported castor oil has the highest viscosity being 7 times higher than other vegetable oils. Mutlu and Meir (2010), stated the high viscosity over a wide range of temperatures makes castor a valuable ingredient for lubricants and that castor oil is one of the most promising renewable raw materials for the chemical and polymer industries due to its manifold uses and to a series of well well-established industrial procedures that yield a variety of different renewable platform chemicals. The relationship of the viscosity and temperature is presented in Figure 2.6. The properties of castor oil are presented in Table 2.2.

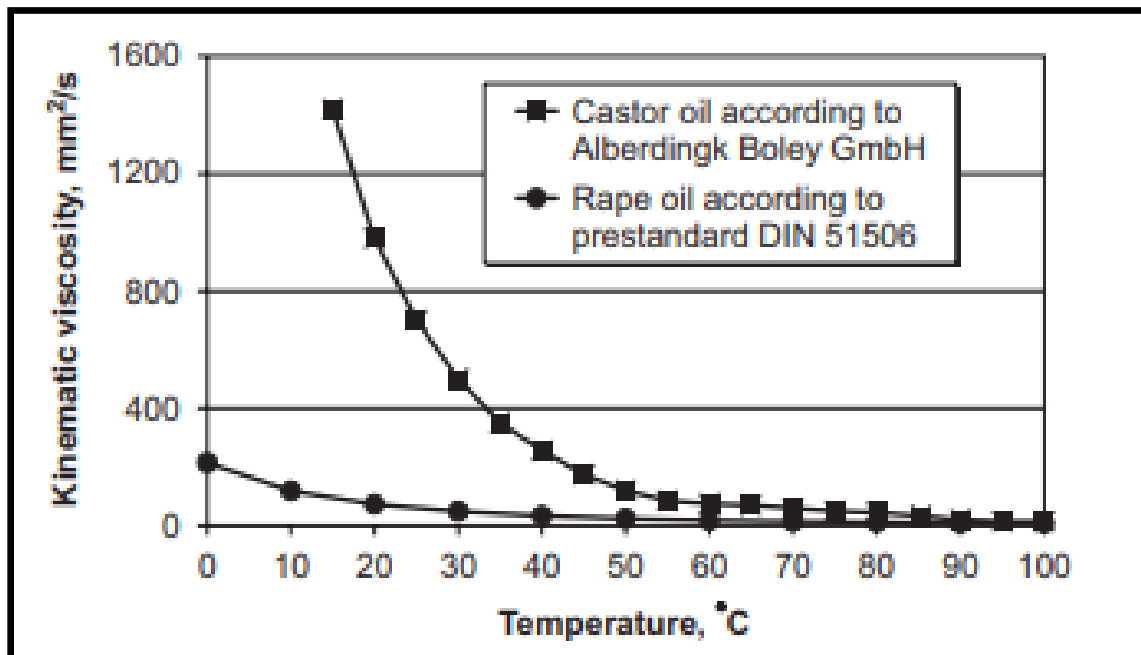


Figure 2.6 Viscosity versus temperature (Belaid *et al.* 2011)

Table 2.2 Physical properties of castor oil (Belaid *et al.* 2011)

Parameter	Value	Units
Viscosity	889.3	centistokes
Density	0.959	g/ml
Thermal conductivity	4.727	W/m°C
Specific heat	0.089	kJ/kg/K
Flash point	145	°C
Pour point	2.7	°C
Melting point	-2 to -5	°C
Refractive index	1.480	

Table 2.3 Fatty acid composition of castor oil (Patel *et al.* 2016)

Fatty acid composition	Molecular formular	Type of fatty acid	Weight percentage composition
Ricinoleic	C ₁₈ H ₃₄ O ₃	Monosaturated	85-90%
Oleic	C ₁₈ H ₃₄ O ₂	Monosaturated	3-4%
Palmitic	C ₁₆ H ₃₂ O ₂	Saturated	1-2%
Stearic	C ₁₈ H ₃₆ O ₂	Saturated	1-2%
Linolenic	C ₁₈ H ₃₀ O ₂	Unsaturated	0.5-0.7%
Linoleic	C ₁₈ H ₃₂ O ₂	Polyunsaturated	4-5%

2.1.6 Castor seeds agronomy

Milani and Nobrega (2013), reported that the castor seed yield could be rapidly increased with the use of improved agronomical practices. The use of good seed quality, selection of appropriate cultivar, appropriate planting date, irrigation, soil fertilization, management of weed, pest, and diseases, optimized plant population, mechanical harvesting, and postharvest are the main technologies that promote higher seed yield. The optimization of planting population is reported to be an inexpensive practice that could significantly increase castor seed yield. The optimum plant population, however, varies as it is influenced by the genotype, environmental conditions, and agricultural practices.

A study conducted by (Baldwin and Cossar 2009), reported that castor seed yield is influenced by planting date. The study was conducted over a period of 3 years (2002- 2004) in 4 different locations in the States of Mississippi and 7 different planting dates, castor 3seed yield varied from 89 to 1954 kg ha⁻¹ among four locations, greatest yields were obtained with early spring planting.

In a study by (Manickan *et al.* 2009), it was reported that India has been able to successfully develop high yielding hybrid castor seeds. A 72% seed yield increase was obtained in the State of Tamil Nadu, (Manickan *et al.* 2009) believed that higher yields could still be achieved. In India the average seed yields range from 1864 kg ha⁻¹ in the State of Gujarat to 371 kg ha⁻¹ in the State of Andra Pradesh, where the crop has been predominantly grown without irrigation on marginal soils (Basappa 2007).

The State of Parana in Brazil, has the highest average seed yield in the country (1600 kg ha⁻¹) due to better soil fertility and agronomical practices (Silva *et al.* 2009).

Damage to the castor plants leaves causes a reduction on seed yield, each 1 m² of lost leaf area leaves reduces production by 37.8 g of seed and 24.4 g of oil leaves are damaged by pests, diseases, wind, hail, machinery traffic, and inappropriate use of herbicides and defoliant. A castor plant can recover from a drastic defoliation; but damage of leaves will still decrease yield (Lakshamma *et al.* 2009; Lakshmi, Lakshamma and Lakshmi 2010).

In a study by (Koutroubas, Papakosta and Doitsinis 1999), stated that successful cropping in Greece depends on the yielding ability and yield stability of the cultivars (hybrids or inbred) as well as the reliability of production systems.

Moshkin (1986), stated that scientists needed to investigate the issue of slow, irregular, and cold sensitive germination of castor seed. The minimum temperature that is required for germination is 14 to 15 °C, the optimum temperature is 31 °C, and the maximum temperature is 36 °C. Often low soil temperatures caused delay germination and seedling emergence resulting in irregular stands.

In a study by Patel *et al.* (2016), reported that there are various challenges that make castor crop cultivation difficult to pursue. Amongst them being climate adaptability, which is restricting castor plantation in the U.S. It also requires a labour-intensive harvesting process, which makes it almost impossible for the U.S. and other developed countries to pursue castor plantation. The production of castor oil from the different parts of the world since the 1970's is represented by Figure 2.7 and Figure 2.8.

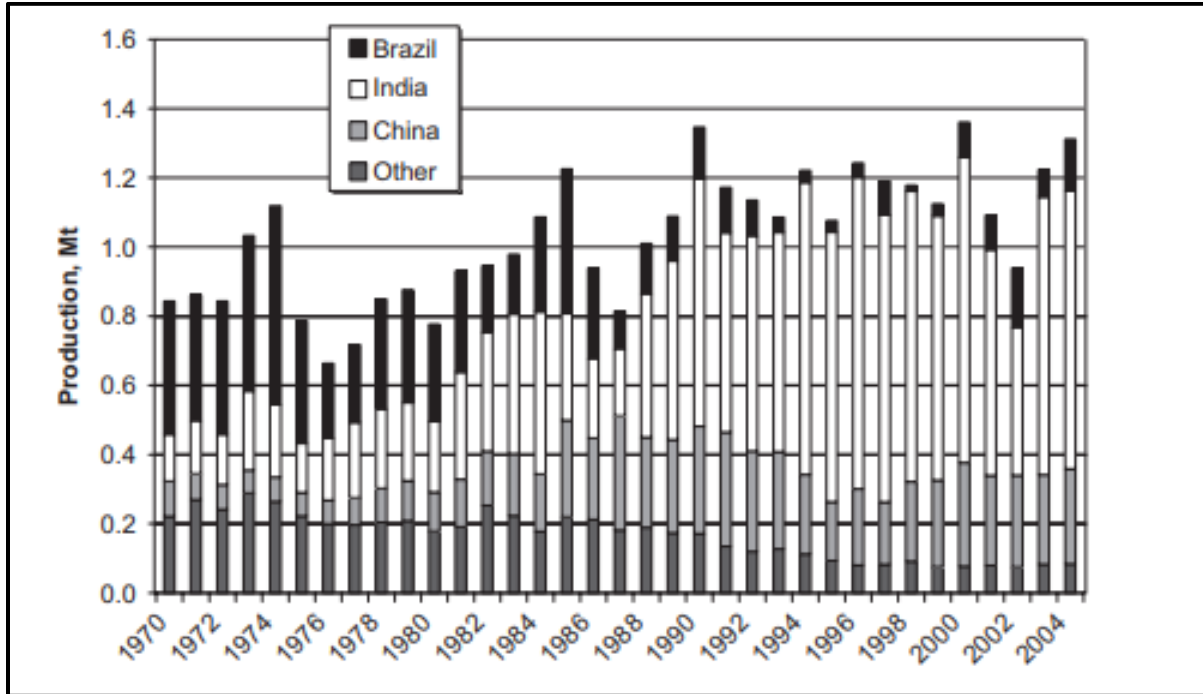


Figure 2.7 World production of castor seeds as at 2004 (FAOSTAT 2005; Patel *et al.* 2016)

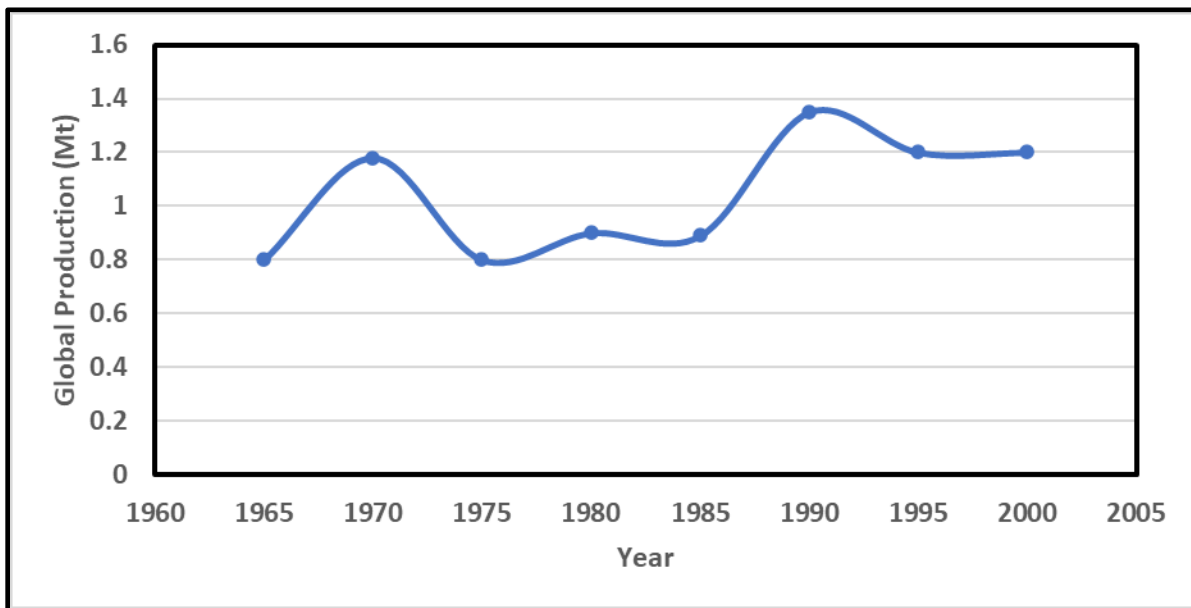


Figure 2.8 World production as at 2010 (Belaid *et al.* 2011)

2.1.7 The benefits of castor oil

Castor oil and the derivatives of castor oil are reported to be found in the production of many products (Ogunniyi 2006; Mutlu and Meier 2010) such as oil-based formulations of lubricants, grease, functional fluids and process oils, oleochemicals, reactive components for paints, coatings, inks, polymers and foams, textile finishing agents, emulsifiers, stabilizers in vinyl compounds, wetting agents, fuel and biodiesel, soap and cosmetic production, fertilizer as well as castor meal serves as cattle feed after the meal has been detoxified.

Characteristics of castor oil such as , high lubricity, high melting point, and insolubility in aliphatic petrochemical fuels and solvents, make it useful as a lubricant for equipment operating under extreme conditions (Mutlu and Meier 2010; Yao *et al.* 2010).

A large class of polymers known as the polyurethanes with vast uses, commonly used for liquid painting coating to rigid insulations. Polyetheranes have a vast variety of applications and were initially produced from petroleum based polyols now castor oil have been found to have an ability to act as a raw material in the production of these polyurethanes (Oprea 2010). Due to energy and environmental concerns the use of renewable and biodegradable materials for production of polyurethanes is increasingly demanded by both industry and society (Sharma and Kundu 2006). Castor oil is reportedly the only commercially available natural oil polyol (Scholz and Da Silva 2008; Severino *et al.* 2012; Sbihi *et al.* 2018).

A study by Ogunniyi (2006), reported that some semi-rigid foams that have potential uses in thermal insulation were produced when castor oil and polyether mixture was reacted with toluene diisocyanate. A 10-carbon dicarboxylic acid, known sebacic acid is manufactured by heating castor oil to high temperatures (about 250 °C) with alkali. The treatment results in saponification of castor oil to ricinoleic acid that is then cleaved to give capryl alcohol (2-octanol) and sebacic acid (Vasishtha, Trivedi and Das 1990).

It was found that methyl esters of castor oil can be used as a biodiesel alternative feedstock when blended with diesel fuel (Berman, Nizri and Wiesman 2011) . The maximum blending level however is limited to 10% due to the high levels of RA present in the oil, which directly affects biodiesel's kinematic viscosity and distillation temperature.

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. Recently, the use of castor oil has attracted attention for producing and optimizing biodiesel production, due to high content of ricinoleic fatty acid and the possibility to esterify with only methanol, which assures low production costs (Osorio-González *et al.* 2020).

Castor oil has a low pour point property which is useful in the manufacturing of lubricants, the low pour point property helps to provide full lubrication when the equipment is started and is easier to handle in cold weather, lubricant base stocks are produced through the synthesis of acyloxy castor polyol esters (Kamalakar *et al.* 2015). Castor oil has been in the past extracted using mechanical pressing, but with mechanical pressing a lot of castor oil was still left behind in the castor cake, thus researchers have looked into methods to enhance the extraction such as using solvents for the extraction of castor oil these methods of solvent extraction will be discussed further in the study.

2.2 Traditional solvent

In the chemical industry, solvents play a crucial role in industrial processes. Volatile non-polar (VNP) have a vast number of applications where they are employed such as in synthetic chemistry, coatings industry and liquid–liquid extraction, where facile removal is by evaporation. Many conventional VNP solvents, such as aliphatic hydrocarbon solvents (hexane or cyclohexane) and aromatic solvents (toluene or benzene), exhibit high persistence, bioaccumulation, and toxicity (PBT). Byrne *et al.* (2018) reported that hexane is suspected of causing fertility and respiratory problems, toluene is suspected of harming an unborn child, and benzene is known to be a carcinogen. As a result, substitutes for this class of solvents that comply with green chemistry principles are desired. Farmer and Mascal (2015) reported that there is difficulty in developing non-polar solvents from biomass is that biomass is strongly functionalized with electronegative O atoms, resulting in high polarity. Hydrocarbons (e.g., hexane, cyclohexane, toluene) and chlorinated hydrocarbons (e.g., carbon tetrachloride, chloroform) were reported to be the traditional non-polar solvents (Byrne *et al.* 2017). It was reported that to lower the polarity, it was feasible to remove functionality of the biomass, but this was reported to closely mimic the conventional target solvents, as it was reported that removing functionality in glucose could

produce hexane (Alder *et al.* 2016). As improvements are being made to processes for the extraction of castor oil, research is conducted into finding alternative greener solvents for the extraction of castor oil. Research into greener solvents has been carried out as it is believed that green solvent does not pose immediate threat to the environment and to human life.

2.3 Green solvents

A study by Wan *et al.* (1995), reported that hexane had been used for decades to extract cotton seed oil, however regulations were put in place against hexane as it was reported to have potential health risks. Therefore, the oil industry needed to alternative hydrocarbon solvents to replace hexane.

In a study conducted by Liu and Mamidipally (2005), reported that edible oils from low oil content were extracted using organic solvents. Hexane is reported to have been the solvent of choice because of its boiling point range of 63-69 °C, excellent oil solvent in terms of oil solubility and ease of recovery. However, hexane as a solvent is also responsible for serious environmental problems such as fire, explosion, and air pollution, in addition to other health hazards due to its toxicity (Liu and Mamidipally 2005).

The alternative of using hexane or other petroleum solvents was the development of green methods such as using green solvents and technology aimed to developing an environment friendly process with simultaneous reduction of pollutant (Kumar *et al.* 2017).

Green solvents are derived from the processing of agricultural crops. These solvents are reported to be environmentally friendly solvents. The use of petrochemical solvents is the key to most chemical processes but not without severe implications on the environment. Green solvents were developed as a more environmentally friendly alternative to petrochemical solvents (Doble and Kruthiventi 2007).

Green solvents that have been derived naturally, from agricultural residues (terpenes), they reported to have good solubilizing properties like conventional solvents. A study by (Kumar *et al.* 2017), reported that advances on 'green' approaches had great impetus in oil industry because of green solvents i.e., terpenes (d-limonene, p-cymene and α -pinene). Terpenes are isoprene units

(C₅H₈) derived chiefly from agriculture source. D-limonene, p-cymene and α -pinene are derived is derived from citrus peels, tree oils and pine tree respectively, and employed in many applications.

Interestingly, these solvents have good Hansen solubility properties (HSP) to dissolve the like molecules. The behaviour of given solvent is determined by the use of the Hansen properties, based on the energy of dispersive (δ_d), dipolar (δ_p) and hydrogen bond forces (δ_h), between the molecules (Dejoye Tanzi *et al.* 2012).

Advantages of using green solvents

Green chemistry has gained popularity amongst scientists over the years as there is a growing need to produce sustainable, renewable solvents and co-solvents this being due to the risk that has been associated with the use of organic solvents in the production of chemicals and in separation processes. Green solvents or green chemistry has great benefits not only on human health, but also on the environment, economic and business sector (EPA 2022).

Human health advantage:

- The release of hazardous chemicals to air leading to damage of respiratory organs is minimized, the air is cleaner.
- Cleaner drinking and recreational water as the release of hazardous chemical waste to water is minimized
- Increased safety for industrial workers as the risk of explosions, fires and accidents is minimized as there is less use of toxic material
- Production is made with less waste, safer products for consumers will be produced, cleaning products and pesticides can be replaced with safer products
- Food can be made safer as there is elimination of toxic chemicals that can enter the food chain
- Pesticides are made to be toxic to only the pests they are engineered for and degrade after use
- There is less exposure to toxic chemicals as endocrine disruptors

Environmental advantage:

- Green Chemicals or green solvents are recovered for further use or degrade to innocuous products, there is no intentional release into the environment during production or use or through disposal
- Plants and animal encounter less harm from toxic chemicals release into the environment
- The potential of global warming, ozone depletion and smog formation are lowered
- There are minimized chemical disruptions of the ecosystem
- The use of hazardous waste landfills is minimized

Business and economic advantage:

- Chemical reactions give off higher yields, while consuming smaller amounts of feedstock to obtain the same amount of product
- Synthetic processes are minimized, allowing for faster production of products
- Increased plant capacity
- Saving on energy and water
- Reduction of waste, elimination of costly remediation, hazardous waste disposal, and end of pipe treatments
- Replacement of purchased feedstock by a waste product
- Less product is required to achieve same function through better performance
- Reduction of petroleum products, slowing their depletion and avoiding their hazards and price fluctuations
- Improved competitiveness of chemical manufactures and customers
- Increased consumer sales from safer product labelling and reduced footprint through increased throughput

Hackl and Kunz (2018), reported that chemical solvents constitute to approximately 80% of the total volume of chemicals used in many important chemical processes, especially in fine chemical manufacturing. Some of the applications for solvents are:

- Paints and coatings
- Pharmaceuticals

- Adhesives
- Printing inks
- Cosmetics
- Household/car care
- Metal degreasing/ Dry cleaning /Domestic cleaning
- Formulations: Dispersant /Lubricant /Surfactant /Adhesives /Viscosity modifier/ Diluent
- Coatings: Paints/ Varnishes
- Chemical's production: Reaction medium/ Product purification / Chromatographic solvent

2.4 The extraction of castor oil

The extraction of castor oil can be done through a series of process either through mechanically pressing (hot or cold) the castor seeds or by solvent extraction. It can be done using the combination of the mentioned process (Dasari and Goud 2013). There are different types of extraction processes, which include traditional method, solvent extraction, conventional extraction and Soxhlet extraction.

2.4.1 Traditional method

The castor seeds were taken through a process of cleaning to remove debris it would then be dehulled by hand. The dehulled castor seeds would then be boiled using water at a temperature of 96 °C for 10 minutes. Once the seeds had completed the boiling process, then be sundried to remove the moisture. The seeds would then be crushed using a manual grinding machine. It would be grounded to a paste; the paste would be mixed with water using a ratio of 1 kg of paste to 2 litres of water. The castor and water mixture would be taken through a process of cooking. As the water evaporates and the product becoming sticky, the oil would then surface and settles on the surface. This process is reported to have been able to extract 19.42% by weight of castor oil which was about 38.84% of the oil present in the seeds. This process was reported to be time consuming, labour intensive and inefficient (Oluwole *et al.* 2012).

A spindle oil press machine that would be manually operated was designed, constructed, and tested to evaluate its performance. The machine gave a satisfactory maximum oil recovery of 78.1% and the cake obtained was of the same quality when compared with those produced from the traditional method. The machine was reported to not only be able to eliminate the rigors involved in the traditional method of extracting seed oil in rural areas but it would also reduce the processing time (Oluwole, Aviara and Papu 2003).

It is reported that the yield of oil extracted using cold pressing is lower than that obtained when using hot pressing (hot-pressing using the pressing machine with the aid of heating by assembling heat element in front of the extruder),(Ayo *et al.* 2012; Bhatol 2013). In the study of hot pressing an oil yield of 54% was obtained. In another study by Muzenda *et al.* (2012a), it was reported that a combination of pressing and solvent extraction was applied and a maximum yield of 50.16%, the mechanical pressing conducted was the hot press with pressing time of 60 minutes.

In a study conducted by , it was reported that castor seeds were taken through a process of cold-pressing, the castor oil that was obtained was 39,43% by weight. Upon further characterization and refining the virgin oil obtained was a clear, viscous, pale-yellow liquid, it was further purified by filtration through sintered glass (fine mesh screen). The physicochemical characterization of the purified oil revealed low acid value (2.07), low iodine value (84.18), low peroxide value (38.00), but relatively high specific gravity (0.959), hydroxyl (163.64) and saponification (175.31) values. These values were reported to compare favourably with ASTM standards and general specifications for industrial grade castor oil suggesting that the oil has good industrial potential.

2.4.2 Solvent extraction

The process of selectively removing a desired compound, natural product or product from the raw material is known as extraction. Extraction methods include solvent extraction, distillation method, pressing and sublimation according to the extraction principle. Solvent extraction is the most widely used method. The extraction of natural products has 4 stages: (1) the solvent penetration into the solid matrix; (2) the solute dissolving into the solvent; (3) the solute diffusing out of the solid matrix; (4) the extracted solutes being collected. The extraction is enhanced by the factors that affect diffusivity and solubility. The properties of the extraction solvent, the particle size of

the raw materials, the solvent-to-solid ration, the extraction temperature and the extraction duration will affect the extraction efficiency (Zhang, Lin and Ye 2018). Selecting solvents to use for the extraction requires that it be given thought, as the selectivity of the solvent, solubility, safety and cost play an important role in the extraction process. The process of extraction of oil using green solvents is depicted in Figure 2.9, where pre-treatment of the material is conducted before the oil is extracted using terpenes and the oil-solvent mixture is separated through the process of distillation.

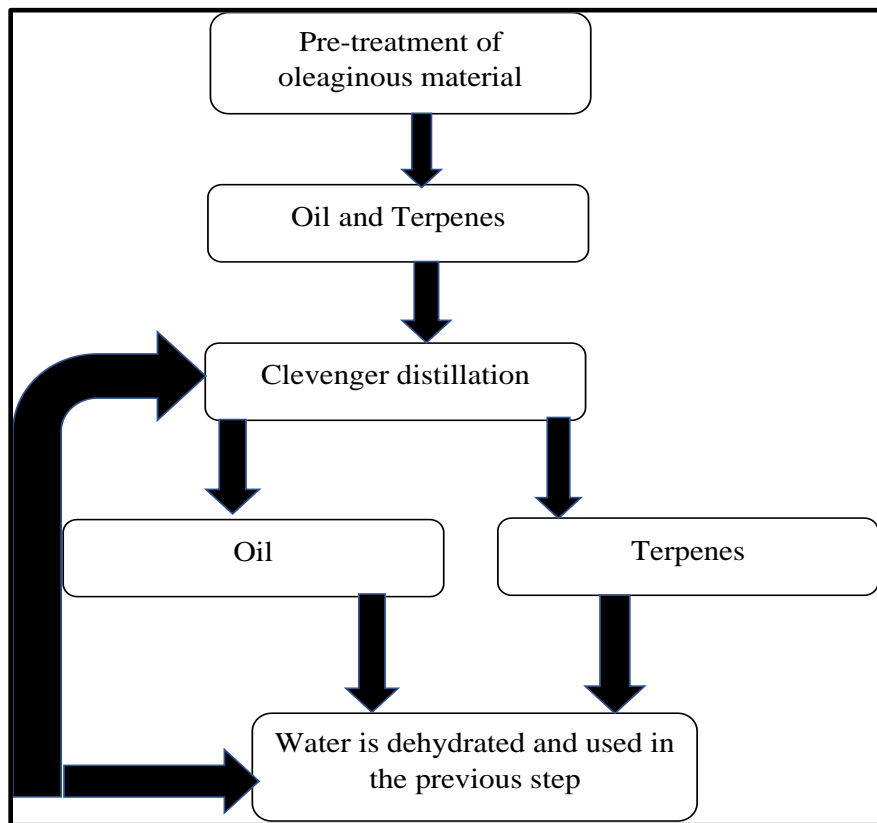


Figure 2.9 Schematic flow diagram of process of oil extraction using green solvents (Kumar *et al.* 2017)

2.4.3 Conventional extraction

The conventional extraction methods for oil seeds, comprise of hydraulic pressing, expeller pressing and solvent extraction. Solvent extraction is reported to being widely adapted for economical and practical concerns. The oil seeds are first crushed or pressed to allow a wide

surface area for the solvent to penetrate for an enhanced process recovery of oil from the seeds (Kumar *et al.* 2017)

The preferential dissolution of oil by contacting oilseeds with a liquid solvent, is the solvent extraction process. This is reported to be the most efficient technique to recover oil from oilseeds. The efficiency depends on the oilseed preparation prior to extraction, temperature, mode of operation (batch vs. continuous and co-current vs. counter current operations) and equipment design. It is expected that residual oil in the meal to be less than 1 percent after commercial solvent extraction (Dunford 2016). A schematic flow diagram in Figure 2.10 depicts the process of extraction using hexane as the solvent.

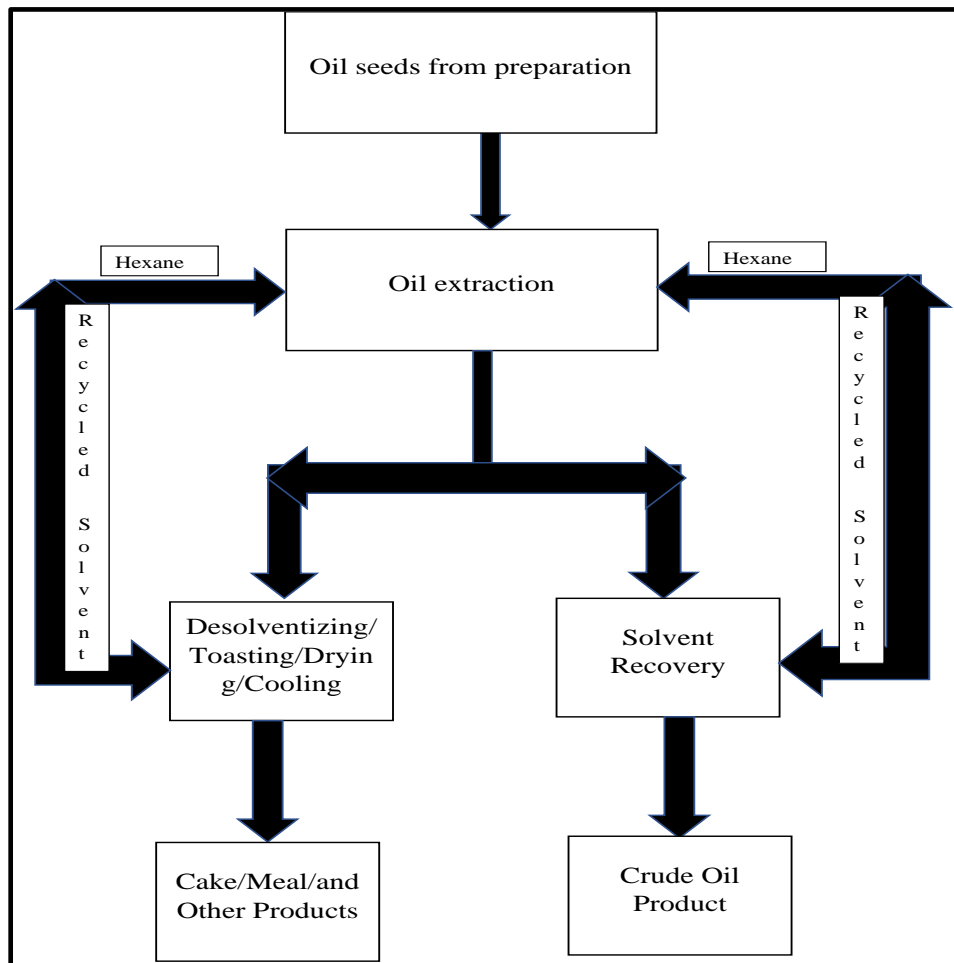


Figure 2.10 Schematic diagram of the process of the solvent extraction (Dunford 2016; Zhang, Lin and Ye 2018)

2.4.4 Soxhlet extraction

A Soxhlet extractor is a piece of laboratory apparatus invented in 1879 by Franz von Soxhlet. It was originally designed for the extraction of a lipid from a solid material (Harwood and Moody 1989). The Soxhlet extraction method is typically used when the desired compound has a limited solubility in a solvent, and the impurity is insoluble in that solvent. It allows for unmonitored and unmanaged operation while efficiently recycling a small amount of solvent to dissolve a larger amount of material. The Soxhlet extraction was selected to carry out this study. Figure 2.11 presents the simple typical Soxhlet extractor. Since it selected to extract castor oil in this study then more detailed description in Chapter 3.

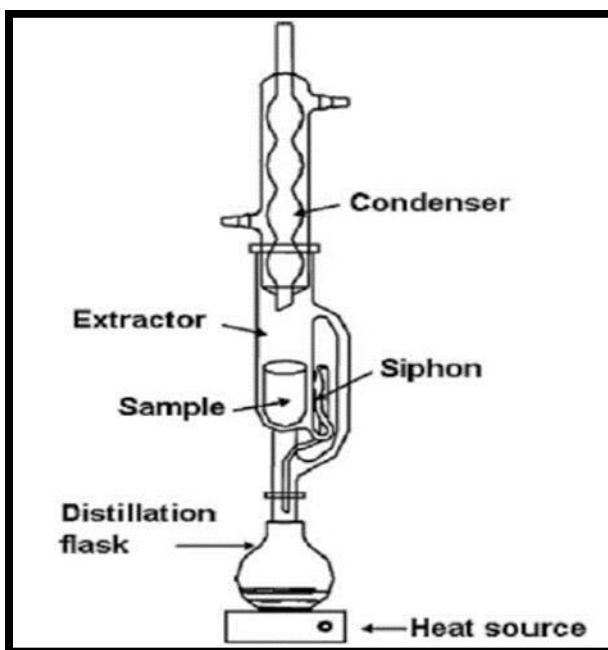


Figure 2.1 A diagram of the Soxhlet extractor (De Castro and Priego-Capote 2010)

Advantages of using a Soxhlet extractor (De Castro and Priego-Capote, 2010)

- The sample is repeatedly brought into contact with fresh portions of extractant, which facilitates displacement of the transfer equilibrium.
- The system remains at a relatively high temperature by effect of the heat applied to the distillation flask reaching the extraction cavity to some extent.

- No filtration is required after leaching.
- Sample throughput can be increased by performing several simultaneous extractions in parallel.
- Low cost of the basic equipment.
- Soxhlet extraction is a very simple methodology that requires little training.
- Extract of more sample mass than most of the latest alternatives (microwave-assisted extraction, supercritical fluid extraction, etc.)

Disadvantages of using a Soxhlet extractor (Viro *et al.* 2008a; De Castro and Priego-Capote, 2010)

The most serious drawbacks of Soxhlet extraction as compared to other techniques:

- Long time required for extraction
- Large amount of extractant wasted which is not only expensive to dispose of, but also the source of additional environmental problems.
- Samples are usually extracted at the solvent boiling point over long periods, which can result in thermal decomposition of thermolabile target species
- Conventional Soxhlet device provides no agitation
- The large amounts of extractant used call for an evaporation concentration step after extraction.
- The Soxhlet technique is limited by extractant and difficult to automate
- Energy consuming and conventionally used high amount of petroleum solvents

The advantages and shortcomings of the conventional Soxhlet extraction, have reported to have been used as starting point for the development of a variety of modifications intended to alleviate or suppress the latter while keeping or even improving the former. Most of the modifications reported over the last few decades have been aimed at bringing Soxhlet closer to that of the more recent techniques for solid sample preparation, by shortening leaching times with the use of auxiliary forms of energy and automating the extraction (De Castro and Priego-Capote 2010).

2.5 Parameters affecting the extraction

The oil solubility in solvent increases with extraction temperature, high temperature has a positive effect on viscosity and diffusivity of oil as viscosity decreases while diffusivity increases as the extraction temperature increases, resulting in shorter extraction times. The required energy for solvent recovery decreases when higher operating temperature is used for extraction. However, too high of temperatures may cause deterioration and denaturation of some oil and meal components. Hence, temperature selection is based on type of oil and required specifications of the final product (Olaniyan 2010; Dunford 2016; Patel *et al.* 2016; Kumar *et al.* 2017; Zhang, Lin and Ye 2018). Figures 2.12 and 2.13 represent the effect of time on the extraction when using different solvents.

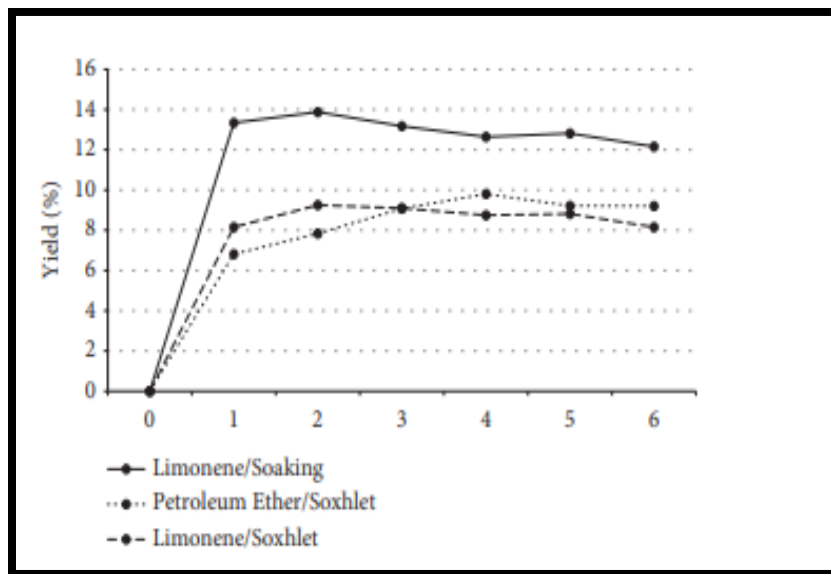


Figure 2.12 Effect of time on extraction (Hamza, Elfalleh and Nagaz 2021)

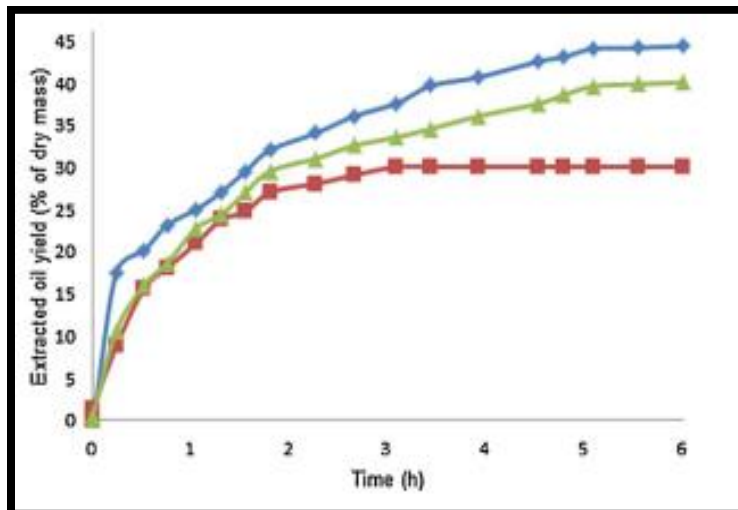


Figure 2.13 Depicting the effect of time on extraction (Li *et al.* 2014; Li, Smith and Stevens 2016)

Among mentioned extraction processes, the Soxhlet extractor was utilized to carry out experiment in this study using green solvents. As mentioned earlier that single and co-solvents were used to evaluation the highest yield of castor oil. Consequently, the following green solvents, which include d-limonene, α -pinene, *p*-cymene, furfural, and ethanol as well as co-solvents were used in this study.

2.6 Selected green solvents

D-limonene

D-limonene is a renewable cyclic monoterpene that is easily obtainable from citrus peel, it is commonly used as a nutraceutical ingredient, antibacterial, biopesticide and green extraction solvent. It is also used as an additive in healthcare, fragrance and food and beverage industries because of its characteristic citrus-like smell. Its lack of toxicity makes d-limonene a promising green-alternative for the development of a wide range of effective products in modern biorefineries. Therefore, industrial demand reportedly largely exceeds supply now. D-limonene can also be used as starting substrate for the preparation of building block chemicals, including *p*-cymene which is an important intermediate in several industrial catalytic processes. Figure 2.14 present the structure of d-limonene.

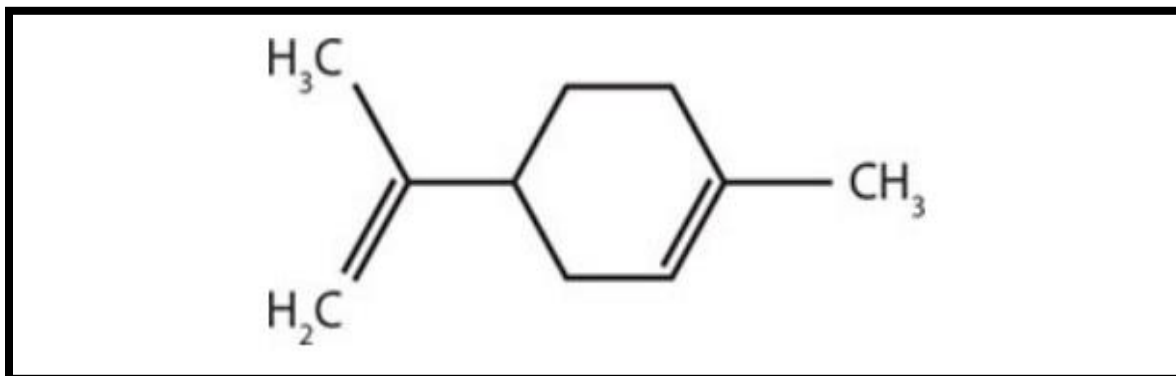


Figure 2.14 Chemical structure of d-limonene

D-limonene has positive attributes which makes it a good candidate to replace hexane or the petroleum solvents. It reported not be carcinogenic or mutagenic, it is biodegradable and contains no ozone depleting chemicals, it is deemed safe by the Food and Drug Administration (FDA) therefore it is approved for use in food contact applications also the Environmental Protection Agency (EPA) approved for its use as an inert ingredient (Liu and Mamidipally 2005).

In a comparison study carried out using hexane and d-limonene for the extraction of crude-rice bran oil, it was reported that d-limonene extracted significantly more oil than hexane. It was reported that no significant increase in the percentage oil yield when the extraction time was increased by 1 hour for both solvents (Liu and Mamidipally 2005). A solvent-to-rice bran ratio of 5:1 and extraction time of 1 hour presented the conditions for maximum yield (22.98%) of crude rice bran oil. The application of d-limonene solvent as an alternative to hexane in edible and non-edible oil extraction could potentially eliminate the safety, environmental, and health issues associated with the use of hexane (Liu and Mamidipally 2005).

Viro *et al.* (2008) carried out a study of lipid extraction in food using d-limonene as an alternative to hexane, for the study the yield obtained for the lipid extraction using d-limonene was 48.6% compared to that of hexane which was 40.3%. D-limonene's extracts were found to be almost equivalent to those obtained using n-hexane. However, it was noted that the performance of the extraction obtained using d-limonene is slightly higher than that obtained by using n-hexane. This observation was reported to be the possibility of the slightly polar nature of d-limonene compared

with n-hexane and to a higher dissolving power of d-limonene for triglycerides. Furthermore, at higher temperatures used to boil d-limonene lower viscosity resulted and therefore a better diffusion rate of oil in the matrix.

A study conducted for extraction of oil in date palm seeds using a green solvent extracted from orange peels, was reported to be successful. D-limonene from the orange peels was reported to present a promising approach for bio-oil extraction from date seeds, as the extraction yield obtained was 13.88% and the yield obtained when the extraction was carried out using petroleum ether was 9.25% (Hamza, Elfalleh and Nagaz 2021). This proved that the green solvents extracted higher oil amount and significantly improved its quality.

***p*-cymene**

The *p*-cymene is a naturally occurring aromatic organic compound, it is a colourless liquid with pleasant smell. This solvent is reported to be member of monoterpenes and toluene. The *p*-cymene is a natural product that is found in *Nepeta nepitella*, *Xylopi aromatic* and cranberries (Balahbib *et al.* 2021). It is insoluble in water and but miscible with organic solvents. It was reported to be present in several food-based plants such as carrots, orange juice, grapefruit, tangerine, raspberries, and several spices. Several studies have reported that *p*-cymene has demonstrated pharmacological properties of been antioxidant, anti-inflammatory, antiparasitic, antidiabetic, antiviral, antitumor, antibacterial, and antifungal activities. Figure 2.15 present the structure of *p*-cymene. It had been reported to act as an analgesic, antinociceptive, immunomodulatory, vasorelaxant and neuroprotective agent and also has demonstrated anticancer effects which makes it an ideal green solvent (Balahbib *et al.* 2021).

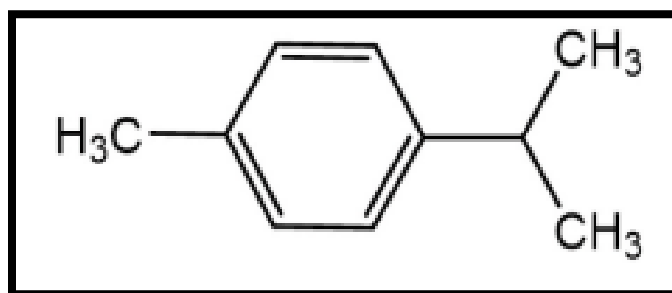


Figure 2.15 Chemical structure of *p*-cymene

Ethanol

Ethanol also known as ethyl alcohol, is a member of a class of organic compounds known as alcohols. It is an industrial chemical used as a solvent in the synthesizing of other organic chemicals. Ethanol is also found in automotive gasoline as additive, it is also an ingredient in many beverages as wines, beer, and distilled spirits (Augustyn *et al.* 2022). Ethanol is manufactured in two main processes through the fermentation of carbohydrates (this method is used for alcoholic beverages) and the hydration of ethylene. Oklu, Matsinha and Makhubela (2019), reported to the most produced through the biological transformation of sugars. Sugarcane, corn, and nonedible (cellulose) are usually used as feedstock for these processes. With growing concerns of food prices increasing due to edible feedstock, processes of optimizing cellulosic ethanol have been initiated and the first cellulosic ethanol commercial -scale production plant was commissioned by Beta (van Zyl *et al.* 2011). Figure 2.16 presents the structure of ethanol.

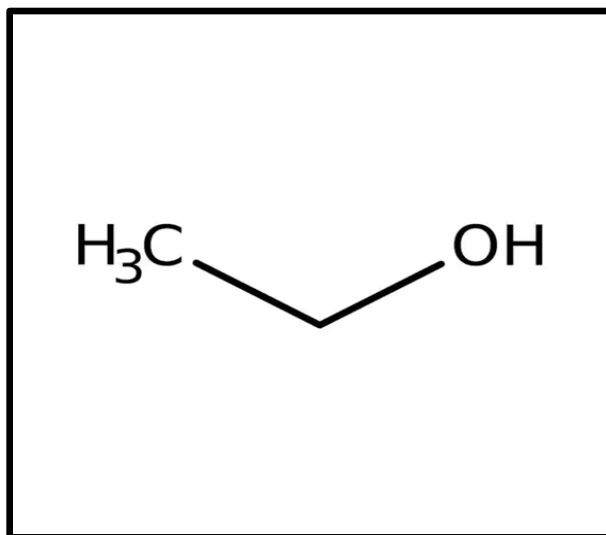


Figure 2.16 Chemical structure of ethanol

Ethanol and water were reported to be classified as less hazardous, bio-renewable, and cheap (Castejón, Luna and Señoráns 2018). Baumler, Carrín and Carelli (2016), reported that ethanol is classified as a bio-renewable material because it can be obtained from a wide variety of biological matter. Bhutada *et al.* (2016), reported that ethanol has high polarity which gives the ability to

engage in strong interactions with the other polar molecules and, as a result ethanol can extract nonglyceride components.

In a study carried out to evaluate the efficiency of solvent on castor seeds and plant, ethanol and hexane were used as solvents and the results were compared. It is reported that the seed oil yield and sterol content were higher when ethanol was used as the extracting solvent than when hexane was used for both varieties of plants studied. While castor oil extracted with hexane had a higher tocol content than that extracted with ethanol, castor oil from Zanzibar seeds had a higher tocol content than castor oil extracted from Impala seeds. The fatty acid profile of the castor oils showed high levels of oleic and linoleic acids. Extractions performed with hexane afforded oils with a greater variety of fatty acids (Sbihi *et al.* 2018).

In a study by Baümler, Carrín and Carelli (2016), investigating the diffusion of tocopherols, phospholipids and sugars during oil extraction from sunflower collects, using ethanol as a solvent. The study was carried out at temperatures of 50 to 60 °C in a batch reactor, the sugars were reported to have been extracted in large proportion, especially the indigestible raffinose, increasing the nutritional value of the meal. The sugar reduction percentage in the sunflower collets was reported to have increased over extraction time to up to 60 and 80% at 50 and 60 °C. As a result of this study, it was reported that the use of ethanol could increase the quality of oil and that of the meal. It could also help get a third phospholipid-rich phase after fractionation.

A study carried out to evaluate the efficacy using solvents for the extraction of lipids from algal biomass by the Soxhlet extraction method, thirteen solvents with varying characteristics were used in the extraction of algal biomass amongst the solvent's ethanol, chloroform and hexane produced average of above 10% lipid extracts. The time-based trials showed optimum extraction efficiency at 3 hours, the binary mixtures that gave the greatest extraction efficiency with a ratio of 1:1 was chloroform: ethanol (Ramluckan, Moodley and Faizal 2014).

α -pinene

α -pinene is an organic compound of the terpene class, one of two isomers of pinene. It is an alkene, and it contains a reactive four-membered ring. It is found in the oils of many species of many coniferous trees, notably the pine. It is also found in the essential oil of rosemary and Satureja

myrtifolia (Simonsen 1957). Figure 2.17 present the structure of α -pinene. It is reported to be a key compound of the essential oils extracted from many species of coniferous trees and it is known for its biological activities (Bouzennaa *et al.* 2017).

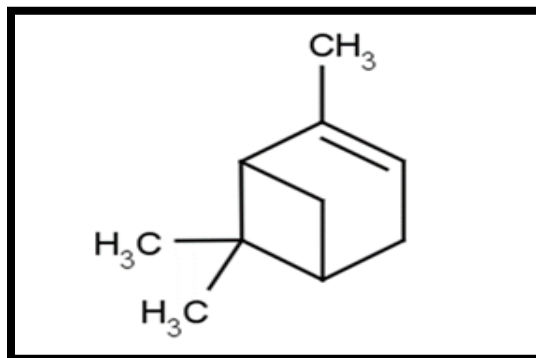


Figure 2.17 α -pinene chemical structure

In a study to investigate the possibility of replacing hexane with alpha-pinene. It was reported that α -pinene had a higher polarity than hexane. The results obtained for the extraction were reported to be satisfactory when using α -pinene, allowing for a large reduction in toxicity for both operator and the environment. Furthermore, the use of by-products resulting from renewable raw materials as solvent and the high recycling rate of α -pinene presented an additional interest as reported by (Bertouche *et al.* 2013a). Figure 2.18 presents the relation between α -pinene versus hexane where α -pinene shows higher trend in extraction as the time of extraction increased (Dejoye Tanzi *et al.* 2012).

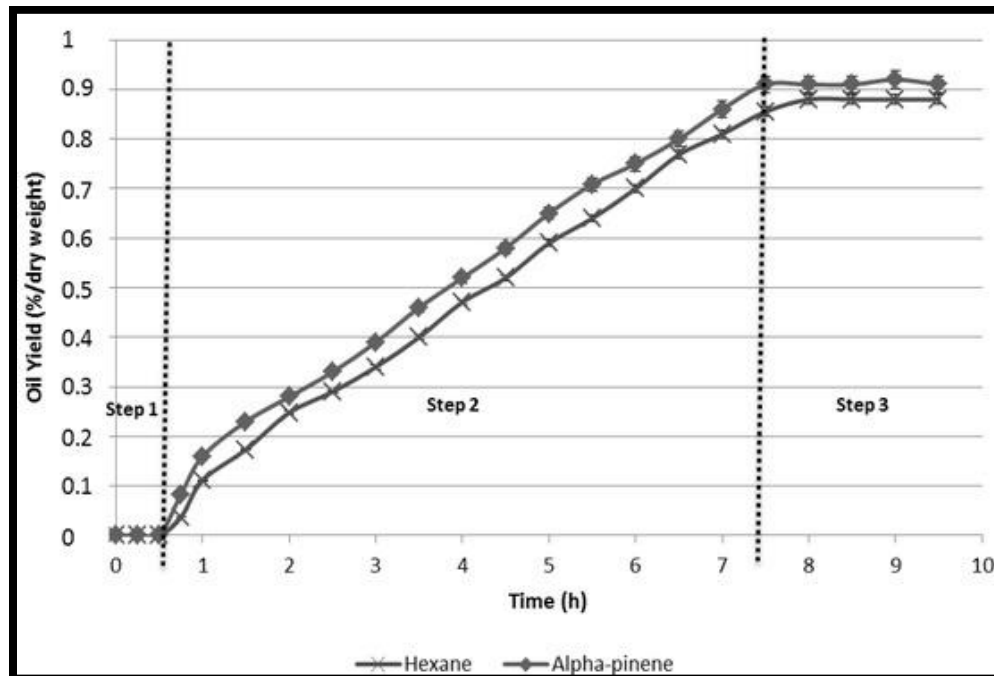


Figure 2.18 Graph of performance of α -pinene to hexane (Dejoye Tanzi *et al.* 2012)

Green solvents *p*-cymene, d-limonene and α -pinene were reported to be feasible alternatives over n-hexane for the extraction of vegetable oils. The large-scale utilization of these solvents, however, is reported to be limited owing to their high boiling points and latent heats of vaporization. When these solvents were used to extract canola oil the highest solvent fluxes were observed with oil/limonene mixtures whereas the oil rejections were comparable in the different oil/solvent mixtures and up to 90% was achieved (Abdellah *et al.* 2019). Figure 2.19 present the physiochemical properties of the terpenes, alcohols and hexane.

Relevant physiochemical properties of various solvents and extracts.							
Solvent	<i>n</i> -Hexane	<i>n</i> -Limonene	α -Pinene	<i>p</i> -Cymene	Ethanol	Isopropanol	<i>n</i> -Butanol
Chemical structure							
Molecular formula	C ₆ H ₁₄	C ₁₀ H ₁₆	C ₁₀ H ₁₆	C ₁₀ H ₁₄	C ₂ H ₆ O	C ₃ H ₈ O	C ₄ H ₁₀ O
Molecular weight (g mol)	86.18	136.23	136.24	134.22	46.07	60.09	74.12
Density 25 °C (g cm)	0.675	89	0.879	.861	0.780	0.791	0.805
Flash point (°C)	-23.3	42.8	32.2	47.2	8.9	11.7	35
Boiling point (°C)	69	176	155	176	73	73	118
Viscosity, 25 °C (cP)	0.31	0.83	1.32	0.83	0	1.96	3
Enthalpy of vaporization (kJ mol)	29.74	39.49	37.83	39.34	38.56	39.85	43.29
Surface tension, 25 °C (dyne cm)	20.3	25.8	25.3	28.5	22.3	22.6	26
Dielectric constant, 20 °C	1.87	2.44	2.58	2.34	24.5	17.9	17.5
Hansen solubility parameters							
δ_{total} (MPa ^{1/2})	15.0	17.1	16.6	17.6	25.4	22.3	23
δ_{dH} (MPa ^{1/2})	15.0	16.7	16.4	17.3	16.2	15.8	15.9
δ_p (MPa ^{1/2})	0	1.8	1.3	2.3	8.6	6.7	6.4
δ_h (MPa ^{1/2})	0	3.1	2.2	2.4	17.6	15.2	15.2
Extracts	Triglyceride	Tocopherol	α -Tocotrienol	Brassicasterol	Campesterol	β -sitosterol	Fatty acids
Hansen solubility parameters							
δ_{total} (MPa ^{1/2})	17.0	16.9	17.8	17.9	17.6	17.4	17.7 ± 0.4
δ_{dH} (MPa ^{1/2})	15.8	16.6	17.5	17.5	17.2	17.1	16.5 ± 0.2
δ_p (MPa ^{1/2})	4.7	0.9	0	1.7	1.8	1.7	3.1 ± 0.3
δ_h (MPa ^{1/2})	2.2	2.8	3.5	3.3	3.2	3	5.7 ± 0.7

Figure 2.19 Physiochemical properties of various solvents and extracts (Li *et al.* 2014)

Furfural

Furfural is reported to be an outstanding extractant for separating compounds with double bonds from compounds without double bonds, the reason being that the double bonds of furfural attract double bonds of other molecules since energy is liberated when a double bond system is enlarged. One such application of furfural is the extraction of vegetable oils such as soybean oil to get an extract rich in double bonds, and a raffinate depleted of double bonds. The extract rich in double bonds can be used as a "drying oil" for paints and varnishes, where the double bonds react with oxygen of the ambient air to form cross-linked polymers. On the other hand, the raffinate depleted of double bonds is a more desirable product for the food industry than the no-extracted soybean

oil. Thus, two advantages are obtained in a single operation. Unlike customary extraction, in such a column the dispersed phase and the continuous phase change roles. Figure 2.20 present the structure of furfural. In the upper portion, furfural droplets fall through a continuous oil phase, whereas in the lower portion oil droplets rise through a continuous furfural phase, with an interface between these two regions.

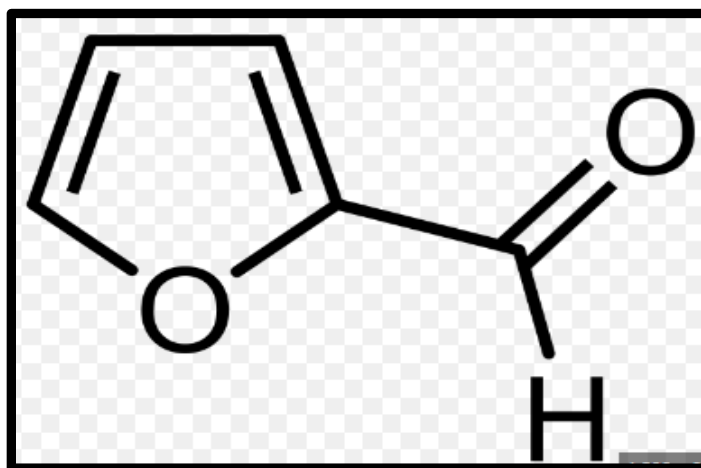


Figure 2.20 Furfural structure

2.7 Extraction of oil using n-hexane as solvent

In a study carried out by (Muzenda *et al.* 2012b), for the optimization of process parameters for the extraction of castor oil. Hexane was used as a solvent together with isopropanol, the maximum recovery achieved was 50.16% for the isopropanol and this was dependent on the nature of the solvent. High oil yields were obtained when extracting with 150 ml of isopropanol for 45 minutes at its boiling point the influence of temperature was also observed. Extraction with hexane gave the lowest yield of 38.68% at 45 minutes and the same volume.

In a study carried to produce detergent using castor oil, hexane was used to extract castor oil from castor seeds. It was reported that the oil yield obtained was low at 29.11 %. This result reported to be relatively low compared to a previous study that was conducted where an average oil yield of 32.1 % was attained (Isah A. G., Mohammed A. and Garba M. 2005). This is further explained to have been attributed to type of seed that was used. The quality of oil was however reported to be satisfactory (Isah 2006).

Ngusale , Kipkemboi and Mitie (2017), carried out a study for the synthesis and characterization of biodiesel from non-edible castor oil. In the study it was reported that the extraction was carried out using Soxhlet extraction and the solvent that was used was hexane, the resulting oil yield that was achieved was 33.2%.

In a study carried out by Akpan, Jimoh and Mohammed (2006), the percentage yield of oil obtained using hexane as a solvent was 33.2% and this was within the range of castor oil content (30-55%). Salimon *et al.* (2010) reported that the oil yield obtained using hexane for extraction on African castor seed oils was at 43.3%.

After the solvent extraction process, the oil is refined to remove harmful components making it appropriate for industrial process and human use. This was achieved by refining which takes place in 3 stages: degumming, bleaching and deodorization.

Degumming

Is a chemical refining process that removes phospholipids, which are classified as hydratable or non-hydratable. Hydratable-phospholipids can be removed by washing the oil with water but non-hydratable phospholipids need the addition of phosphoric or citric acid (Aukema and Campbell 2011). During the process of water degumming, the oil is heated up to 75 °C, mixed with water by 5% volume of water, and then the mixture is centrifuged for 30 min to precipitate gums, reducing the oil content of phospholipids to about 200 ppm (Kővári 2004). The process of acid degumming acid is carried out using, citric acid (30% concentrated.), which is added to 2% of total oil volume. The acid forms complex compounds with potassium, calcium, and phosphorus that precipitate and that can be separated via centrifugation. Usually, citric acid is used not only for decomposition of metal salts but as a chelating agent to keep the metals as water-soluble complexes (Zufarov, Schmidt and Sekretár 2008).

Bleaching

It is a chemical absorption process where oil is filtrated usually through a natural clay filter (bleaching earth) but may also include activated charcoal that removes contaminants and unattractive colour compounds, including chlorophyll, oxidation compounds, and iron. This step is performed under vacuum for about 5 to 30 min at 100–110 °C. The colour and suspended contaminants are absorbed by the clay particles and/or activate carbon (charcoal) (Wrigley *et al.* 2015).

Deodorizing

It is the last step of the refining process where unpleasant odours are removed, this process is carried out at high temperatures above 200 °C with steam at high vacuum. Modern deodorizing equipment utilizes packed columns that provide a very high efficiency in stripping the free fatty acids and other volatiles from the oil (Wrigley *et al.* 2015). The process of extraction to the refining final step is represented Figure 2.21.

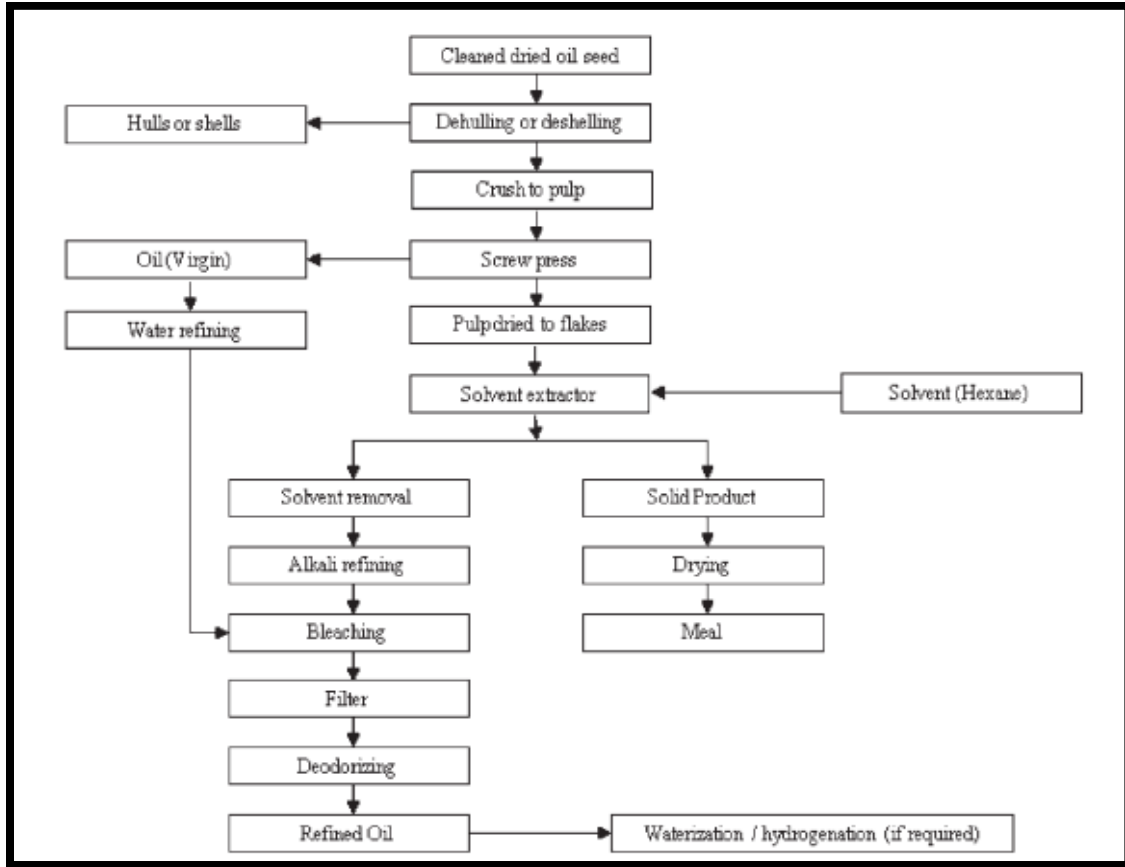


Figure 2.21 A process flow of the refining of castor oil (Mamidipally and Liu 2004a; Mutlu and Meier 2010; Aukema and Campbell 2011)

Figure 2.22 presents a schematic diagram that explains the removal of impurities or improvement that take place on each stage of the refining.

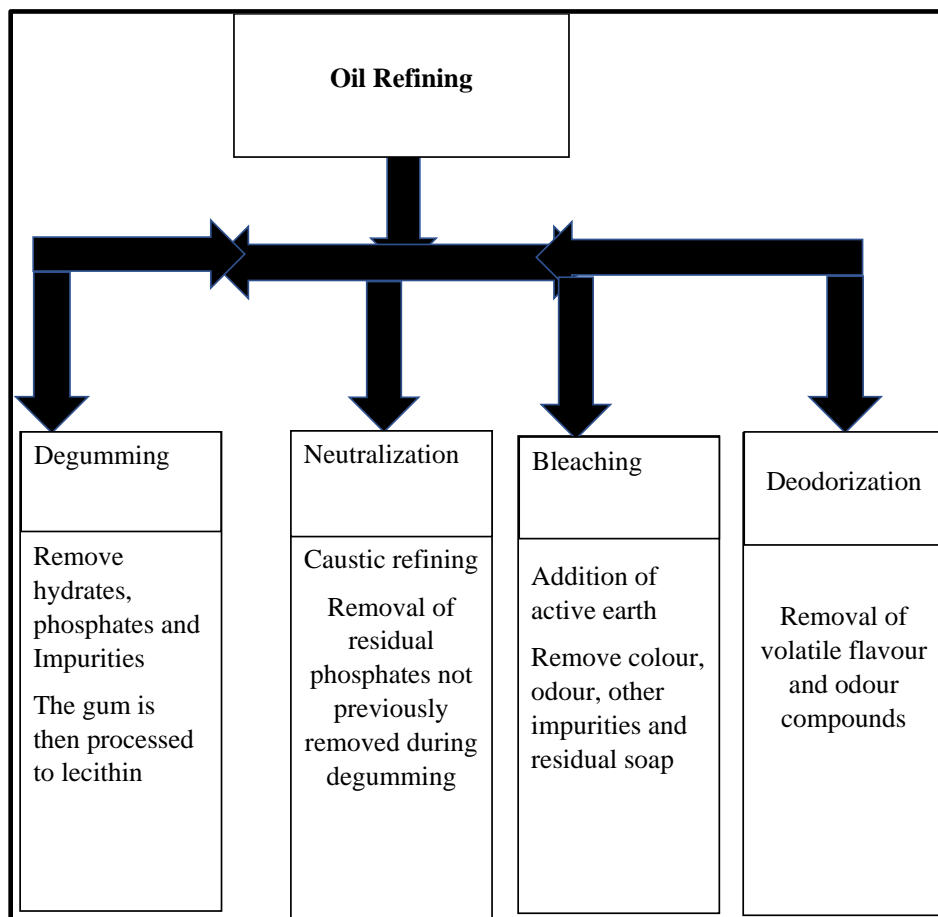


Figure 2.22 A schematic representation of the refining process (Belaid *et al.* 2011)

Characterization of the castor oil specifications were determined according to the techniques reported in the standard methods or applied by researchers investigating in the same or related field.

2.8 Physical characterization

The physical properties of oils depend on their chemical composition as well as operation parameters such as pressure and temperature. For an unknown physical parameter of an oil, it can be determined and compared to the cited standard (Omari, Mgani and Mubofu 2015).

2.8.1. Yield

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 2.1 (Muzenda *et al.* 2012a):

$$Y = (Y_1 - Y_2) / Y_1, \dots\dots\dots \text{Equation 2.1}$$

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. (Muzenda *et al.* 2012a)

2.8.2. Refractive index

The refractive index is a useful rapid measure of purity and quality of an oil (Warra *et al.* 2011). Anton Paar a DMA 4100M model with uncertainties of ± 0.0001 was used to measure refractive index and density of the castor oil at 25 °C. About one drop of the sample was spread over the glass slide of the refractometer. Through the refractometer's eyepiece, the dark portion view was adjusted to be in line with the intersection of the cross. Five repetitions were done and recorded for the castor oil (Akpan, Jimoh and Mohammed 2006; Omari, Mgani and Mubofu 2015; Ospina *et al.* 2016). The results are present in Chapter 4.

2.9 Market demand for castor oil

According to current production and demand trends in South Africa, a possible extraction facility should have a capacity of around 60 kg/day, or 21,9 t/year. South Africa's market for castor oil is said to be quite significant (Belaid *et al.* 2011).

Grandview (2022) reported that global castor oil and derivatives market demand was assessed at 813.2 kilotons in 2018 and is predicted to rise in capacity at a CAGR of 4.1% from 2019 to 2025 as shows in Figure 2.23. This growth can be attributed to the rising use of the product as a biodiesel feedstock.

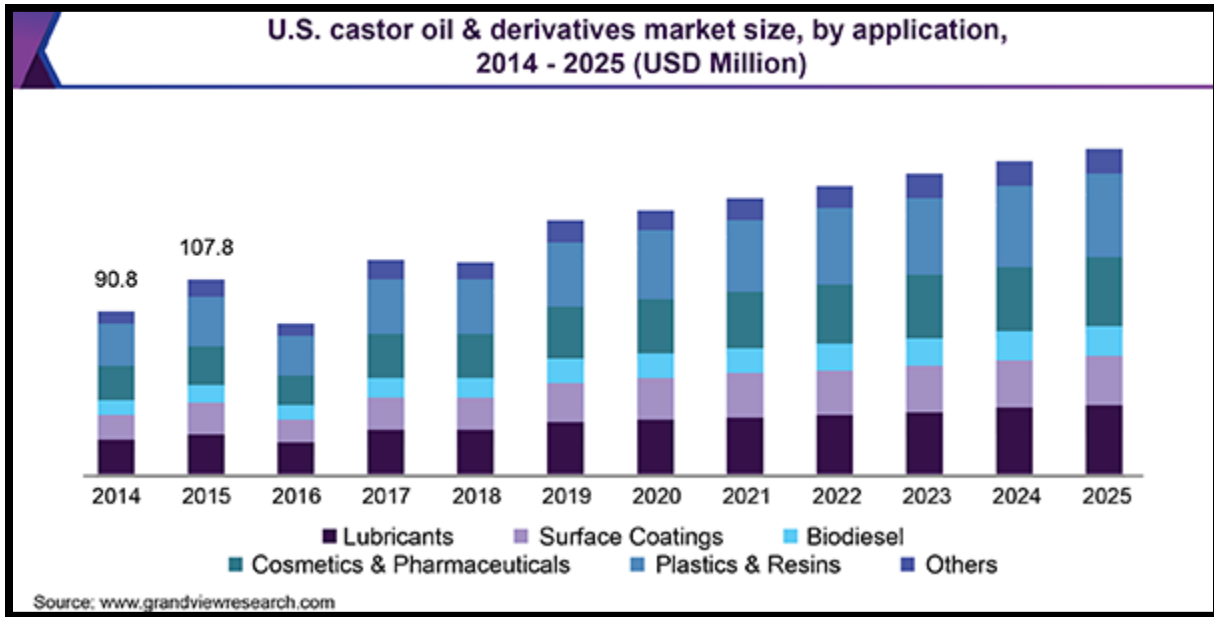


Figure 2.23 A depiction of the uses of castor oil and the derivatives of castor oil in industry
(Grandview, 2022)

It is reported that the United State of America imports on average 76 kilometric tons of castor oil, which is used to produce fatty acids, paints, varnishes, soaps, lubricants, and cosmetics products. The country imports the product from India, Mexico, and Brazil for its domestic needs.

Growing demand for derivatives, particularly hydrogenated castor oil, as a pressure mould releasing component in the plastics industry, is likely to drive market expansion. Castor wax is used in the production of cosmetics and soaps, as well as high-quality aviation grease and multipurpose Calcium/Lithium grease. Crayons, pencils, anti-deodorant sticks, and lipsticks all employ the substance as a component of speciality wax blends. It's also utilized as a mould release agent in the production of rubbers and plastics, as well as sealants and hot-melt coatings that need to be water-resistant. As a result, the market for castor oil and derivatives is expected to grow even further. Due to its low solubility, 12-hydroxy stearic acid (12-HSA) became the most popular product segment in 2018 as represent in Figure 2.24.

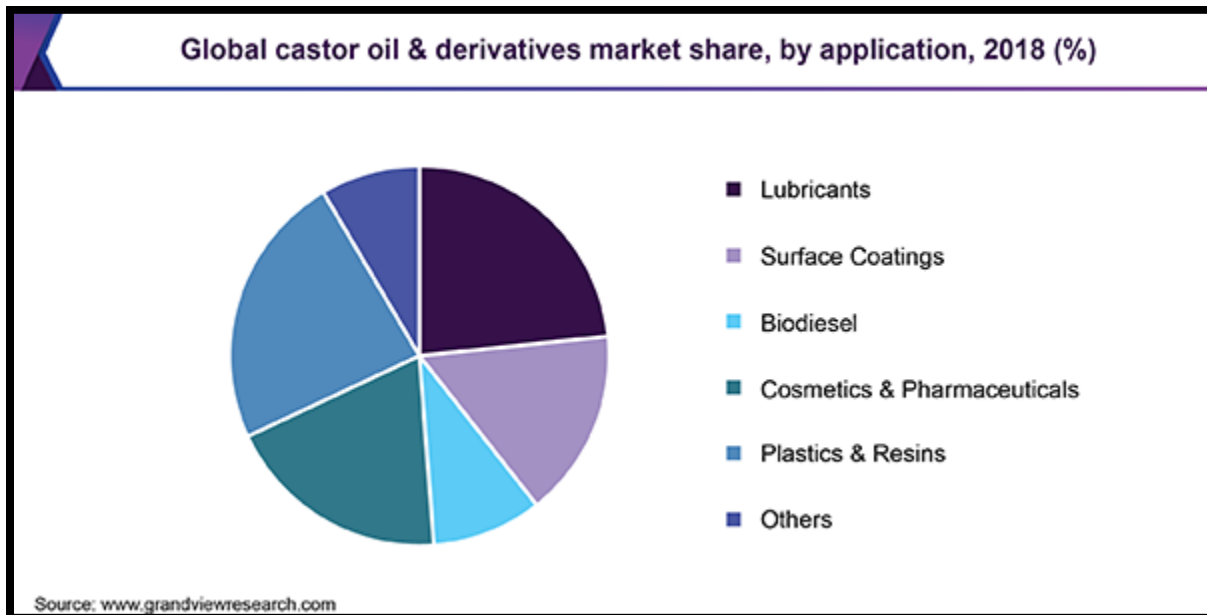


Figure 2.24 Global castor oil and its derivatives by application (Grandview, 2022)

Grandview, 2022 reported that castor oil and castor oil derivatives have a well-established global market with major applications in the plastics and resins industries. Castor oil and derivatives have seen an increase in demand in recent years. As a result, manufacturers and suppliers in the industry have significant opportunities to supply quality and consistent products through an auditable supply chain.

China is reported to have consumed the most castor oil and derivatives in 2018, owing primarily to the gradual expansion of its downstream industries. Sebacic acid dominates overall industrial usage in China, it is reported to be used in the manufacture of a wide range of products (Grandview, 2022).

Plasticizers, candles, lubricants, hydraulic fluids, and resins are examples of industrial products. The industry's challenges include a demand-supply gap as well as the availability of substitutes such as palm oil, sunflower oil, rapeseed oil, sugarcane, corn, and wheat.

As the product becomes more popular in local newspapers and radio stations, more people are becoming interested in the product. It was reported that Sasol Technology had agreed to assist a castor oil producer with additional market research, costing, and pricing to achieve high profit margins ((Belaid *et al.* 2011)). The market price of castor oil was reported to have been at R9-00

per 100 mL; at 100% sales, the net income would be around R1 971 000 per year. For this study, the design of the extraction column and its economic feasibility are calculated based on the mentioned information. The design of extraction and economic are presented in later Chapter. The design was based on experimental data produced from the laboratory. Experimental work was carried out at the Thermodynamics laboratory, the process is explained in further detail in the next Chapter 3.

CHAPTER 3

Materials and Methods

This chapter presents a detailed description of the experimental procedure that was followed to obtain results for this study. The list of apparatus and material used are presented as well as the equations of how to calculate the yield. The detailed description of the Soxhlet extractor is presented in this Chapter. It is used to carry out the experimental work of this study.

3.1 The Soxhlet extractor

The Soxhlet extractor was originally invented in 1879 by Franz von Soxhlet. It was originally designed for the extraction of lipids from a solid material. The Soxhlet extractor allows for unmonitored and unmanaged operation while efficiently recycling small amounts of solvent, it is used when the desired compound has limited solubility in a solvent. The Soxhlet extractor has three main sections: a percolator (boiler and reflux) which circulates the solvent, a thimble (usually made of thick filter paper) which retains the solid to be extracted, and a siphon mechanism that periodically empties the thimble as presented in Figure 3.1. The Soxhlet extractor consist of the condenser; siphon tube; Soxhlet extraction main chamber; a vapor tube; cold water outlet; cold water inlet and heating mantle.

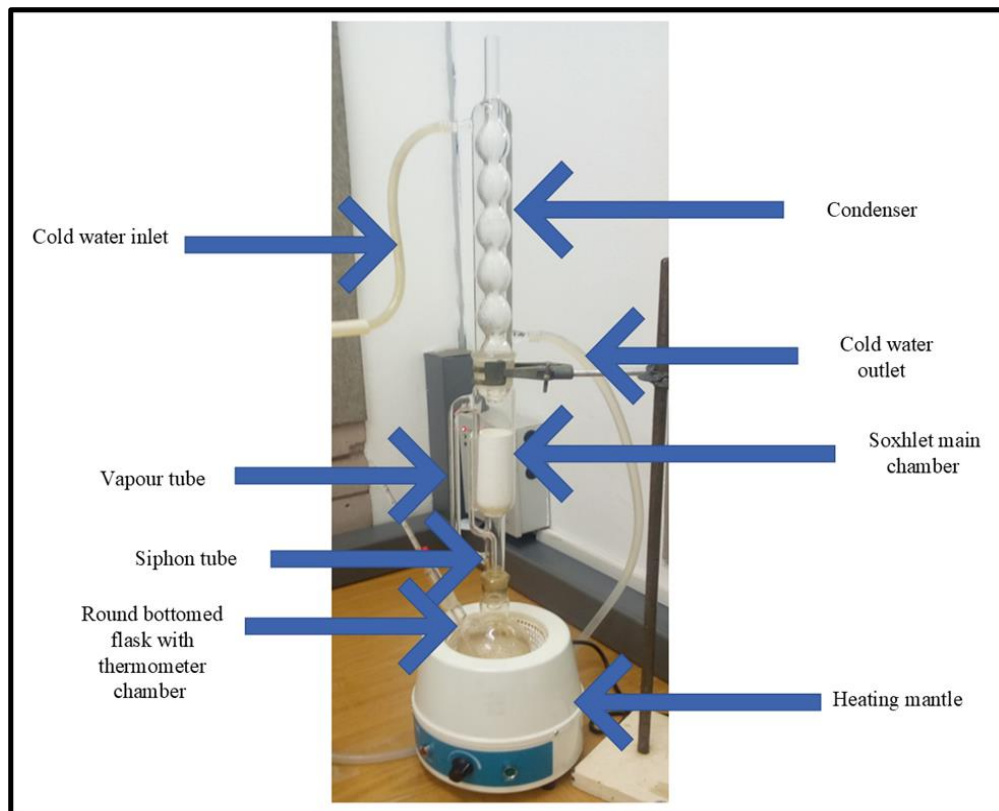


Figure 3.1 An assembled Soxhlet extractor

The vapor tubes provide a path for the solvent vapours to travel up to the main Soxhlet chamber. The siphon tubes provide a path for the extracted fluid to travel down to the round-bottomed flask. The condenser plays the role in condensing the solvent vapours during the extraction process, when the vapours condense, they travel down as droplets into the thimble. The condenser consists of the inlet cold water tube and the outlet cold-water tube. The water flow is counter current. The cold-water tube transports the cold water from the chiller unit at a temperature of 5 °C into the condenser and circulate it.

List of equipment used

- ❖ Oven
- ❖ Soxhlet extractor
- ❖ Digital heating mantle

- ❖ Refractometer
- ❖ Density meter
- ❖ Mass balance scale
- ❖ 10 ml measuring cylinder
- ❖ 20 ml measuring cylinder
- ❖ 250 ml round-bottomed flasks ×2
- ❖ 100 ml round-bottomed flask
- ❖ Mortar and pestle
- ❖ Coldwater bath/Chiller
- ❖ Rotameter evaporator
- ❖ Distillation unit (lab scale)
- ❖ Thermometers
- ❖ Erlenmeyer flask 500 ml

Heating mantle

A digital heating mantle present in Figure 3.2 was used to heat the solvent that was to extract the castor oil from the castor seeds. The heating mantle comes with a temperature probe to measure the temperature of the solvent in the round-bottomed flask during extraction. It is an HMD 2 model that has an uncertainty of ± 0.5 °C, it has the capacity to hold up to 250 ml, the surface temperature goes to a maximum of 450 °C. The temperature control ranges from RT +20 to about 250 °C and it has a heating element made of nichrome wire.



Figure 3.2 The digital heating mantle

Low-temperature water bath/chiller unit

Figure 3.3 presents the low-temperature water bath/chiller unit LTB 25/20 HP CPM is the source of the cold water that will be used for the operation of the condenser in the Soxhlet extractor. The manufacturing uncertainty of ± 1 K was reported.



Figure 3.3 The cold-water bath/chiller

Distillation unit

Figure 3.4 presents a lab scale distillation unit with three essential parts: a round bottomed flask housing the solvent oil mixture which would be heated in the process of distillation, a condenser in which the vapor is cooled and a receiving flask in the distillate is collected. This unit was used to recover the solvent in this study and to measure castor oil produced.

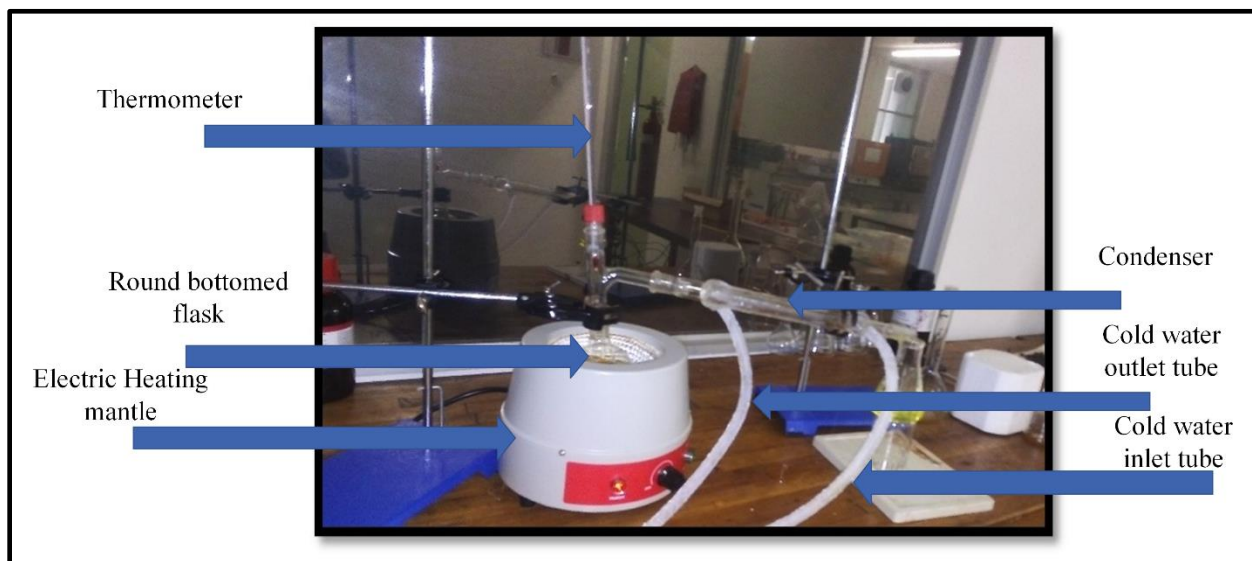


Figure 3.4 The distillation unit apparatus that was used to recover the solvent

Table 3.1 presents all the green solvents and traditional solvent information used to carry out experiments in this study.

Table 3.1 Solvents used

Solvent name	Chemical formula	Molecular weight (g/mol)	CAS number	Purity	Boiling points	Supplier
D-limonene	C ₁₀ H ₁₆	136.238	138-86-3	97%	176 °C	Sigma-Aldrich
Ethanol	C ₂ H ₅ OH	46.07	64-17-5	99%	78.37 °C	Sigma-Aldrich
<i>p</i> -cymene	C ₁₀ H ₁₄	134.21	99-87-6	99%	177 °C	Sigma-Aldrich
α-pinene	C ₁₀ H ₁₆	134.21	7785-26-4	98%	155 to 156 °C	Sigma-Aldrich
Furfural	C ₄ H ₃ OCHO	96.1	98-01-1	99%	161.6 °C	Sigma Aldrich
Hexane	C ₆ H ₁₄	86.81	110-54-3	99%	69.1 °C	Sigma Aldrich

3.2 Experimental procedure

Preparation of castor seeds

Castor seeds were cleaned of debris and stones found in them. The mortar and pestle were used to deshell and ground the castor seeds by pressing hard on the seeds till the hard covering popped open exposing the soft inside of the seeds. The castor seeds before being processed and after being processed are presented in Figure 3.5 to 3.8. The crushed deshelled seeds were then dried in an oven at 75 °C for 18 hours. The size distribution was not taken into consideration because it has no effect. After 18 hours the seeds were further air dried for 48 hours at room temperature before using them.



Figure 3.5 The castor seed before being processed



Figure 3.6 Crushed castor seeds before extraction and drying



Figure 3.7 Crushed castor seed after drying before extraction



Figure 3.8 Crushed castor seed after solvent extraction and drying

To evaluate the moisture content, Equation 3.1 was used (Muzenda *et al.* 2012b; Yusuf 2015; Yusuf *et al.* 2015):

$$\% \text{ moisture} = \frac{w_1 - w_2}{w_2} \dots \dots \dots \text{Equation 3.2}$$

where, w_1 weight of castor seeds before drying and w_2 weight of castor seeds after drying.

The dried castor seeds were further grounded to a smooth paste using the mortar and pestle for ease when extracting.

3.3 Operation procedure

The round bottom flask, Soxhlet apparatus and condenser were flashed or rinsed with acetone to remove impurities, before using them in this study. The castor seeds were first weighed for initial

weight before crushing and placed in a ceramic mortar and crushed using a ceramic pestle, the seeds were then placed in convectional heat oven for drying. The oven was switched on and placed to dry at 60 °C, the crushed seeds which weighed were then taken and weighed the weighed 80 g, before drying they were placed in the oven for drying. The castor seeds were again weighed after drying for 72 hours. The set-up of Soxhlet extractor presented in Figure 3.1 was used to conduct experiments.

- Varying masses of the dried castor seeds were weighed starting 10 g to 15 g.
- 250 ml of the extraction solvent was poured into the round the bottom flask.
- The thimble was placed into the main soxhlet chamber. Then castor seeds were then placed in a cellulosic extraction thimble.
- The Soxhlet was connected to the condenser, which was connected to the chiller.
- The Soxhlet extractor was connected to the round bottom flask, and it was placed into the heating mantle.
- The temperature of the heating mantle was set to 60 °C initially.
- Allowed the extraction to be carried out at different temperatures at extraction times of between 2-6 hours.
- The process is carried out for 3 hours . After the 3-hour interval the process is stopped and the thimble is lifted up using a twizzer and it is allowed to drip dry.
- The castor seeds were emptied on to a square filter paper and placed in the oven for drying.
- The castor seeds were placed in the oven for drying for a time period of an hour at a temperature of 75 °C.
- After drying the seeds were then taken out of the oven and weighed to obtain the weight after extraction and drying.
- The process was repeated for all the solvents at different temperatures closer to their respective boiling points as they all have different boiling points.
- Hexane was used as the test system to verify the the procedure and results produces. The result was compared to the previous works by other researchers. The hexane results are presented in the Chapter 4.
- The extraction was carried out using D-limonene; α -pinene; p-cymene; furfural and ethanol as solvent.

3.4 The recovering of solvent and oil

The process of separating the solvent-oil mixture was carried using a lab scale distillation unit, which consisted of a heating mantle, thermometer, a condenser, an elbow (used for directing flow) and a low temperature water bath as presented in Figure 3.4. The solvent-oil mixture was poured into a 100 ml round bottomed flask and placed inside the heating mantle which was already pre-set at the desired temperature according to the respective solvent. The heating mantle was set just above the boiling point of particular solvent to allow evaporation.

As the mixture started to boil the solvent vapours travelled up to the condenser where the condensed vapours were collected into a 100 ml Erlenmeyer flask and the oil remained in the round bottom flask. The process was continued until no droplets of solvent were present. The amount of the solvent collected was compared to the initially loaded amount. This was done to check how much solvent was lost or consumed and to also calculate how much solvent was recovered. The process was done for all the solvents and co-solvents used. Figure 3.9 presents the samples of the castor oil that was extracted from castor seeds, using the green solvents.



Figure 3.9 Sample of oil extracted using α -pinene and d-limonene

3.5 Characterization of the castor oil

Refractive index and density

For qualitative analysis of the castor oil the Anton Paar was used to measure the refractive index and density. The refractometer is built into the density meter DMA 4100 M for the measurements displayed on the refractometer screen.

Figure 3.10 presents the DMA 4100 M that has an accuracy of ± 0.0002 nD, within a measuring range of 1.26 to 1.72 nD and temperature range of 4 °C to 125 °C. The high accuracy of up to ± 0.03 °C is achieved by precise Internal Peltier temperature control. The optical bench is sealed, and temperature stabilized to protect it from outside influence.



Figure 3.10 Anton Paar DMA 4100 M refractometer with density meter

For calibrating the DMA 4100 M distilled water was used first clean out any dirt or residue left inside the pipes or the system. The built-in fan was open to blow the path to dry it out before beginning calibrating. A syringe was then filled with about 10 ml of distilled water, which was injected into the inlet of the density meter and readings for the distilled water was $998.2 \text{ kg}/\text{m}^3$ at room temperature which corresponded to that reported by (Daimon 2007).

The refractive index eye was wiped with a clean, soft cloth before placing a drop of distilled water a reading of 1.3333 which corresponded to that reported by (Daimon 2007) as presented in Table 3.2. Equation 3.2 was used to calculate the absolute error.

Table 3.2 Measured refractive index of water

Component	Literature (Daimon 2007).	This study	Absolute Error
Water	1.3331	1.3333	0.0002

$$\Delta P = |P_{lit} - P_{meas}| \dots \dots \dots \text{Equation 3.2}$$

Viscosity

The viscosity of castor oil was measured using the Anton Paar oscillation U-tube DSA 5000 M presented in Figure 3-11. Prior to the experimental analysis, ethanol was used to clean the cell, and acetone for drying using the automatic X sample 452 Module. Prior to the viscosity measurements, the distilled water was used at 298.15 K to calibrate Anton Paar oscillation U-tube DSA 5000 M. The measured value was compared to the literature value as presented in Table 3.3. This was to verify that the equipment will produce valid results. The vial filled with sample was placed into the X sample 452. The bubbles formed inside the U-tube pipe were removed by adding more samples automatically until all bubbles were eliminated, and this was done through the camera. The desired temperature was set on the instrument, and it was allowed to stabilize. The viscosity results were displayed in the LED screen and the measurements were repeated three to four times to evaluate repeatability.



Figure 3.21 Anton Paar oscillation U-tube DSA 5000 M.

Table 3.3 Calibration of Anton Paar oscillation U-tube DSA 5000 M using double distilled water at 298 K.

Experimental (mPa.s)	Literature (Pa.s) (Whitakeroil. 2018)	Absolute Error
8.88×10^{-4} Pa. s	8.90×10^{-4} Pa. s	0.02×10^{-4}

The results in Table 3.2 and 3.3 provide confident that this equipment can give valid results for the measurement of this study.

3.6 Safety in the laboratory

1. Lab coat worn before starting any work
2. Keep work area(s) tidy and clean.
3. Make sure that all eye wash stations, emergency showers, fire extinguishers, and exits are always unobstructed and accessible.

4. Only materials that were require were kept in the work area. Everything else was stored safely in the storage room or cabinet.
5. Any equipment that requires air flow or ventilation to prevent overheating should always be kept clear.
6. Fume cupboards were used
7. When working with equipment, hazardous materials, glassware, heat, and/or chemicals, always wear face shields or safety glasses.
8. When handling any toxic or hazardous agent, always wear the appropriate gloves.
9. Before leaving the lab or eating, always wash your hands.
10. After performing an experiment, you should always wash your hands with soap and water.
11. When using lab equipment and chemicals, be sure to keep hands away from the body, mouth, eyes, and face
12. Every chemical should be treated as though it were dangerous.
13. Do not allow any solvent to touch the skin.
14. All chemicals should always be clearly labelled with the name of the substance, its concentration, the date it was received, and the name of the person responsible for it.
15. Before removing any of the contents from a chemical bottle, read the label twice.
16. Do not put unused chemicals back into their original container.
17. Chemicals or other materials should never be taken out of the laboratory.
18. Chemicals should never be dumped in the sink drains.
19. Flammable and volatile chemicals should only be used in a fume hood.
20. If a chemical spill occurs, clean it up and report the incident to the supervisor or lab technician.
21. Ensure that all chemical waste is disposed of properly.
22. Material Safety Data Sheet (MSDS) for all green solvents and castor oil are available in the workplace.

CHAPTER 4

Results and Discussion

This chapter presents the results of the experimental work carried out in the solvent extraction of castor oil from hybrid castor seeds using green solvents. It discusses the effects of the process parameters on the yield of castor oil from castor seeds. The temperature, mass of dry seeds and solvent type were varied and discussed. Five different potential green solvents and co-solvents are discussed in the process to study the effects of each solvent. Best recommended solvent that produced higher yield compared to hexane. The greatest potential solvent that can replace hexane in the process of castor oil extraction is discussed.

4.1 Introduction

Solvent extraction has been the most widely used form of extraction for natural products for in the past years. The extraction process progresses from the solvent penetrating the solid matrix, to the solvent diluting the solute and to the final stage where the solute diffuses out of the solvent. Solvent extraction of solid material is commonly known as solid-liquid extraction, but the correct use of the physicochemical terminology, is leaching or lixiviation. This is one of the oldest ways of solid sample pre-treatment. For this technique of leaching a Soxhlet extractor has been used for over a century (M.D. Luque de Castro* and Garcõa-Ayuso 1998). The Soxhlet extractor is used as the main reference in assessing other leaching methods performance. Initially the Soxhlet was used to determine the fat content in milk (Soxhlet 1879). A solid sample is placed in a thimble and inserted into a thimble holder; the process starts with the solvent boiling once condensed it gradually fills the thimble the process continues with fresh solvent from a distillation ask continually filling the thimble. When the liquid reaches the overflow level, a siphon aspirates the solute of the thimble-holder and unloads it back into the distillation flask, carrying the extracts into the bulk liquid. This operation is repeated until complete extraction is achieved.

This performance makes Soxhlet a hybrid continuous-discontinuous technique (M.D. Luque de Castro* and Garcõa-Ayuso 1998). The process can be considered as a continuous batch process.

The advantages of using the conventional Soxhlet is its ability to continuously bring the sample brought into contact with the fresh solvent, this helps to displace the transfer equilibrium.

The temperature of the system remains relatively high since the heat applied to the distillation flask reaches the extraction cavity. There is no filtration that is required after the leaching step. The sample throughput can be increased by simultaneously extracting in parallel, since the basic equipment is inexpensive. It is a very simple methodology that needs little specialized training, has the possibility to extract more sample mass than most of the latest methods such the microwave-extraction, supercritical fluids, etc, (De Castro and Priego-Capote 2010).

4.2 Green solvents used

Table 4.1 presents all green solvents used to conduct all experiments for this study. Before using green solvents for experiments, it is essential to check for impurities and possible contaminants. One method to verify was to measure refractive index and density then compared to the literature values. Table 4.1 and 4.2 presents refractive index and density, which confirms and provide confidence that all green solvents used were not contaminated. Absolute error was calculated using Equation 4-1. It shows an acceptable error, which is below 1%.

Table 4.1 Refractive index of green solvents

Solvent	Reference		Literature	This study	Absolute Error
Hexane	(Aminabhavi <i>et al.</i> 1996))		1.3749	1.3758	0.0001
D-limonene	(Jiménez Riobóo <i>et al.</i> 2009))		1.4701	1.4730	0.0029
<i>P</i> -cymene	(Pajić <i>et al.</i> 2020))		1.4912	1.4907	0.0005
α -pinene	(Pajić <i>et al.</i> 2020))		1.4631	1.4658	0.0027
Furfural	(Jiménez Riobóo <i>et al.</i> 2009))		1.5235	1.5261	0.0025
Ethanol	(Bonomi <i>et al.</i> 2016))		1.3614	1.3618	0.0004

$$Error = |P_{lit} - P_{calc/meas}| \dots \dots \dots \text{Equation 4.1}$$

Table 4.2 Densities of green solvents used

Solvents	References	Literature (kg/m ³)	This study (kg/m ³)	Error
Hexane	(Aminabhavi <i>et al.</i> 1996))	660.60	660.64	0.04
D-limonene	(Clará, Marigliano and Sólamo 2009))	838.30	838.35	0.05
P-cymene	(Pajić <i>et al.</i> 2020))	857.30	857.38	0.08
α-pinene	(Pajić <i>et al.</i> 2020))	858.00	858.10	0.01
Furfural	(Jiménez Riobóo <i>et al.</i> 2009))	1160.00	1159.92	0.08
Ethanol	(Bonomi <i>et al.</i> 2016))	789.45	789.47	0.02

4.3 Hexane test system

Hexane was used as a test system for this study to validate a Soxhlet extractor and procedure used to perform experiments. This brings confidence to the results obtained when using the green solvents to extract castor oil using a Soxhlet extractor. Table 4.3 presents the castor oil yield obtained using a traditional solvent, which is hexane. The extracted oil yield increases as temperature increases with time (Omari, Mgani and Mobofu 2015). In some cases, the yield results differ because of the geographic location of the seeds that were used in the particular study. In this study, hybrid castor seeds from South Africa were used, then fortunately, they produced a similar yield in the literature of Muzenda *et al.* (2012b). The absolute average deviation (AAD) was calculated using Equation 4.2, and the results are presented in Table 4.3. The reproducibility of the results of hexane brings confidence that all results for green solvents for this study are correct, as well as the procedure.

Table 4.3 Castor oil yield obtained using hexane

Temperature (°C)	Time (hours)	^a Literature (%)	This study (%)	AAD
56	2	31.99	31.36	0.019
60	3	33.44	33.67	0.007

^a(Isah A. G., Mohammed A. and Garba M. 2005; Muzenda *et al.* 2012b))

$$AAD = \left| \frac{P_{lit} - P_{meas}}{P_{lit}} \right| \dots\dots\dots \text{Equation 4.2}$$

4.4 The effect of solvent type on the extraction of castor oil yield

Traditional solvents have been known to be volatile organic compounds, harmful to health and environment and they contribute to troposphere ozone formation and the contamination of water and soil (Bertouche *et al.* 2013b), therefore the type of solvent used in extraction is important.

Figure 4.1 presents the castor oil yield obtained when green solvents d-limonene; ethanol; α -pinene; furfural and p-cymene were used to extract the castor oil from the castor seeds at varied temperatures, varied castor seed weights and solvent content and the extraction obtained when hexane is used. Table 4.4 presents an overall result of the yields obtained from green solvents compared to castor oil yield obtained when hexane is used. For this study the castor oil yield is presented in terms of weight percentage per dry weight of castor seeds. The highest yield obtained 47.13% was obtained using furfural this was followed by ethanol with a yield of 45.37%, the highest oil yield obtained with hexane as the solvent was 31.36%. More description for each green solvents is discussed later in this Chapter.

Table 4.4 Castor oil yield per solvent used

	Percentage yield obtained of castor oil per solvent							
Solvent	Run 1	Run 2	Run 3	Run 4	Run 5	Run 6	Run 7	Run 8
Furfural	39.05	41.14	47.13	23.67	37.33	20.56	41.92	27.21
Ethanol	45.37	28.36	42.59	40.94	37.94	39.15		
D-limonene	39.15	38.66	34.89	30.63	25.20	37.96		
<i>p</i> -cymene	34.33	35.44	32.81	32.13	39.15	35.20		
α -pinene	32.60	22.55	36.07	38.11	26.42			
Hexane	17.4	23.1	29.51	23.67	31.36			

The extraction yield obtained for each solvent was as indicated on table 4.4. The highest yield obtained for each solvent respectively was recorded as follows, d-limonene and p-cymene both obtained a yield of 39.15% respectively and alpha-pinene obtained the least yield at 38.11%. This result could be explained to be attributed to the difference in solvent polarities of the different solvents. Terpenes and alcohols are generally known to be more polar than hexane. It is reported that different solvents yield different natural compounds from a given material, resulting in extract composition between different for each solvent (Bhargavi, Nageswara and Renganathan 2017). Terpenes have a higher dissolving ability for lipids due to their high boiling point which calls for lower viscosity resulting in a higher diffusion rate. The solvents that were ordered were of different volumes therefore some runs were limited at 6 to 8 runs. The runs were repeated three times for reproducibility.

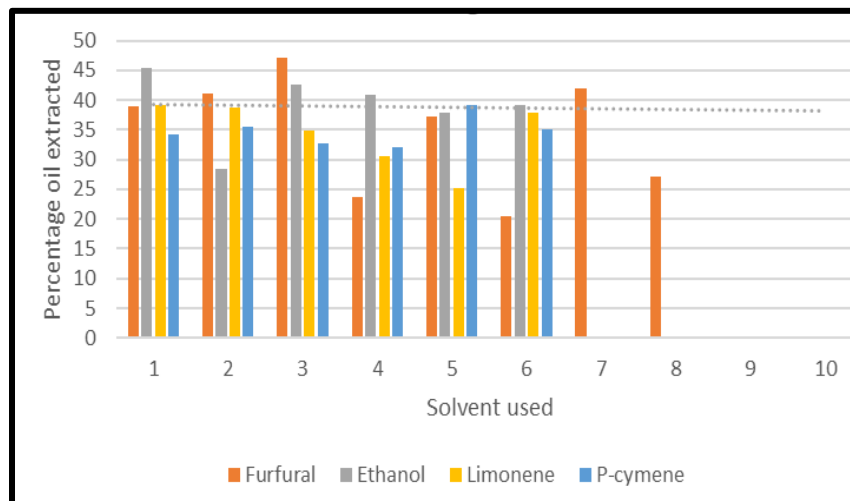


Figure 4.1 A depiction of the castor oil yield obtained per solvent used

It is reported that oil content and oil yield are affected by genotype and location (Koutroubas, Papakosta and Doitsinis 1999). In this study high yielding hybrid castor seeds were used from South Africa. It is reported that the first commercial castor seeds hybrid, GCH 3, was developed in India. This hybrid had potential seed yields 88% higher than the existing cultivars, medium maturity (140–210 d), and high oil content (466 g kg⁻¹) (Severino *et al.* 2012) .

In a study conducted by Mamidipally and Liu (2004b) for the extraction of rice bran oil using d-limonene, d-limonene evidently extracted a significantly higher amount of rice bran oil than hexane. This observation was reported to contributed to by the polar nature of d-limonene. In a study conducted by Li *et al.* (2014) for the extraction of rapeseed oil solvents (α -pinene, limonene, ethanol, *p*-cymene, hexane, isopropanol and butanol) the highest yield was reported to have been obtained using *p*-cymene followed by d-limonene the least yield was from ethanol, this is was reported to have been due to the difference in solvent polarity. This was further reported to have been due to the affinity of ethanol to oil being temperature dependent and the temperature of extraction was reportedly low, hence leading to not achieving solvation (Li *et al.* 2014).

Crushing the castor seeds ensured that the walls are broken down which allowed for ease of penetration by solvent to achieve maximum or almost maximum yield of castor oil. Terpenes have the highest boiling temperature which leads to a lower viscosity of the solvent and this allows for a better diffusion rate of the solute from the solid phase to the solvent (Li *et al.* 2014). Ethanol

and the terpenes (d-limonene; furfural; p-cymene and α -pinene) portrayed qualities of good extractive ability and selectivity by achieving higher oil yields.

4.4.1 The effect of time on the castor oil yield

The castor oil yield extracted from castor seeds using d-limonene; α -pinene; p-cymene; furfural and ethanol as solvents are presented in Figure 4.2 to 4.6. The results shows that the yield increase with increasing time in hours. After an hour of heating the solvent, the yield of extracted oil increased as the extraction time increased. The extraction time had a direct impact on the extraction of castor oil, and this was reported by (Akaranta and Anusiem 1996).

In Figure 4.2, it is observed that the oil extraction using d-limonene was conducted for 2 hours and 30 minutes where the oil extracted was 37.96% this was within the range that was suggested by (Akaranta and Anusiem 1996; Li *et al.* 2014), when the extraction time was at just above the 3 hour mark the yield had attained was 35.74%. A significant drop in oil yield was observed at 6 hours 17 minutes where the extraction yield obtained was 25.20% which was the lowest yield obtained for extraction using limonene as a solvent. At the interval time of 5 hours 17 minute and 5 hours 3 minutes the oil yield obtained was the highest at 39.15% and 38.66% as at these intervals the extraction was not continuous but was rather conducted at 2–3-hour intervals and left to rest before continuing with the extraction. Oil extraction carried out using limonene experienced the least level drop of oil extraction, as the percentage difference was recorded to be 5.85%. This observation suggested that extraction was high when the extraction time was shorter (between 2-3 hours), as when extraction is carried out for longer periods the extraction yield significantly decreased therefore extraction time is to be kept at period of 2-3 hours for the best extraction yield.

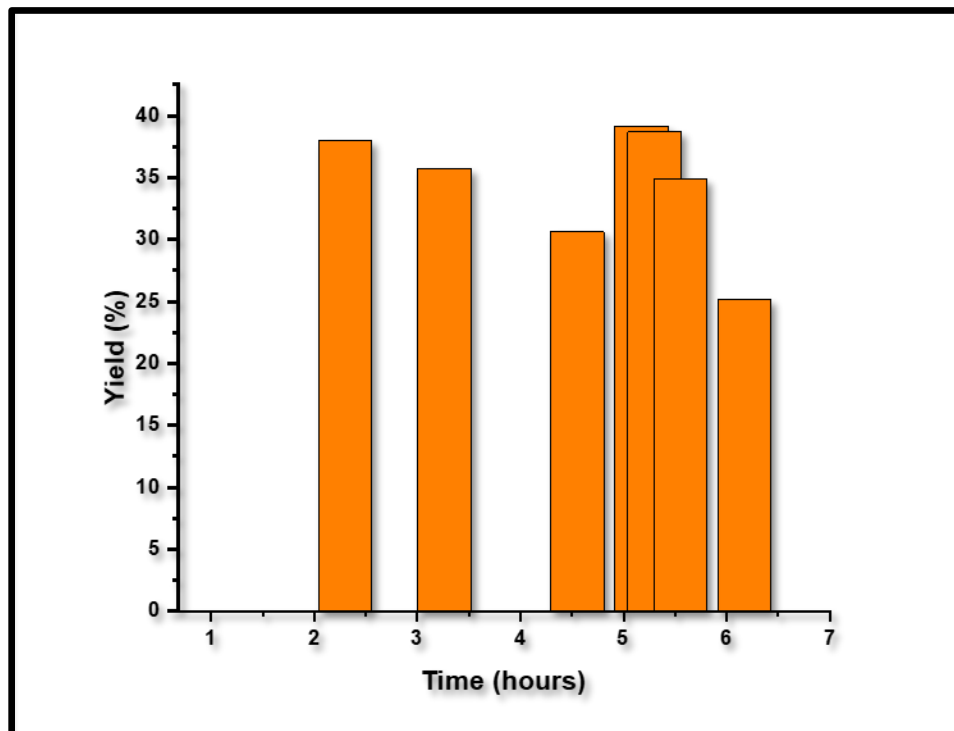


Figure 4.2 Graph depicting the castor oil yield obtained over time when d-limonene was used as solvent

Figure 4.3 presents an extraction of castor oil using ethanol as a solvent for extraction. This green solvent had the highest castor oil yield with oil yield ranging from the highest yield obtained of 45.37% to the lowest yield of 28.36%. The highest yield was obtained at a duration of 2 hours and 20 minutes, a significant drop to 28.36% was observed at 3 hours and 38 minutes this could be attributed to other factors such as temperature and the mass of castor seeds as at 3 hours and 40 minutes the yield was at a high of 42.59%. It is reported that the high polarity of ethanol gives it the ability to engage with other polar molecules (Bhutada *et al.* 2016). During prolonged intervals the oil yield slightly dropped to 39.05%, which was oil yield that was still well within the range of 30-53% as reported by (Li *et al.* 2014). It is reported that oil yield is also affected by the water content in both the solvent and castor seeds could affect the oil yield obtained, the oil yield obtained for seeds that have 0% moisture was higher than that of those that had a moisture content of 7.83% more energy is required for extraction if there is moisture in the material to be extracted (Santos *et al.* 2015).

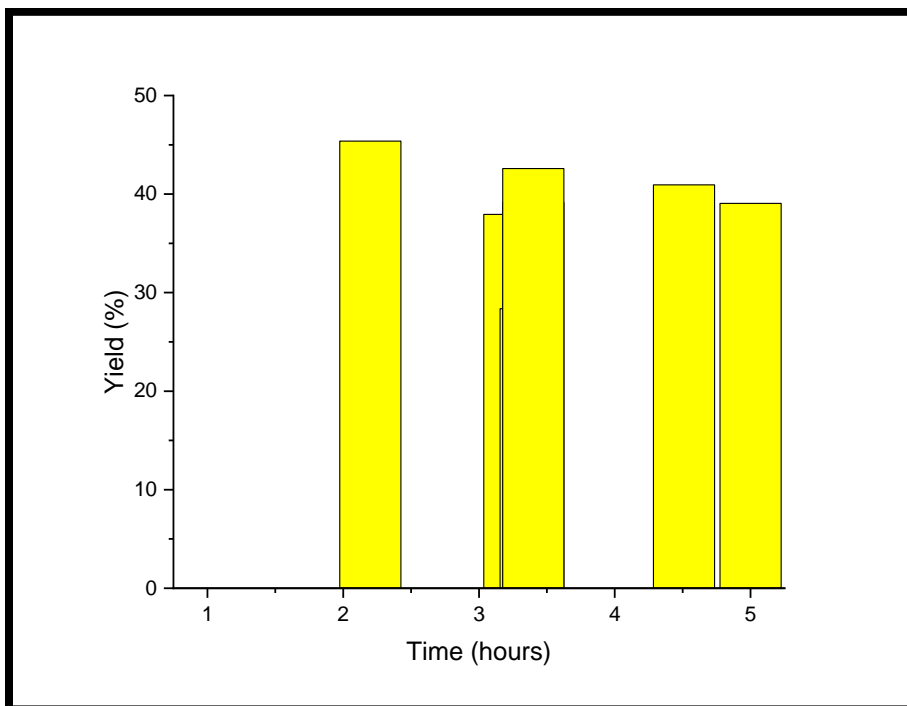


Figure 4.3 Graph showing castor oil yield obtained using ethanol as the solvent

The results for the extraction of castor oil using α -pinene are presented in Figure 4.4; the highest oil yield was 38.11% for a time interval of 3 hours and 23 minutes, the oil yield obtained was within the 43-53% that was reported in literature of (Akaranta and Anusiem 1996). The lowest yield was between the time interval of 5 hours where a yield of 22.55% and 26.42% respectively. It is important to that the extraction time is presented with additional 5 minutes to account for the warmup phase. The oil yield obtained is also as a result of the mass that was weighed for extraction therefore the extraction time and extraction yield will differ per solvent as different masses were used for the solvents, the lesser the mass of the castor seeds taken for extraction the lesser time it took to extract the oil but then this had an impact on the oil yield obtained also, meaning lesser yields where there was lesser mass to extract oil from.

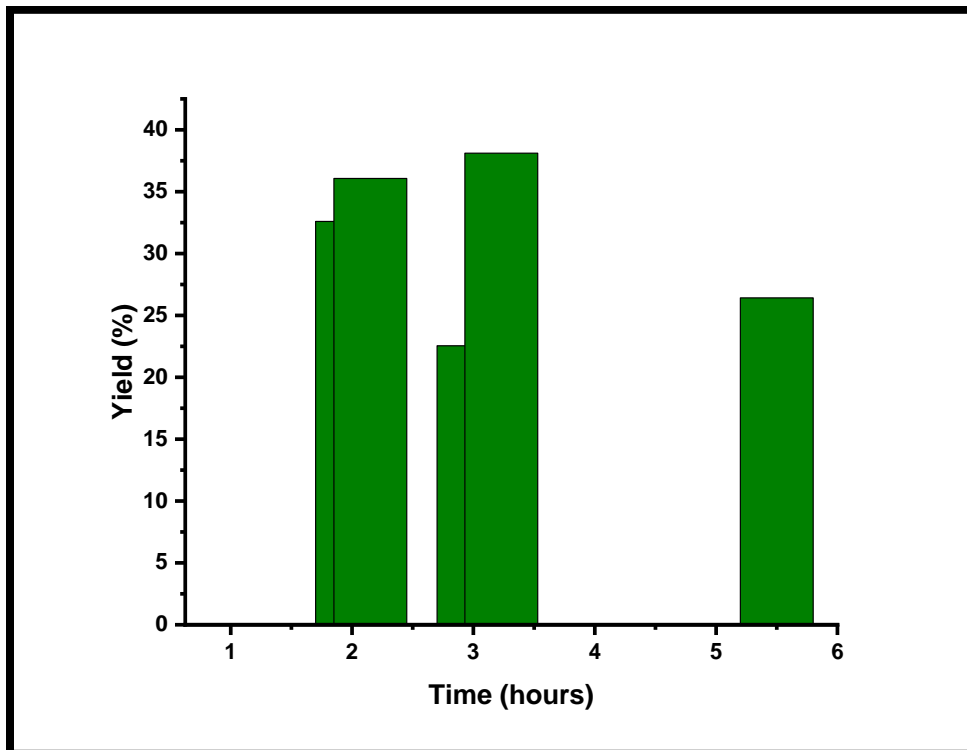


Figure 4.4 Graph of castor oil yield obtained when using α -pinene as the solvent

In Figure 4.5 extraction was conducted using *p*-cymene as a solvent for the oil castor oil extraction, this green solvent yielded oil ranging from the highest yield obtained of 39.15% to the lowest yield of 35.13%. The highest was obtained at duration of 7 hours and 35 minutes; the 7 hours 35 minutes were reached running at intervals of 4 hours and 3 hours over 2 days. When extraction was carried out within the 2-to-3-hour interval the extraction achieved oil yield of 35.13%, 35.20%, 35.33%, 36.44% and 36.81% the oil achieved had did not have significant changes as the time was increased. The percentage oil yield was well within the specified range of oil yield. When considering energy usage, the extraction carried out 3 hours 30 minute was the more favourable as it achieved good oil yield, with lesser energy been used than the extraction that was carried out in 2 days though more oil yield was obtained.

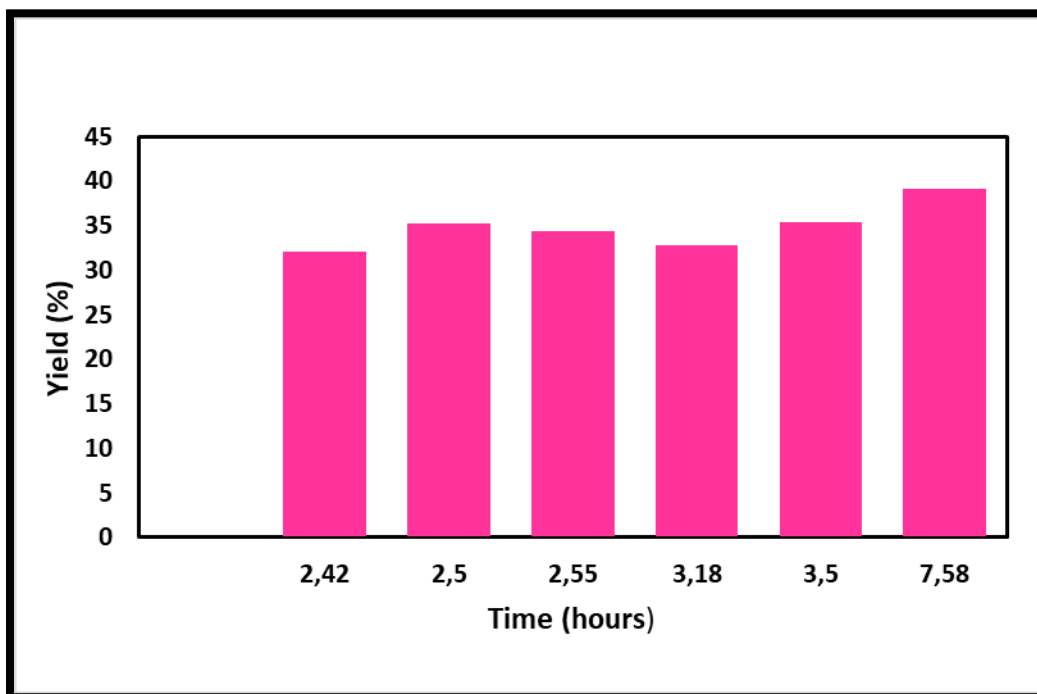


Figure 4.5 Graph showing castor oil yield obtained when using *p*-cymene as the solvent

Figure 4.6 presents the results of the oil yield obtained from extraction using furfural, in the first 2 hours of extraction the yield of oil extracted was 37.33%. The yield of oil extracted gradually decreased with increase in time when the time of extraction was extended to 3 hours and 4 hours the oil yield decreased to 27.21% and 23.67% respectively. The extraction was then conducted for 2 hours then it was left to rest or soaked the solvent and then restarted being ran for a further 2 hours, when the extraction was conducted in this manner the yield increased. The oil yield for an extraction time of 4 hours 30 minutes resulted in 41.92% and for an extraction time of 5 hours was 47.13%. When the extraction was conducted in the manner of running the Soxhlet extraction for 2 hours or 3 hours and then letting it rest to continue at a later stage there was evidently higher extraction but when the extraction was conducted to a further 3 hours (6 hours interval) the oil yield decreased to an extraction of 39.05%.

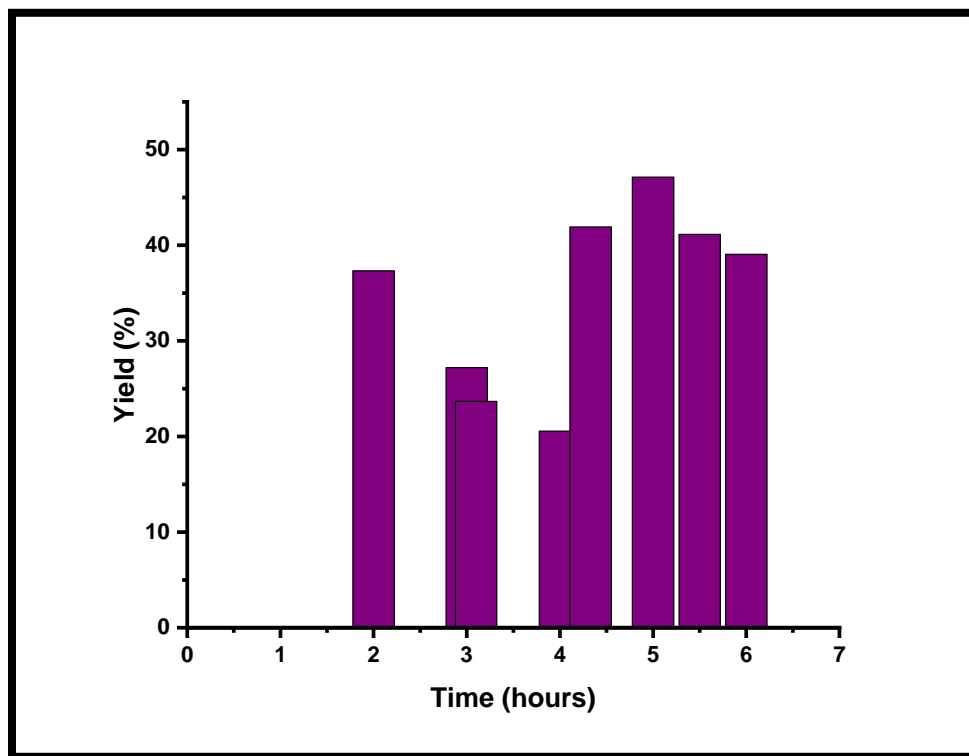


Figure 4.6 Graph showing castor oil yield obtained when using furfural as a solvent

4.4.2 The effect of temperature on the castor oil yield

In this study temperature has showed a positive effect on the oil extraction yield as oil yield increased as the temperature increased, this is shown in the Figure 4.9 to 4.12. In a study conducted by (Muzenda *et al.* 2012b) it was also observed that with an increase in temperature the yield also increased. This was the explained to have been due to the viscosity of the solvent decreasing at elevated temperatures which caused an increase in the diffusivity of solutes and solvents resulting in an increase in the extraction rate. The oil yield was observed to have been greater for the terpenes and alcohol, though oil yield increased with increased temperature for the extraction carried out with hexane it did not compare to that of terpenes. Terpenes (α -pinene, p-cymene, d-limonene, and furfural) naturally have high boiling points, so their extraction took place at high temperatures, hence the oil yield was more. In a study conducted by (Li *et al.* 2014) it was reported that terpenes solubility parameters were generally found to be more stable at higher temperatures than alcohols because of the hydroxyl group.

For this study a digital heating mantle was used, for accuracy a thermometer was inserted into the round bottomed flask to give the exact temperature of the solvent vapours as they flowed to the condenser. As the temperature reading rose bubbles started forming but this would last a little while but as the solvent continued to heat up and the temperature rose to close to the boiling point. The solvent bubbled and vapours started flowing up to the condenser through the vapor tube, this happened till the Soxhlet chamber filled with the solvent and extraction took place. The digital heating mantle was set at the respective temperatures, but the actual temperatures read on the thermometer were the actual boiling point temperatures or close to the boiling temperatures, this was a result of slow transition on the mantle. When hexane was used for the extraction at 30 °C there was no extraction observed but when temperature on the heating mantle was set to 56 °C, bubbling of the solvent was observed when the temperature reading was at 56 °C.

For the rest of the solvents the same observation was made that at lower temperatures there was no evident extraction taking place hence the temperatures were raised to temperatures closer the boiling point temperatures of each solvent respectively. At temperatures higher than that of the boiling point temperatures the solvents would boil to a point of overflowing, hence the temperatures were kept at temperatures close to the boiling point. At higher temperatures the solvent filled the extraction chamber faster, the castor seeds were observed to have a change in colour after the extraction had taken place, they turned from a brownish colour to a whiteish colour a picture of the observation in Chapter 3 Figure 3.12.

In Figure 4.7 presents the oil yield of castor oil extracted using ethanol, it is evident that the extraction increased from 37.94% at the temperature of 50 °C. The oil yield increased to 40.94% as the temperature increases to 60 °C. At the temperature of 70 °C, the yield obtained was 42.59% and a maximum yield of 45.37% was obtained at the temperature of 78 °C. The boiling point temperature of ethanol is 78.37 °C. The results obtained at 78 °C which was the highest yield proves that ethanol near or at boiling point temperature is a good solvent for the extraction of vegetable oils, but at ambient temperatures and at decreasing alcohol concentrations the oil solubility decreases appreciably (Akaranta and Anusiem 1996). At higher temperature of 90 °C, which is above the boiling point therefore there is not enough contact between the castors crushed seeds and solvent. This leads to lower castor oil yield of 28.36%. Consequently, it is not recommended to run experiment above the temperature of the solvent.

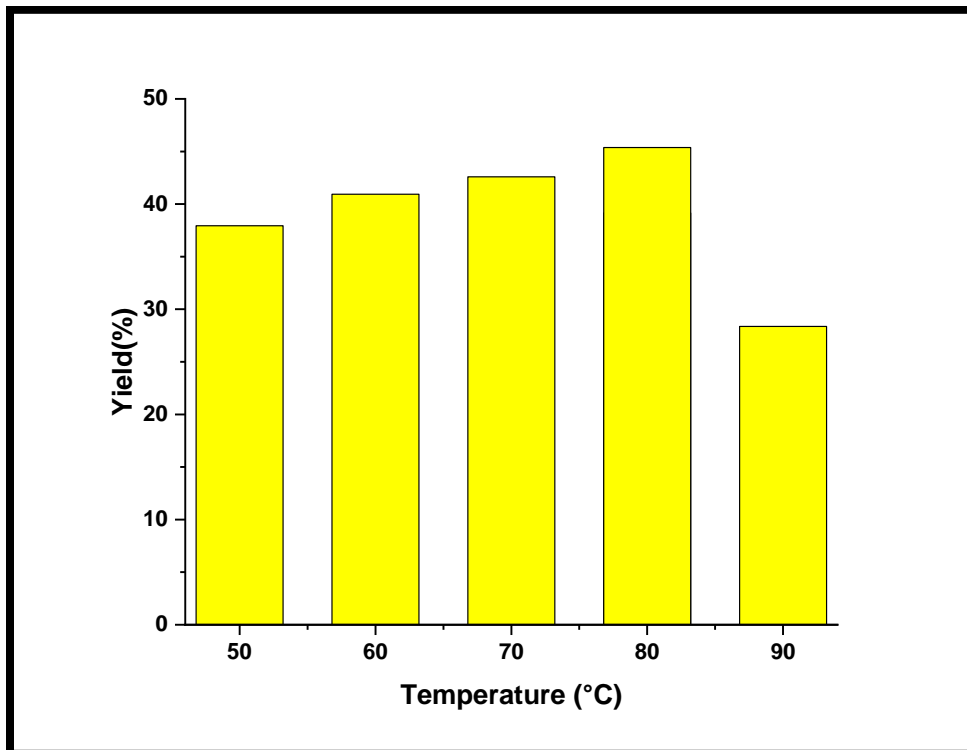


Figure 4.7 Graph showing the effect of temperature on yield using ethanol as solvent

The relationship between temperature and castor oil yield during extraction using furfural as a solvent is depicted in Figure 4.8. It is observed that when the extraction was conducted at the temperature of 73 °C, the yield obtained was 41.92%. Then, when the temperature was increased to 80 °C, the yield obtained was 40.33%. The boiling point temperature of furfural was reported is 162 °C as a result of furfural having such a high boiling point temperature it was evident that furfural was able to extract the highest yield of oil, at 95 °C the oil extracted was 47.13%. At the temperature above 100 °C, the yield shows a rapid decrease, this shows that furfural has limitation on temperature. Furfural is one of the most promising solvent for replacing hexane but has challenges observed in this study. Furfural is not a recommendable solvent to use in the near future to replace hexane although it produced the highest castor oil yield, as it is difficult to recover.

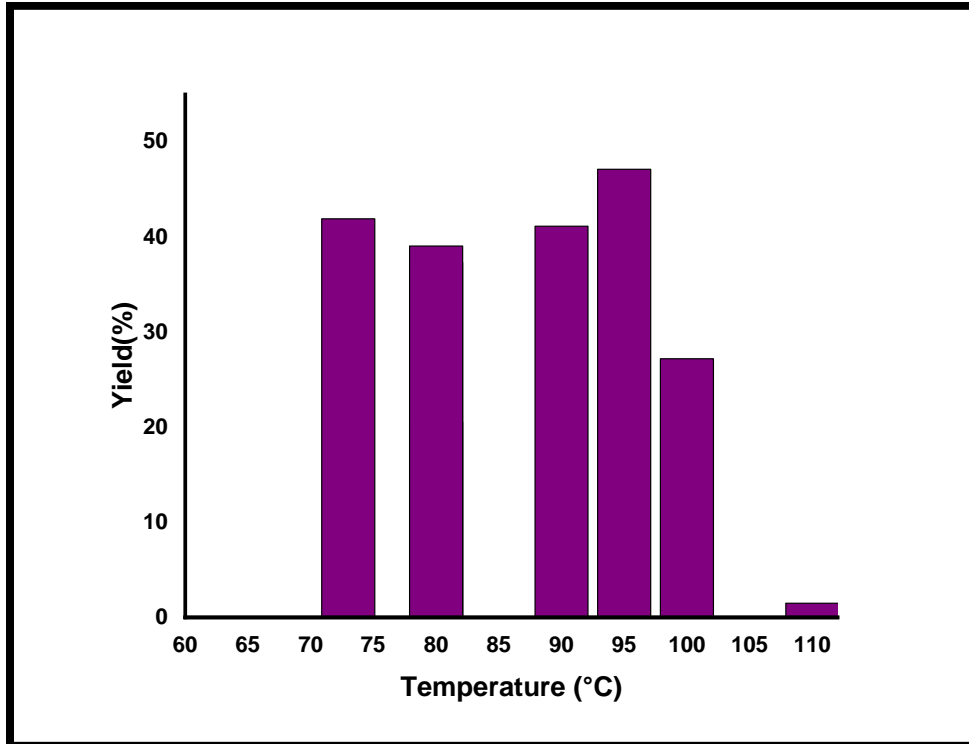


Figure 4.8 Graph showing the effect of temperature on the oil yield using furfural

Figure 4.9 presents the effect of temperature on castor oil yield using d-limonene as solvent. The extraction was started at a temperature of 80 °C where the oil yield extracted was 34.89%. When the temperature was increased to 90 °C and the yield increased to 39.15%. An effect that time had on yield was that the temperature was increased with increased time, and this led to the decreased castor oil yield. This observation was made when the temperature was increased to 95 °C, the oil yield extracted was 30.63%, which was dropped by 12%. When the extraction temperature is raised to higher temperatures, it was observed that castor oil yield of 37.11% was obtained. It is reported that prolonged extraction time at high temperatures causes oxidation and degradation of the desired compounds (Spigno, Tramelli and De Faveri 2007; Che Sulaiman *et al.* 2017).

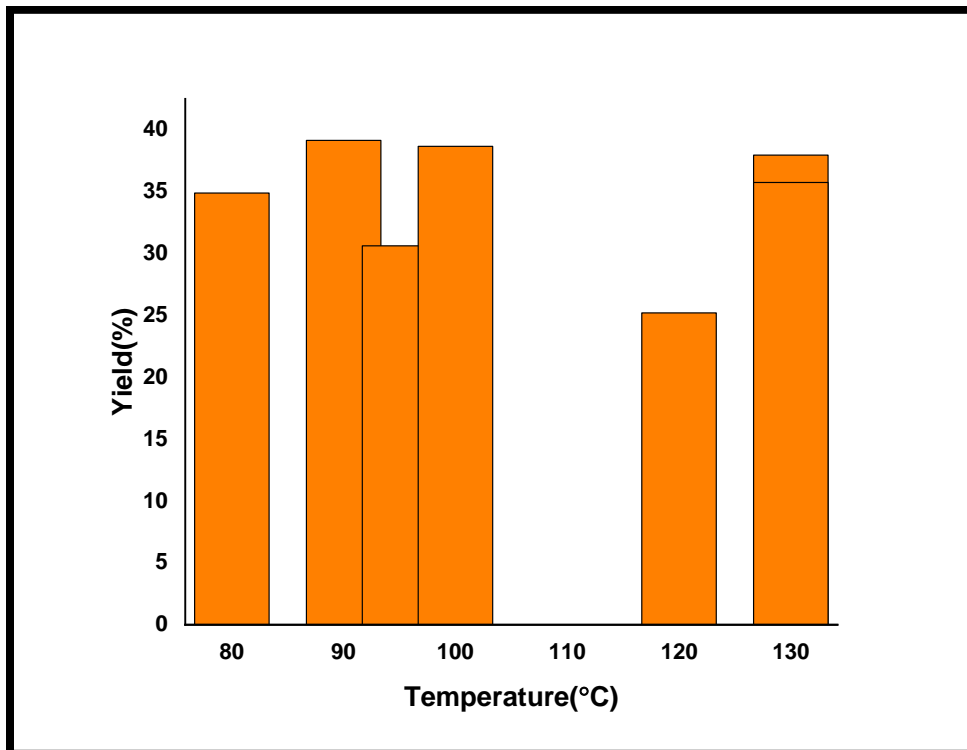


Figure 4.9 Graph showing the effect of temperature on oil yield using d-limonene as solvent

Figure 4.10 shows the relationship of the temperature and castor oil extracted when *p*-cymene was used as solvent. The extraction obtained when the temperature was at 80 °C the oil extracted was 39.15%. The castor oil extracted was observed to decrease the yield as the temperature increases.. The castor oil yield obtained at the temperature of 120 °C is 32.13% that is below of the hexane. Therefore, *p*-cymene is not recommended green solvent to use.

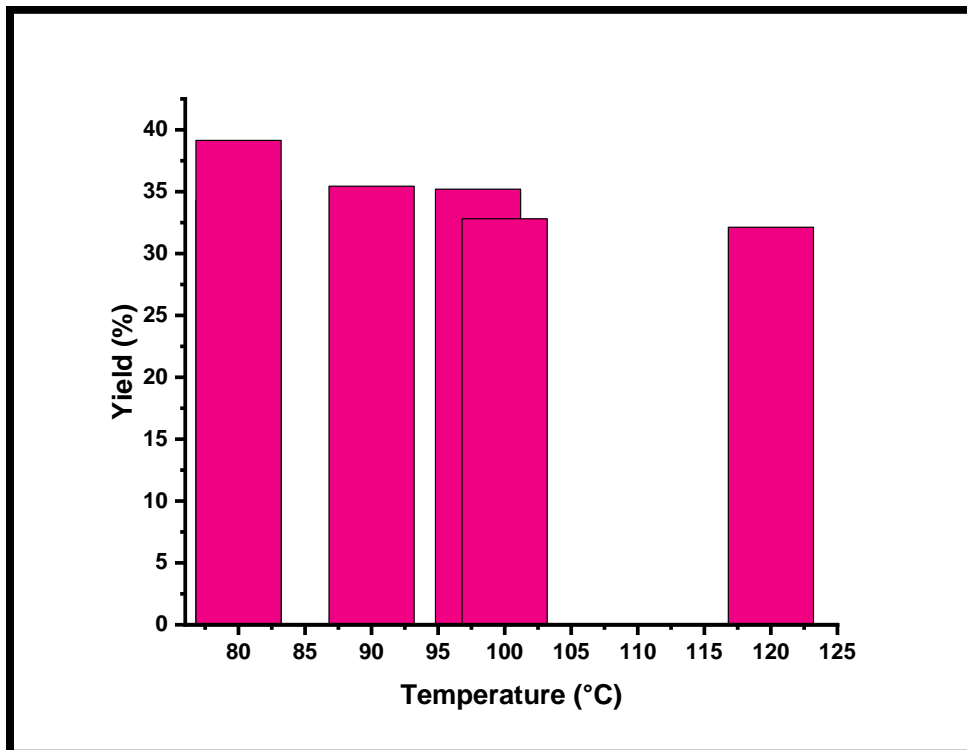


Figure 4.10 Graph showing the effect of temperature on oil yield using p-cymene as solvent

Figure 4.11 presents the results of castor oil yield using α -pinene as solvent for extraction. A similar observation was made when the extraction was carried out using *p*-cymene, when the extraction temperature was 75 °C the oil yield was 32.6%. When the temperature was increased to 80 °C the oil extracted increased to 36%, but gradually decreased with increased temperature. When the time of extraction was shortened, and the extraction temperature was increased to 100 °C the oil yield was obtained was 38.11%. Therefore, α -pinene is not recommended green solvent to use over hexane because when the temperature increases the oil yield decreases. This shows that the solvent is not spending enough in the castor crushed seeds.

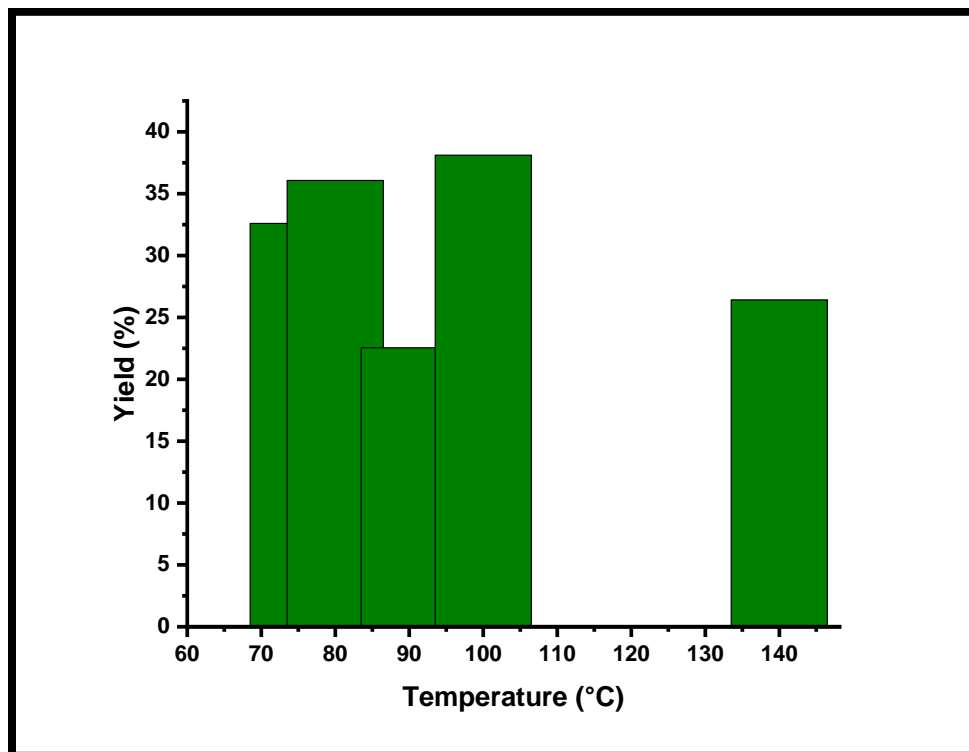


Figure 4.11 Graph showing the effect of temperature on oil yield when α -pinene is used

Optimum conditions for the castor oil yield are presented in Table 4.5 for each of green solvent investigated in this study. Table 4.5 shows highest or best castor oil yield obtained at different times. Furfural shows the highest castor oil yield obtained in longer time of 6 hours. This is time consuming and energy, which is costly. The real process needs the solvent that produced higher castor oil yield at the shortest time to maximum the production and profit. Consequently, ethanol shows the percentage of castor oil extracted at 45.37% at the shortest time of 2 hours and at the temperature of 78 °C, which makes it more favourable.

Table 4.5: Optimum conditions for highest castor oil yield

Solvent	Temperature (°C)	Time (hours)	Castor oil yield (%)
Furfural	95	6 hours	47.13
d-Limonene	90	5 hours 17 min	39.13
α -pinene	100	3 hours 23 min	38.11
P-cymene	80	7 hours 35 min	39.15
Ethanol	78	2 hours 2 min	45.37

4.5 Castor oil produced

Castor oil extracted from castor seeds is a viscous, pale yellow, non-drying and non-volatile drying oil (Hincapié, Mondragón and López 2011). The initial observation that was made as the extraction was taking place. The change in colour of the solvent shows that there was indeed extraction taking place. The solvents used were clear in colour except for furfural which had a dark brownish-purple colour. It is reported by (Ogunniyi 2006) that has different physical and chemical properties that vary with the method of extraction. Cold-pressed castor oil has low acid value, low iodine value and a slightly higher saponification value than solvent-extracted oil, and it is lighter in colour.

The experimentally obtained castor oil was darker in colour when compared to standard castor oil obtained from industry as shown in Figure 4-12. It was reported that castor oil is a pale straw colour but turns colourless or slightly yellowish upon refining and bleaching (Akpan, Jimoh and Mohammed 2006). Due to time constraints and limited resources, for this study the castor oil was not taken through the refining and bleaching process hence the darker colour.



Figure 4.12 Samples of extracted castor oil from green solvent

The density of a liquid or material is defined as the measure of its mass per unit volume (e.g., kg/m^3). The density of vegetable oil is lower than that of water and the difference in density of

vegetable oils are quite small, particularly amongst the common vegetable oil (Kazeem *et al.* 2014; Patel *et al.* 2016). The density of oil generally decreases with molecular weight yet increases with unsaturation level. Table 4.6 presents measured physical properties of castor oil at the temperature of 25 °C after removing the solvent. The physical properties results show that it is pure castor oil obtained and there are no traces of solvent. The measured data of castor oil were compared to the literature data of (Omari, Mgani and Mubofu 2015). The absolute error was calculated using Equation 4.1, it is acceptable error.

Table 4.6 Physical properties of castor oil produced

Parameter	^a Literature	This study	Units	Absolute Error
Refractive index	1.4746	1.4751	nD	0.0005
Density	674.31	674.34	mPa.s	0.03
Viscosity	961.10	961.12	kg/m ³	0.03

^a(Omari, Mgani and Mubofu 2015)

From the initial amount of mass of castor, crushed seeds of 100 g were introduced into the round bottom with 150 ml of green solvents. Table 4.7 presents an amount of castor oil produced at optimum conditions, showing different amounts obtained because of different times. Ethanol shows the highest amount of castor oil obtained in the shortest time. The results show that ethanol has been recommended to be used to replace hexane in industrial processes.

Table 4.7 Castor oil produced

Solvent	T/ (°C)	Time (hours)	Castor oil yield (%)	Amount produced (ml)
Furfural	95	6.0	47.13	14.6
d-Limonene	90	5.17	39.13	13.2
α-pinene	100	3.23	38.11	7.8
p-cymene	80	7.35	39.15	11.4
Ethanol	78	2.20	45.37	15.3

4.6 Green solvents recovery after castor oil extracted

It is important to separate the mixture of castor oil produced and green solvents used in that particular time. Green solvents were recovered using a simple distillation unit presented in Chapter 3 in Figure 3.6. The process of recovery of each solvent was discussed earlier, where the set temperature of heating mantle is just above the boiling point of the solvent, except for furfural that was difficult to recover. This was done to ensure there is no solvent traces in the castor oil produced. The boiling point of castor is 313 °C, therefore all investigated green solvents had the boiling point far below of the castor oil. The vapours of solvent were condensed. The condensed liquid was collected until there is no droplets. There is no specific time during the recovery of the solvent. The physical properties such as refractive index and density of each recovered solvent was measured. Table 4.8 presents the measured physical properties at the temperature of 25 °C after it completed to cool, then the recover solvent was compared to the literature values. This was done to ensure that the recovered solvent is still pure and there is no reaction take place during the extraction, which can alter the physical properties. From the Table 4.8 shows pure green solvents that were recovered. Absolute error was calculated using Equation 4.1.

Table 4.8 Physical properties of the recovered green solvent

Solvent	This study Refractive index (nD)	Literature Refractive index (nD)	Absolute Error	This study density (kg/m ³)	Literature density (kg/m ³)	Absolute Error
Ethanol	1.3661	^a 1.3614	0.0047	789.22	^a 789.47	0.25
D-limonene	1.4873	^b 1.4701	0.0185	840.61	^d 838.35	2.26
<i>p</i> -cymene	1.4886	^c 1.4912	0.0026	861.88	^c 857.38	4.50
α -pinene	1.4706	^c 1.4631	0.0075	860.83	^c 858.10	2.73
Furfural	–	^b 1.5235	–	–	^b 1159.92	–

^a(Bonomi *et al.* 2016)); ^b(Jiménez Riobóo *et al.* 2009)); ^c(Pajíc *et al.* 2020)); ^d(Clará, Marigliano and Sólino 2009))

There was no castor oil produced when furfural was used as the solvent. It is too difficult to separate the mixture. Several methods, including simple distillation, and rotary vacuum

distillation, were used to recover furfural, but these methods were proved to be unsuccessful. However, furfural obtained the highest yield compared to other green solvents. It is not recommended green solvent be used in the industrial process to replace hexane. One has to investigate more why furfural is not easily separated from the mixture of castor oil and furfural. Maybe there is an unawareness of the reaction occurring during the extraction process. In Table 4-8, the refractive index and furfural density are unavailable because nothing was recovered.

4.7 Moisture content of castor seeds

The moisture content of the castor seeds was calculated for the crushed castor seeds before the extraction process, to minimize the water content in the seeds. The castor seeds were dried in an oven at temperature of 75 °C for the period of 18 hours. After drying the castor seeds, the moisture content was measured. It was found that the moisture content was 6.50%. The moisture content was calculated using Equation 3.1 in Chapter 3. It was revealed that the moisture content was within the range of 5-7% reported by (Doan 2004). Therefore, the result of the moisture shows that the castor seeds are matured. The moisture content of 4.15% was reported by (Akaranta and Anusiem 1996). The composition and moisture content of castor seeds some time differ because it is dependent on the geographical location it is planted and harvested (Patel *et al.* 2016). In a study carried out by (Vallejos, Rondanini and Wassner 2011), it was stated that physiological maturity is attained when seeds had a water content of $21.8 \pm 2.4\%$. Therefore, the result of the moisture shows that the castor seeds are matured.

4.8 Production of castor oil using co-solvents

Co-solvents are substances that are added 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 boundary layer of both reactants. Kusdiana and Saka (2004), 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.

From the green solvents that were used (d-limonene, *p*-cymene, ethanol, and α -pinene) for the extraction of castor oil. The ratios of 1:2 was measured for each solvent which would then be used as co-solvent mixtures. Since ethanol was observed to produce higher yield of castor oil even when the system was manipulated where 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 volume ratio of ethanol was measured to be twice that of the respective co-solvent. The co-solvent mixtures were prepared as follows: *p*-cymene-ethanol; α -pinene-ethanol and d-limonene-ethanol. Table 4.9 presents castor oil yield obtained for co-solvent mixtures; the mixture of *p*-cymene-ethanol solvent mixture produced the highest yield of 43.29%. Figure 4.13 presents the extracted castor oil at the period of 2 hours. An amount of 9.8 ml of castor oil was produced after the separation the mixture of co-solvents and castor oil using the simple distillation equipment. After the separation of the mixture, the co-solvent was not separated.

Table 4.9 Castor oil yield obtained per co-solvent mixture

Co-solvent	Castor oil yield extracted (%)
d-limonene-ethanol	34.80
α -pinene-ethanol	41.09
<i>p</i> -cymene-ethanol	43.29

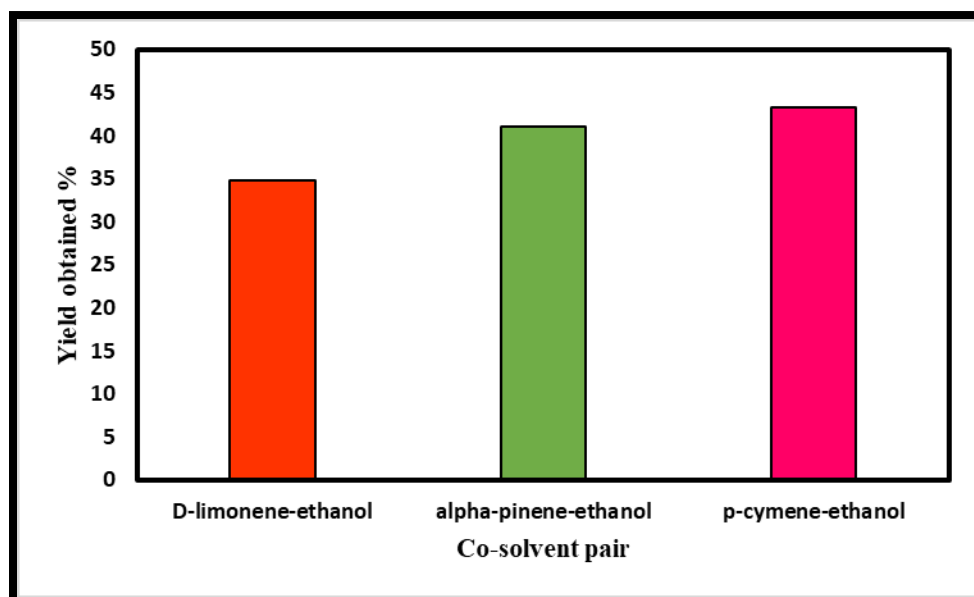


Figure 4.13 Co-solvents mixtures on yield of castor oil yield

4.9 Scaling up the castor oil production to meet industry expectations

The castor oil yield obtained experimentally from ethanol was used to calculate weight of seeds that would be required to produce castor oil at a larger scale. In a feasibility study carried out by (Belaid *et al.* 2011), it was stated that the current production and demand trends required that possible extraction facilities meet a capacity of close to 60 kg/day, which is equivalent to 21.9 ton/year. The highest yield was obtained from ethanol which also showed selectivity and extractability qualities that are desirable in a solvent.

The highest yield was obtained over a period of 2 hours, this time was then converted to a weight per day rating as the capacity is in weight per day. The castor oil obtained after extraction was 15.3 ml. The highest oil yield was used to scale up as the highest oil yield was obtained at optimal conditions. Converting the measurement to match those of the required production per day in Table C1 in Appendix C. The conversion factor was to be 3201.559. The scale up factor was calculated the method and equations in the literature of (Hassim *et al.* 2019). In a study on animal feed using castor cake (Heuzé *et al.* 2020), reported that one ton of castor seeds produced 300-500 kg of castor oil and 500-700 kg of castor cake. The extraction of castor oil produces a by-product called the castor oil cake or castor oil meal. This castor oil cake is valuable for animal feeding but needs to be detoxified first as it is high in a toxic protein ricin. For the optimal condition the highest castor oil yield was obtained using a mass of 0, 01016 kg castor seeds which produced 0,4537g castor oil. This was used to up scaled by scaling factor that was calculated using the original oil yield obtained, dividing by the new yield that we needed for a possible pilot scale production. Then, the data obtained was used to design the extraction column, which is presented in the next chapter.

CHAPTER 5

Design of extraction column and Economic study

This chapter presents the design of the extraction column that can be used in industry. Other equipment in the process of the production of castor oil was not designed. The extraction column was selected to design because it is the critical equipment where the extraction is taking place. There are two types of extraction process, the liquid-liquid extraction process also known as solvent extraction and there is the solid-liquid extraction which is known as leaching. Both these extraction types follow the same principle, which is the separation of compounds, based on their relative solubilities in two different immiscible either liquid or solid matter compound (Donau, 2022).

5.1 Solid-liquid extraction column design

For the purpose of this study the solid-liquid extraction was used to extract castor oil from solid castor seeds. The principle for the solid-liquid extraction is that the soluble compounds of a solid matter are extracted by a solvent. Therefore, solid-liquid extraction column was designed. It can be included in the cells like oil in oil seeds or as fine dispersion on the solid matter like caffeine.

Extraction process is recommended for separation of:

- Non-volatile components
- Mixtures which cannot be separated using other separation procedures
- Mixtures whose vapour-liquid-phase equilibria show azeotropic features
- Temperature sensitive

Figure 5.1 shows the typical industrial process in the production of castor oil. Using the results of the castor oil yield obtained in this study an extraction unit was designed for a pilot scale extraction plant. A batch stirred solid-liquid extraction column was designed to produce 60 kg per day of castor oil. Appendix B present the detailed design of solid-liquid extraction column. The height of the extraction column was calculated to 2 m and the diameter of the tank was calculated to be 2 m. The extraction column will have an impeller which has a diameter of 1 m and height of 1.5 m. The design extraction column has 4 baffles. A safety factor of 2% was considered for the design and a

filling capacity of 80% was considered. The extraction column has a separate entrance for the castor seeds and the solvents.

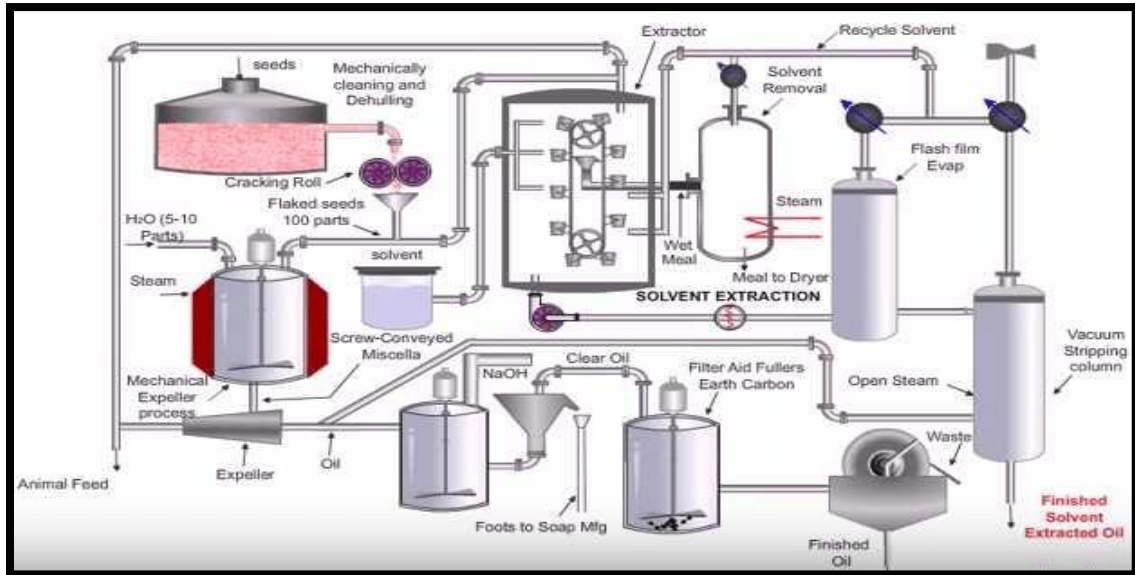


Figure 5.1 Castor oil extraction process flow diagram (Lonescu *et al.* 2016)

5.2 Preliminary economic study

A preliminary economic study was conducted for the batch extraction column for the pilot plant. The estimated capital investment for a 60 L capacity batch extractor was R 3 326 831,90. Sigma Aldrich of Merck is currently selling castor oil at a price of R460.60 per 250 ml to R1000 per litre depending on the quality of the oil. Taking into consideration the prices of castor oil above, the tank capacity, the yield that was obtained and assuming 24 hours, 330 days production cycle sales projection was made for both the scaled-up yield and the un-scaled up yield. For the scaled-up production yield of 60 kg per day at a castor oil cost and a converted amount of castor oil per kg, the sales projected before removing any operations cost were as follows, for the amount of R1919.17 castor oil per kilogram castor oil, the annual sales were estimated to be R37 999 566. Using the price of R651.97 per kilogram of castor oil, the annual sale was estimated at R12 909 006 these estimates are not the true value of the projected sales as the operating costs were not considered but rather the extraction column refer to Appendix B for the estimates calculation.

Estimated annual sales were also projected for the un-scaled castor oil yield again the extraction unit was taken into consideration and the same parameters as for the scaled-up yield. The projected annual sales were projected for the price of R1919.17 per kilogram of castor oil, the sales were R842 323.71 and for the price of 651.97 per kilogram of castor oil, the sales were at R286 149.63. The estimated or projected annual are not a true indication of the actual sales as these values are overestimated as per the scaling factors by Peter and Timmerhaus (1991).

CHAPTER 6

Conclusion and Recommendation

6.1 Conclusion

The objectives of this study were stated in the introduction as follows:

- ✓ Evaluating the potential solvents that are environmentally friendly, not harmful, not expensive and give the best yield of castor oil
- ✓ To design extraction column for the production of castor oil.
- ✓ To evaluate an economical design for the extraction process to produce oil from the seeds.

The Soxhlet extractor was a selected method to extract castor oil from castor seeds. The Soxhlet extractor apparatus was set up and the hexane test system was conducted to extract the castor oil. The results obtained agreed with the literature values from previous studies. This was gives confident on the procedure and equipment itself that it can produced an accurate result for unknown systems that include green solvents and co-solvents.

All objectives were met for this study. In the process of finding the most suitable solvent for the extraction of castor oil, the parameters that affected the yield of the castor oil were investigated. The type of solvent on the yield obtained the effect of temperature on yield and the time of extraction was investigated to understand the effect each parameter had on the yield. The high-ranking solvents will used to experimentally verify the performance of solvents for the extraction of the oil from the castor seed. It was found that green solvents extraction capabilities can be ranked as follows: the castor oil yield of furfural was 47.13% at an extraction time of 6 hours at the temperature of 95⁰C; ethanol was 45.37% at an extraction time of 2 hours and 2 minutes at the temperature of 78⁰C; D-limonene was 39.15% extraction time of 5 hours and 17 minutes at the extraction temperature of 90⁰C; *p*-cymene was 39.15% at an extraction time of 7 hours and 35minutes at the extraction temperature of 80⁰C and α -pinene was 38.11% at an extraction time of 3 hours and 23 minutes at the extraction temperature of 100⁰C. While the extraction using furfural obtained a higher yield, the recovery of furfural proved difficult. Distillation was used to separate the oil and solvent

combination, recovering the solvent that was used in the process. Ethanol was found to be the next best solvent for the extraction since it yielded 45.37%. Consequently, ethanol is an environmentally friendly, not harmful, not expensive and give the best yield of castor oil, meets one of the mentioned objectives. Co-solvent was also measured, it was found that p-cymene-ethanol mixture provides the highest yield compared to other co-solvent mixtures.

An extraction column was designed using the data obtained using ethanol as a solvent as it gave the best results amongst the other green solvents. For a pilot scale production, the yield obtained was scaled up to the theoretically accepted yield. An economic study was carried out to determine the annual sales which were projected using two different prices as castor oil has different price ranges because of the difference in the quality of castor oil. The annual sales were projected to be R37 999 566 and R12 909 006 for the price of R1919.17 per kilogram castor oil and R651.97 per kilogram castor oil, respectively. These sales estimates were for scale up values and ranges, the operational costs were not considered therefore these sales were overestimated, but these prove that there is a potential for profits in castor oil production.

6.2 Recommendations

It is recommended that one has to investigate why furfural is not separated from the mixture of castor oil and furfural. What can be the best method for the separation? Investigate whether there is any reaction that is taking place during the extraction. It is recommended that one Design the whole industrial equipment using the data for the best green solvent, ethanol. Then, a full economic feasibility study that shows profit margins is recommended to be done. The optimization of the process is required using engineering software such as Aspen, Design expects, etc.

The kinetics model of the best green solvent in the production of castor oil is recommended to be studied in detail.

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APPENDIX A

A.1 Calculation of the percentage castor oil yield

Sample calculation of the yield:

The yield of the castor oil was calculated using the equation (Yusuf *et al.* 2015), the yield is by % by weight.

$$\%yield = \frac{y_1 - y_2}{y_1} \times 100 \dots\dots\dots \text{Equation A-1}$$

Temperature of T=80 °C

Duration 10: 36 am to 15 :45 pm

$$y_1 = 10.83 \text{ g}$$

$$y_2 = 6.60 \text{ g}$$

$$\%yield = \frac{10.83 - 6.60}{10.83}$$

$$= 39.058\%$$

2. Temperature of T = 90 °C

Duration 12: 42 pm to 16:20 pm stopped and continued from 08:46 am to 11:25 am

$$y_1 = 15.02 \text{ g}$$

$$y_2 = 8.84 \text{ g}$$

$$yield = \frac{15.02 - 8.84}{15.02} \times 100$$

$$41.14\%$$

3. Temperature of T=95 °C

Duration 11: 40 am to 16:30 pm

$$y_1 = 12.37 \text{ g}$$

$$y_2 = 6.54 \text{ g}$$

$$\%yield = \frac{12.37 - 6.54}{12.37} \times 100$$
$$= 47.13\%$$

4. Temperature of T = 90 °C

Duration 13: 40 pm to 16 :40 pm

$$y_1 = 12.42 \text{ g}$$

$$y_2 = 9.48 \text{ g}$$

$$\%yield = \frac{12.42 - 9.48}{12.42} \times 100$$
$$= 23.67\%$$

APPENDIX B

B.1 Sales estimation

Price of castor oil <https://www.sigmaaldrich.com/>

250 ml is R460,60

1 l is R625,24

$$\frac{250\text{ml}}{1} \times \frac{1}{1000\text{ml}} \times \frac{1\text{ m}^3}{1000\text{ l}} \times \frac{959\text{ kg}}{\text{m}^3} = 0.23975\text{ kg} = 0.24\text{ kg}$$

Therefore, castor oil per kg is $\frac{460.60}{0.24} = \text{R}1919.17/\text{kg}$

$$\frac{1\text{ l}}{1} \times \frac{1\text{ m}^3}{1000\text{ l}} \times \frac{959\text{ kg}}{\text{m}^3} = 0.959\text{ kg}$$

Therefore, castor oil per yield $\frac{625.24}{0.959} = \text{R}651.97/\text{kg}$

Production rate is 60 kg/day

Sales forecast for the upscaled production

$$60\text{ kg/day} \times \text{R}1919.17/\text{kg} \times 330\text{ days} = \text{R}37\,999\,566$$

$$60\text{kg/day} \times \text{R}651.97/\text{kg} \times 330\text{ days} = \text{R}12\,909\,006$$

Production rate is kg/day

Sales forecast for if not scaled up assuming operation is 24 hours a day 2 hourly run ,330 days

Mass by weight of oil yielded 45.37%

Mass of oil 4.61 g in 2 hours 2min

Conversion G to kg

$$\frac{4.61}{1000} = 0.00461\text{ kg oil}$$

Rate of extraction

$$0.00461 \text{ kg oil} / 2 \text{ hours} = 0.002305 \text{ kg/hour}$$

Therefore, 0.002305 kg in 1 hour assuming the plant operates 24 hours rate will be 0.05532 kg/hour

Conversion to kg /day

$$0.05532 \text{ kg/hour} \times 24 \text{ hours} / 1 \text{ day} = 1.33 \text{ kg/day}$$

$$1.33 \text{ kg/day} \times R1919.17 / \text{kg} \times 330 \text{ days} = R842\,323.71$$

$$1.33 / \text{day} \times R651.97 / \text{kg} \times 330 \text{ days} = R\,286\,149.63$$

APPENDIX C

Extraction column design

Table C.1 Extraction unit design

Extraction Unit Design			
Data/Assumptions			
	Units	Value	
Feed rate of castor seeds	Kg/batch	500	
Feed rate of Solvent	Kg/batch	1500	
Density of castor seeds	kg/m ³	538	
Density of Ethanol	kg/m ³	789	
Reaction temperature	°C	80	
Charging time (tf)	min	10	
time to reach temperature(tH)	min	25	
Reaction time (Tr)	min	120	
Time take to empty extractor(tE)	min	25	
Thermal conductivity of insulator	w.m/k	0,063	
Tank design			
1. Total Batch Time	$tF + tH + tR + tE$	min	180
2. Tank Capacity	$V = (mc/qc + (ms/qs))$	m ³	2,830509
20% safety factor	$v * 1,20$	m ³	3,39661
80 % filling capacity	$v / 0,80$	m ³	4,245763
3. Tank diameter	$v = \pi D^2 h / 4$	m ²	1,755343
Tank diameter	D _{tank use}	m	2
4. Tank height	$HT = D$ (rounded of to 2m)	m	2
Height of head	H _h =0,10H	m	0,2
Height of bottom	H _b =0,10H	m	0,2
Total height of tank	H _t =H _h +H _b +H _t	m	2,4
5. Allowable max tensile strength	$S = S_u + F_m + F_a + F_r + F_s$	psi	15000
6. Density of solution	$q = m/v$	kg/m ³	706,5868
7. Internal pressure	$P = H \rho g + P_{atm}$	pa	16737,2
Impeller design			
8. Impeller diameter	$Da / DT = 0.5$	m	1
9. Length of impeller	60-80% of Tank diameter	m	1,5
10. Width of impeller	$W / Da = 1/8$	m	0,13
11. Elevation of impeller	$C / Dt = 1/3$	m	0,666667
12. Baffel design	$J / Dt = 1/12$	m	0,166667
12.a. Number of baffels			4