Castor Oil: Properties, Uses, and Optimization of Processing Parameters in Commercial Production



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ABSTRACT: Castor oil, produced from castor beans, has long been considered to be of important commercial value primarily for the manufacturing of soaps, lubricants, and coatings, among others. Global castor oil production is concentrated primarily in a small geographic region of Gujarat in Western India. This region is favorable due to its labor-intensive cultivation method and subtropical climate conditions. Entrepreneurs and castor processors in the United States and South America also cultivate castor beans but are faced with the challenge of achieving high castor oil production efficiency, as well as obtaining the desired oil quality. In this manuscript, we provide a detailed analysis of novel processing methods involved in castor oil production. We discuss novel processing methods by explaining specific processing parameters involved in castor oil production.

KEYWORDS: castor oil, castor beans, ricinoleic acid, nonedible oil, crude castor oil refining

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Introduction

Castor oil has long been used commercially as a highly renewable resource for the chemical industry.^{1,2} It is a vegetable oil obtained by pressing the seeds of the castor oil plant (*Ricinus communis* L.) that is mainly cultivated in Africa, South America, and India.^{3,4} Major castor oil-producing countries include Brazil, China, and India. This oil is known to have been domesticated in Eastern Africa and was introduced to China from India approximately 1,400 years ago.⁴ India is a net exporter of castor oil, accounting for over 90% of castor oil exports, while the United States, European Union, and China are the major importers, accounting for 84% of imported castor oil.^{5,6}

India is known as the world leader in castor seed and oil production and leads the international castor oil trade. Castor oil production in this country usually fluctuates between 250,000 and 350,000 tons per year. Approximately 86% of castor seed production in India is concentrated in Gujarat, followed by Andhra Pradesh and Rajasthan. Specifically, the regions of Mehsana, Banaskantha, and Saurashtra/Kutch in Gujarat and the districts of Nalgonda and Mahboobnagar of Andhra Pradesh are the major areas of castor oil production in India.⁷ The economic success of castor crops in Gujarat in the 1980s and thereafter can be attributed to a combination of a good breeding program, a good extension model, $\begin{array}{l} \textbf{COPYRIGHT:} @ \mbox{the authors, publisher and licensee Libertas Academica Limited.} \\ This is an open-access article distributed under the terms of the Creative Commons CC-BY-NC 3.0 License. \\ \end{array}$

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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 produced from this crop is considered to be of importance to the global specialty chemical industry because it is the only commercial source of a hydroxylated fatty acid.⁹ Even though castor oil accounts for only 0.15% of the world production of vegetable oils, worldwide consumption of this commodity has increased more than 50% during the past 25 years, rising from approximately 400,000 tons in 1985 to 610,000 tons in 2010.^{9,10} On average, worldwide consumption of castor oil increased at a rate of 7.32 thousand tons per year. In general, the current rate of castor oil production is not considered sufficient to meet the anticipated increase in demand.

There are various challenges that make castor crop cultivation difficult to pursue. Climate adaptability is one of the challenges restricting castor plantation in the U.S. The plant also contains a toxic protein known as ricin, providing a challenge from being produced in the U.S. It also requires a labor-intensive harvesting process, which makes it almost impossible for the U.S. and other developed countries to pursue castor plantation. Castor plant grows optimally in tropical summer rainfall areas. It grows well from the wet tropics to the subtropical dry regions with an optimum temperature of 20°C–25°C. The high content of the oil in the seeds can be attributed to the warm climate conditions, but temperatures over 38°C can lead to poor seed setting. Additionally, temperatures low enough to induce the formation of frost is known to kill the plant.¹¹

As of 2008, three countries (India, China, and Brazil) produced 93% of the world's supply of castor oil. Because production is concentrated mainly in these three countries, total castor production varies widely from year to year due to fluctuations in rainfall and the size of the areas utilized for planting. As a consequence, this concentration has led to cyclic castor production. Thus, diversification of castor production regions and production under irrigation would hopefully reduce the climatic impact on castor supplies.⁹

In the United States, the hazardous chemical products found in the castor plant, especially ricin has been a major concern.9,12-15 The body of scientific literature related to castor plants, especially on the detailed processing parameters involved in commercial production, has been relatively small over the past century.9 Over the years, there has been considerable interest and research done on the uses and properties of castor but not on a commercial scale. Castor oil studies have shown increasing growth with the number of manuscripts increasing sixfold since the 1980s (Fig. 1). While alternative breeding programs and marketing can lead to economic growth of castor oil production, at the commercial level, various projects fail due to the lack of knowledge about novel processing methods and parameters used in castor oil production. This manuscript discusses those processing parameters in detail. Although the castor bean processing method can typically be considered a simple process, it can also be complicated if the operators are unaware of its exact processing parameters and operating procedures. Specifically, process parameters for castor oil production should be optimized to achieve high oil extraction efficiency through a solvent extraction method.^{16,17} No scientific literature currently exists discussing in detail the







Figure 2. Castor beans

commercial castor processing parameters. This contribution discusses in detail the commercial castor processing parameters and the important key points needed on how to manufacture the desired quality of castor oil, both of which are important to castor oil producers.

Castor Oil and its Properties

Castor beans are cultivated for their seeds (Fig. 2), yielding a viscous, pale yellow nonvolatile and nondrying castor oil.¹⁸ The physical properties of castor oil have been studied (Table 1). Comparative analysis showed that the values of viscosity, density, thermal conductivity, and pour point for

Table 1. Physical properties of castor oil.

PHYSICAL PROPERTIES	
Viscosity (centistokes)	889.3
Density (g/mL)	0.959
Thermal conductivity (W/m°C)	4.727
Specific heat (kJ/kg/K)	0.089
Flash point (°C)	145
Pour point (°C)	2.7
Melting point (°C)	-2 to -5
Refractive index	1.480



Figure 3. Chemical structure of ricinoleic acid, the primary component of castor oil.

castor oil were higher than the values of a standard lubricant (SAE 40 engine oil).¹⁹

The unique structure of castor oil offers interesting properties, making it appropriate for various industrial applications. Castor oil is known to consist of up to 90% ricinoleic, 4% linoleic, 3% oleic, 1% stearic, and less than 1% linolenic fatty acids. Castor oil is valuable due to the high content of ricinoleic acid (RA), which is used in a variety of applications in the chemical industry (Fig. 3).²⁰

The hydroxyl functionality of RA makes the castor oil a natural polyol providing oxidative stability to the oil, and a relatively high shelf life compared to other oils by preventing peroxide formation. The presence of the hydroxyl group in RA and RA derivatives provides a functional group location for performing a variety of chemical reactions including halogenation, dehydration, alkoxylation, esterification, and sulfation. As a result, this unique functionality allows the castor oil to be used in industrial applications such as paints, coatings, inks, and lubricants.²⁰

Castor beans, the source of castor oil, contain some allergenic (2S albumin) proteins as well as ricin; however, processed or refined castor oil is free from any of these substances and can be safely used in pharmaceutical applications. This can be attributed to its wide range of biological effects on higher organisms.^{13,21} Ricin is found exclusively in the endosperm of castor seeds and is classified as a type 2 ribosome-inactivating protein.^{22,23} Type 2 ribosome-inactivating proteins such as ricin from castor oil are lectins, which irreversibly inactivate ribosomes, thus stopping protein synthesis and eventually leading to cell death. This makes ricin a potent plant toxin.²⁴

Applications of castor oil and its derivatives.

Fuel and biodiesel. Castor is considered to be one of the most promising nonedible oil crops, due to its high annual seed production and yield, and since it can be grown on marginal land and in semiarid climate. Few studies have been done regarding castor fuel-related properties in pure form or

as a blend with diesel fuel, primarily due to the extremely high content of RA. In a study by Berman et al,²⁵ it was found that methyl esters of castor oil can be used as a biodiesel alternative feedstock when blended with diesel fuel. However, the maximum blending level 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. Another study by Shojaeefard et al²⁶ examined the effects of castor oil biodiesel blends on diesel engine performance and emissions. They found that a 15% blend of castor oil-biodiesel was an optimized blend of biodiesel-diesel proportions. The results indicated that lower blends of biodiesel provide acceptable engine performance and even improve it. Similar to the study by Shojaeefard et al,²⁶ Panwar et al²⁷ prepared the castor methyl ester by transesterification using potassium hydroxide (KOH) as catalyst. They then tested this methyl ester by using it in a four-stroke, single cylinder variable compression ratio type diesel engine. It was concluded that the lower blends of biodiesel increased the break thermal efficiency and reduced the fuel consumption. Further, the exhaust gas temperature increased with increasing biodiesel concentration. Results of their study proved that the use of biodiesel from castor seed oil in a compression ignition engine is a viable alternative to diesel. The transesterification reactions of castor oil with ethanol and methanol as transesterification agents were also studied in the presence of several classical catalytic systems. Results of their study show that biodiesel can be obtained by transesterification of castor oil using either ethanol or methanol as the transesterification agents.²⁸ Although these studies have shown promising results for the use of castor oil as a technically feasible biodiesel fuel, a major obstacle still exists in its use as a biodiesel in some countries such as Brazil. In Brazil, government policies promoted castor as a biodiesel feedstock in an attempt to bring social benefits to small farmers in the semiarid region of the country.^{29,30} However, seven years after the Brazilian biodiesel program was launched, negligible amounts of castor oil have been used for biodiesel production. It was found that the castor oil produced in this program was not primarily used for biodiesel but sold for higher prices to the chemical industry.³⁰ Another major constraint in the use of castor oil as a feedstock for biodiesel has been the high price paid for the oil as industrial oil rather than its physical and chemical properties. Castor oil is in high demand by the chemical industry for the manufacture of very high value products. For this reason, it is not economical to use this oil as a replacement for diesel.⁹ Finally, although castor oil can be used directly to replace normal diesel fuel, the high viscosity of this oil limits its application.³¹

Polymer materials. Castor oil and its derivatives can be used in the synthesis of renewable monomers and polymers.² In one study, castor oil was polymerized and cross-linked with sulfur or diisocyanates to form the vulcanized and urethane derivatives, respectively.³² In another study, full-interpenetrating polymer networks (IPNs) were prepared from epoxy and castor oil-based polyurethane (PU), by the sequential mode of synthesis.³³ Similar to the aforementioned study, a series of two-component IPN of modified castor oil-based PU and polystyrene (PS) were prepared by the sequential method.³⁴ IPN can be elaborated as a special class of polymers in which there is a combination of two polymers in which one is synthesized or polymerized in the presence of another.^{35,36} Thus, IPN formulation can be considered a useful method to develop a product with excellent physicomechanical properties than the normal polyblends. IPN is also known as polymer alloys and is considered to be one of the fastest growing research areas in the field of polymer blends in the last two decades.³⁴

Castor oil polymer (COP) has also been shown to have a sealing ability as a root-end filling material. A root-end filling material simply refers to root-end preparations filled with experimental materials. The main objective of this type of material is to provide an apical seal preventing the movements of bacteria and the diffusion of bacterial products from the root canal system into the periapical tissues.³⁷ In a study conducted by de Martins et al,³⁸ the sealing ability of COP, mineral trioxide aggregate (MTA), and glass ionomer cement (GIC) as root-end filling materials were evaluated. MTA is primarily composed of tricalcic silicate, tricalcic alluminate, and bismuth oxide and is a particular endodontic cement.³⁹ GICs, on the other hand, are mainstream restorative materials that are bioactive and have a wide range of uses such as lining, bonding, sealing, luting, or restoring a tooth.⁴⁰ Results of their study show that the COP had a greater sealing ability when used as a root-end filling material than MTA and GIC.

Biodegradable polyesters are one of the most common applications using castor oil.⁴¹ Polyesters are the first synthetic condensation polymers prepared by Carothers during the 1930s.^{42,43} They are known to be biodegradable and environmental friendly, with a wide array of applications in the biomedical field, as well in the preparation of elastomers and



packaging materials.44,45 Fatty acid scaffolds are desirable biodegradable polymers, though they are restricted by their monofunctional property. That is, most fatty acids have a single carboxylic acid group. RA, however, is known to be one of the few naturally available bifunctional fatty acids with an additional 12-hydroxy group along with the terminal carboxylic acid (Fig. 3). The presence of this hydroxyl group provides additional functionality for the preparation of polyesters or polyester-anhydrides. The dangling chains of the RA impart hydrophobicity to the resulting polyesters, thereby influencing the mechanical and physical property of the polymers. These chains act as plasticizers by reducing the glass transition temperatures of the polyesters.^{41,46} Castor oil can be combined with other monomers to produce an array of copolymers. Fine-tuning these copolymers can provide materials with different properties that find use in products ranging from solid implants to in situ injectable hydrophobic gel.⁴¹

Soaps, waxes, and greases. Castor oil has been used to produce soaps in some studies.^{47–49} Some studies also utilize castor oil in waxes.^{50–53} One study by Dwivedi and Sapre⁵⁴ utilized castor oil in total vegetable oil greases. Total vegetable oil greases are those in which both the lubricant and gellant are formed from vegetable oil. Their study utilized a simultaneous reaction scheme to form sodium and lithium greases using castor oil.

Lubricants, hydraulic, and brake fluids. Castor oil has also been used for developing low pour point lubricant base stocks through the synthesis of acyloxy castor polyol esters.⁵⁵ The low pour point property helps to provide full lubrication when the equipment is started and is easier to handle in cold weather.⁵⁶ An interesting study by Singh showed the excellent potential of castor oil-based lubricant as a smoke pollution reducer. In his research, a biodegradable two-stroke (2T) oil, a popular variety of lubricating oil used on two-stroke engines in scooters and motorcycles,⁵⁷ was developed from castor oil, which consisted of tolyl monoesters and performance additives, but no miscibility solvent. Their performance evaluations showed that it reduced smoke by 50%-70% at a 1% oil-fuel ratio, and it was on par with standard product specification.⁵⁸ In addition to the possible use as a car engine lubricant, a modified version of castor oil lubricant comprising 100 parts of castor oil and 20-110 parts of a chemically and thermally stable, low viscosity blending fluid, soluble in castor oil showed its potential as a lubricant for refrigerator systems.⁵⁹ Although castor oil has been used as a DOT 2 rating brake fluid, it is considered an outdated type of brake fluid that should not be used in any modern vehicles.60,61

Fertilizers. Production of castor oil generates two main byproducts: husks and meal. For each ton of castor oil, 1.31 tons of husks and 1.1 tons of meal are generated. A study by Lima et al⁶² showed that blends of castor meal and castor husks used as fertilizer promoted substantial plant growth up to the dose of 4.5% (in volume) of meal. However, doses exceeding 4.5% caused reduction in plant growth and even plant death.



Their study showed that castor meal may be used as a good organic fertilizer due to its high nitrogen and phosphorus content, but blending with castor husks is not necessary.

Coatings. Coatings and paints are also another application of castor oil. Castor oil can be effectively dehydrated by nonconjugated oil-maleic anhydride adducts to give useful paint or furniture oil applications (Fig. 4).63 Trevino and Trumbo⁶⁴ studied the utilization of castor oil as a coating application by converting the hydroxyl functionalities of castor oil to β -ketoesters using *t*-butyl acetoacetate. The reaction is known to be relatively rapid and proceeded to high yield under mild conditions. Results showed that the 60° glosses of the films and film flexibilities were good. In a separate study by Thakur and Karak,⁶⁵ advanced surface coating materials were synthesized from castor oil-based hyperbranched polyurethanes (HBPUs), a highly branched macromolecule. The HBPs exhibited excellent performance as surface coating materials with the monoglyceride-based HBPU, exhibiting higher tensile strength than direct oil-based coatings. Both the HBPUs have acceptable dielectric properties with greater than 250°C thermal stability for both the polymers. Ceramer coatings are also another coating application of castor oil. de Luca et al⁶⁶ synthesized ceramer coatings from castor oil or epoxidized castor oil and tetraethoxysilane. Most recently, highperformance hybrid coatings were synthesized by Allauddin et al⁶⁷ using a methodology that included introducing hydrolyzable -Si-OCH₃ groups onto castor oil that have been used for the development of PU/urea-silica hybrid coatings.

Pharmacological and medicinal use. While castor oil is well known as a powerful laxative, the medicinal use of the oil is

relatively minor (<1%). Beyond this infamous application of castor oil, it is considered to be an important feedstock utilized by the chemical industry, particularly in producing a wide array of materials, many of which are superior to equivalent products derived from petroleum. The high percent composition of RA in proximity to the double bond makes this oil poised for various physical, chemical, and even physiological activities, as described in the aforementioned paragraphs.⁵

Owing to the activity of RA in the intestine, castor oil has been widely used in various bioassays involving antidiarrhea activity on laboratory animals. Castor oil is often administered orally to induce diarrhea in rats.^{68–70} This assay has led to a fast and efficient method of preliminary screening of various phytochemicals for potential drug-like candidates from natural products.

In modern-day medicine, castor oil is also used as a drug delivery vehicle. An example is Kolliphor EL or formerly known as Cremophor EL, which is a registered product of BASF Corp. The product is a polyexthoxylated castor oil, a mixture (CAS No. 61791-12-6) that is prepared when 35 moles of ethylene oxide is made to react with one mole of castor oil. This product is often used as an excipient or additive in drugs and is also used to form stable emulsions of nonpolar materials in various aqueous systems. It is also often used as a drug delivery vehicle for very nonpolar drugs such as the anticancer drugs paclitaxel and docetaxel.^{71–73}

Castor Oil Extraction

Castor oil seed contains about 30%-50% oil (m/m).^{74,75} Castor oil can be extracted from castor beans by either mechanical

pressing, solvent extraction, or a combination of pressing and extraction.⁷⁴ After harvesting, the seeds are allowed to dry so that the seed hull will split open, releasing the seed inside. The extraction process begins with the removal of the hull from the seeds. This can be accomplished mechanically with the aid of a castor bean dehuller or manually with the hands. When economically feasible, the use of a machine to aid in the dehulling process is more preferable.

After the hull is removed from the seed, the seeds are then cleaned to remove any foreign materials such as sticks, stems, leaves, sand, or dirt.⁷⁵ These materials can usually be removed using a series of revolving screens or reels. Magnets used above the conveyer belts can remove iron. The seeds can then be heated to harden the interior of the seeds for extraction. In this process, the seeds are warmed in a steam-jacketed press to remove moisture, and this hardening process will aid in extraction. The cooked seeds are then dried before the extraction process begins. A continuous screw or hydraulic press is used to crush the castor oil seeds to facilitate removal of the oil (Fig. 5). The first part of this extraction phase is called prepressing. Prepressing usually involves using a screw press called an oil expeller. The oil expeller is a high-pressure continuous screw press to extract the oil.

Although this process can be done at a low temperature, mechanical pressing leads to only about 45% recovery of oil from the castor beans.¹⁶ Higher temperatures can increase the efficiency of the extraction. Yields of up to 80% of the available oil can be obtained by using high-temperature hydraulic pressing in the extraction process.⁷⁴ The extraction temperature can be controlled by circulating cold water through a pressing machine responsible for cold pressing of the seeds. Cold-pressed castor oil has lower acid and iodine content and is lighter in color than solvent-extracted castor oil.⁷⁵

Following extraction, the oil is collected and filtered and the filtered material is combined back with new, fresh seeds for repeat extraction. In this way, the bulk filtered material



Figure 5. Commercial continuous screw press assembly.



keeps getting collected and runs through several extraction cycles combining with new bulk material as the process gets repeated. This material is finally ejected from the press and is known as castor cake. The castor cake from the press contains up to approximately 10% castor oil content.⁷⁵ After crushing and extracting oil from the bulk of the castor oil seeds, further extraction of oil from the leftover castor cake material can be accomplished by crushing the castor cake and by using solvent extraction methods. A Soxhlet or commercial solvent extractor is used for extracting oil from the castor cake. Use of organic solvents such as hexane, heptane, or a petroleum ether as a solvent in the extraction process then results in removal of most of the residual oil still inaccessible in the remaining seed bulk.

Castor oil filtration/purification. Following extraction of the oil through the use of a press, there still remain impurities in the extracted oil. To aid in the removal of the remaining impurities, filtration systems are usually employed. The filtration systems are able to remove large and small size particulates, any dissolved gases, acids, and even water from the oil.⁷⁵ The filtration system equipment normally used for this task is the filter press. Crude castor seed oil is pale yellow or straw colored but can be made colorless or near colorless following refining and bleaching. The crude oil also has a distinct odor but can also be deodorized during the refining process.

Castor oil refining. After filtration, the crude or unrefined oil is sent to a refinery for processing. During the refining process, impurities such as colloidal matter, phospholipids, excess free fatty acids (FFAs), and coloring agents are removed from the oil. Removal of these impurities facilitates the oil not to deteriorate during extended storage. The refining process steps include degumming, neutralization, bleaching, and deodorization.^{16,74} The oil is degummed by adding hot water to the oil, allowing the mixture to sit, and finally the aqueous layer is removed. This process can be repeated. Following the degumming step, a strong base such as sodium hydroxide is added for neutralization. The base is then removed using hot water and separation between the aqueous layer and oil allows for removal of the water layer. Neutralization is followed by bleaching to remove color, remaining phospholipids, and any leftover oxidation products. The castor oil is then deodorized to remove any odor from the oil. The refined castor oil typically has a long shelf life about 12 months as long as it is not subjected to excessive heat. The steps involved in crude castor oil refining are further discussed in the next section.

Crude Castor Oil Refining

While the previous section briefly discussed the general overview involved in a castor oil refining step, this section thoroughly explains each of the processes involved in it. Unrefined castor oil leads to rapid degradation due to the presence of impurities as mentioned in "Castor oil refining" section, making it less suitable for most applications.¹ Hence, a refining process has to be conducted prior to the derivatization of





the oil. The order of the steps performed in the refining process, which includes degumming, neutralization, bleaching, deodorization, and sometimes winterization, should be taken into consideration for efficient oil refining (Fig. 6) and are described extensively and specifically in a castor oil industry setting in "Degumming", "Neutralization", "Bleaching", "Deodorization", and "Winterization" sections.

Degumming. The first step in the castor oil refining process, called degumming, is used to reduce the phosphatides and the metal content of the crude oil. The phosphatides present in crude castor oil can be found in the form of lecithin, cephalin, and phosphatidic acids.⁷⁶ These phosphatides can be classified into two different types: hydratable and nonhydratable,77 and accordingly, a suitable degumming procedure (water degumming, acid degumming, and enzymatic degumming) has to be performed for efficient removal of these phosphatides. In general, crude vegetable oil contains about 10% of nonhydratable phosphatides.77 However, the amount may vary significantly depending on various factors such as the type of seed, quality of seed, and conditions applied during the milling operation. While hydratable phosphatides can be removed in most part by water degumming, nonhydratable phosphatides can only be removed by means of acid or enzymatic degumming procedures.77

Water degumming. Water degumming is a relatively simple, inexpensive process to remove as much gums as possible in the initial stages of oil refining. In this process, the crude oil is heated to approximately 60°C–70°C. Water is then added to the crude oil and the resulting mixture is stirred well and allowed to stand for 30 minutes during which time, the phosphatides present in the crude oil become hydrated and thereby become oil-insoluble.⁷⁸ The hydrated phosphatides can be removed either by decantation or centrifugation. Water degumming allows the removal of even small amounts of nonhydratable phosphatides along with the hydratable phosphatides. The extracted gums can be processed into lecithin for food, feed, or technical purposes.

Acid degumming. In general, the acid degumming process can be considered as the best alternative to the water degumming process if the crude oil possesses a significant amount of nonhydratable phosphatides.⁷⁹ In the acid degumming process, the crude castor oil is treated with an acid (phosphoric acid, malic acid, or citric acid) in the presence of water.^{77,80} Acid degumming is usually carried out at elevated temperature, typically around 90°C. The precipitated gums are then separated by centrifugation followed by vacuum drying of the degummed oil.⁷⁹

Enzymatic degumming. The conversion of nonhydratable phosphatides to hydratable phosphatides can also be attained using enzymes.⁸¹ Here, the enzyme solution, which is a mixture of an aqueous solution of citric acid, caustic soda, and enzymes, is dispersed into the filtered oil at mild temperatures normally between 45°C and 65°C. A high-speed rotating mixer is used for effective mixing of oil and enzyme. The oil is then separated from the hydrated gum by mechanical separation and is subjected to vacuum drying.⁸² A variety of these so-called "microbial enzymes" exist. The first of these were the phospholipases A1 (Lecitase® Novo and Ultra) and, more recently, a phospholipase C (Purifine®). A lipid acyl transferase (LysoMax®) with PLA2 activity has also become available in commercial quantities. These enzymes have specific functions and specificities. For example, the Lecitases® and the LysoMax® enzymes are capable of catalyzing the hydrolysis of all common phosphatides. The Purifine® enzyme, on the other hand, is specific for phosphatidylcholine and phosphatidylethanolamine.81

Neutralization. Good quality castor seeds stored under controlled conditions produce only low FFA content of approximately 0.3%.⁸² Occasionally, oil seeds that are old or stored for more than 12 months with high moisture content produce a high FFA content of about 5% level.⁸³ This excess FFA present in the castor oil does not provide the same functionality as the neutral oil and has the ability to alter its reactivity with different substances. Hence, it is highly essential to remove the high FFA content so as to produce a high-quality castor oil. This process of removal of FFA from the degummed oil is referred to as neutralization.⁸²

In general, the refining process can be divided into two methods: chemical and physical refining. Physical refining is

usually done by maintaining a high temperature above 200°C with a low vacuum pressure. Under these processing conditions, the low boiling point FFA is vacuum distilled from the high boiling point triglycerides. However, physical refining is not recommended in the case of castor oil, due to its sensitivity to heat as it normally starts disintegrating above 150°C, which can result in the hydrolysis of the hydroxyl groups. On the other hand, chemical refining is based on the solubility principle of triglycerides and soaps of fatty acids.⁸² FFAs (acid) react with alkali (strong base) to form soaps of fatty acids (Fig. 7). The formed soap is generally insoluble in the oil and, hence, can be easily separated from the oil based on the difference in specific gravity between the soap and triglycerides. The specific gravity of soap is higher than that of triglycerides and therefore tends to settle at the bottom of the reactor. Most of the modern refineries use high-speed centrifuges to separate soap and oil mixture.

Alkali neutralization or chemical refining reduces the content of the following components: FFAs, oxidation products of FFAs, residual proteins, phosphatides, carbohydrates, traces of metals, and a part of the pigments. The degummed castor oil is first treated with an alkali solution (2% caustic soda) between 85°C and 95°C with constant stirring for approximately 45–60 minutes.⁸⁴ At this stage, the alkali reacts with FFAs and converts them into soap stock. The obtained soap has a higher specific gravity than the neutral oil and tends to settle at the bottom. The oil can be separated from the soap either by gravity separation or by using commercial centrifuges. Small-scale refiners use gravity separation route, whereas large capacity plants utilizes commercial vertical stack bowl centrifuges. The separated oil is then washed with hot water to remove soap, alkali solution, and other impurities.⁸⁵

Figure 7. Formation of soap with ricinoleic acid.

Castor oil neutralization is a high loss-refining step. This loss is presumably due to the small difference in specific gravity of the generated soap and neutral viscous castor oil.⁸³

Bleaching. Castor oil is used for many applications where the final product's appearance is extremely important. For instance, cosmetics formulations, lubricant additives, and biomaterial manufacturing all demand the final product's color to be within a certain limit. Although castor oil obtained after degumming and neutralization processes yield a clear liquid by appearance, it may still contain colored bodies, natural pigments, and antioxidants (tocopherols and tocotrienols), which were extracted along with the crude oil from the castor beans.86 The color pigments are extremely small ranging from 10 to 50 nm, which cannot be removed from the oil by any unit operation.⁸² However, an adsorption process called "bleaching" can be used to remove such colored pigments and remaining phospholipids, using activated earths under moderate vacuum conditions between 50 and 100 mmHg. The reduction in the oil color can be measured using an analytical instrument, called a tintometer.

Activated earths are clay ores that contain minerals, namely, bentonite and montmorillonite. These types of clay are generally found on every continent generated through unique geographical movements millions of years ago.⁸⁷ The efficiency of bleaching earth, also called the bleachability, depends on the ability to adsorb color pigments and other impurities on its surface. Normally, unprocessed clay has lower bleachability than acid-activated or processed clays. The unprocessed clays when activated by concentrated acid followed by washing and drying acquire more adsorptive power to adsorb color pigments from the oil.⁸⁸

Bleaching of castor oil can be done under vacuum at around 100°C while constantly stirring the oil with an appropriate amount of activated earths and carbon.⁷⁸ The bleaching process requires around 2% bleaching earth and carbon to produce a desirable light colored oil. Under these processing conditions, colored bodies, soap, and phosphatides adsorb onto the activated earth and carbon. The activated earth and carbon are removed by using a commercial filter. The spent earth-carbon, thus obtained, retains around 20%-25% oil content. Bleaching castor oil containing higher phosphatide and soap content often leads to high retention of oil due to the large amount of activated earth used and thus causes filtration issues. Although this retained oil on the spent earth can be recovered by boiling the spent earth in water or by a solvent extraction method, the recovered oil from the spent earth is highly colored with high FFA and high peroxide content, normally greater than 10 mg KOH/g and 20 meq/kg, respectively.88

Deodorization. Deodorization is simply a vacuum steam distillation process that removes the relatively volatile

components that give rise to undesirable flavors, colors, and odors in fats and oils. Unlike other vegetable oils, castor oil requires limited or no deodorization, as it is a nonedible oil where slight pungent odor is not an issue for most of its applications, with the only exception being pharmaceutical grade castor oil.^{89,90} Deodorization is usually done under high vacuum and at high temperature above 250°C to remove undesirable odors caused by ketones, aldehydes, sterols, triterpene alcohols, and short-chain fatty acids.⁸⁵ Pharmaceutical grade castor oil is deodorized at low temperatures, approximately 150°C–170°C under high vacuum for 8–10 hours to avoid hydrolysis of hydroxy group of RA.⁸⁶

Winterization. The majority of vegetable oils contain high concentrations of waxes, fatty acids, and lipids. Hence, it is subjected to the process of winterization before its final use. Winterization of oil is a process, whereby waxes are crystallized and removed by a filtering process to avoid clouding of the liquid fraction at cooler temperatures. Kieselguhr is the generally used filter aid and the filter cake obtained at the end can be recycled to a feed ingredient. In certain cases, a similar process called "dewaxing" can also be utilized as a means to clarify oil when the amount of cloudiness persists.^{91,92}

Conclusions and Future Directions

Castor oil is a promising commodity that has a variety of applications in the coming years, particularly as a renewable energy source.

Essential to the production and marketing of castor oil is the scientific investigation of the processing parameters needed to improve oil yield. In the recent years, machine learning predictive modeling algorithms and calculations were performed and implemented in the prediction and optimization of any process parameters in castor oil production. Utilization of an artificial neural network (ANN) coupled with genetic algorithm (GA) and central composite design (CCD) experiments were able to develop a statistical model for optimization of multiple variables predicting the best performance conditions with minimum number of experiments and high castor oil production.⁹³ In a separate study by Mbah et al,¹⁷ a multilevel factorial design using Minitab software was used to determine the conditions, leading to the optimum yield of castor oil extraction through a solvent extraction method. This study found that optimum conditions that included leaching time of two hours, leaching temperature of 50°C, and solute:solvent ratio of 2 g:40 mL garnered optimum yield of castor oil extraction. Such mathematical experimental design and methodology can prove to be useful in the analysis of the effects and interactions of many experimental factors involved in castor oil production.

With the advent of biotechnological innovations, genetic engineering has the potential of improving both the quality and quantity of castor oil. Genetic engineering can be categorized into two parts: one approach is to increase certain fatty acids, while the second approach is to engineer biosynthetic

pathways of industrially high-valued oils.⁹⁴ For the latter, biosynthetic gene clusters responsible for fatty acid production can be mined for such purpose. In one particular study by Lu et al,⁹⁵ *Arabidopsis thaliana* expressing castor fatty acid hydroxylase 12 (FAH12) was used to mine genes that can improve the hydoxy fatty acid accumulation among developed transgenic seeds. The aforementioned study was able to identify certain proteins that can improve the hydroxy fatty acid content of castor seeds. These proteins include oleosins (a small protein involved in the formation of lipid bodies) and phosphatidylethanolamine (a protein involved in fatty acid modification and is channeled to triacylglycerol).⁹⁶ Through understanding the genetics behind oil production, better yield can be achieved.

With the dawn of the –omics era, genomics, transcriptomics, and proteomics can be key players in understanding the genetics of improving the quality and quantity of oil production. Advances in genomics have drafted the genome sequence of the castor bean, which has led to insights about its genetic diversity.^{97,98} A future direction would include a tandem genomics and transcriptomics that can help reveal differences in gene expression levels across a spatiotemporal parameter affecting oil quality and quantity. Further, proteomics can be used to understand proteins and enzymes that are expressed by the castor bean plant.⁹⁹ Being a nonmodel organism, homology-driven protein identification techniques are possibly to be employed to understand the cellular and biological nature of oil production, leading to improved oil qualities and quantities.

As a source of biodiesel, recent studies showed that the biodiesel synthesis from castor oil is limited by a number of factors that include having the proper reaction temperature, oil-to-methanol molar ratio, and the quantity of catalyst. A study using response surface methodology as a model has been used to optimize the reaction factor for biodiesel synthesis from castor oil.¹⁰⁰ In another similar study, parameters affecting castor oil transesterification reaction were investigated. Using Taguchi method consisting of four parameters (reaction temperature, mixing intensity, alcohol/oil ratio, and catalyst concentration), the best experimental conditions were determined. It was determined that the reaction temperature and mixing intensity can be optimized. Using the optimum results, the authors proposed a kinetic model that resulted in establishing an equation for the beginning rate of transesterification reaction.¹⁰¹ Besides the Taguchi method, a full factorial design of experiment is also another approach that was investigated to optimize biodiesel production from castor oil. Second-order polynomial model was obtained to predict biodiesel yield as a function of these variables. The experimental results for the process garnered an average yield of biodiesel of more than 90%.¹⁰² The use of models and simulations can, indeed, greatly facilitate the efficiency of biodiesel production from castor oil. To add further, a simple model using a ping-pong bi-bi mechanism has been

proposed, which summarizes an efficient method of noncatalytic transesterification of castor oil in supercritical methanol and ethanol.¹⁰³ It is an enzymatic reaction model that involves two substrates and two products (referred to as bi-bi system). An enzyme reacts first with one substrate to form a product and a modified enzyme. The modified enzyme would then react with a second substrate to form a final product and would regenerate the original enzyme. In this model, an enzyme is perceived as a ping-pong ball that bounces from one state to another.

Biodiesel production from castor oil is, indeed, a promising enterprise. Advances in models and simulations have facilitated optimization of key processing parameters necessary to obtain good yields of such biodiesel.

In this review, we present both an extensive and intensive analysis of castor bean oil, ranging from its industrial to pharmacological use. Moreover, this review discussed traditional and modern castor bean oil processing and the future directions as we enter the –omics and computational analysis era.

Abbreviations

ANN, artificial neural network; AV, acid value; CCD, central composite design; COP, castor oil polymer; DCO, dehydrated castor oil; DOC, de-oiled cake; FAH12, fatty acid hydroxylase 12; FFA, free fatty acid; GA, genetic algorithm; GIC, glass ionomer cement; HBPUs, hyperbranched polyurethanes; HV, hydroxyl value; IV, iodine value; IPNs, interpenetrating polymer networks; KOH, potassium hydroxide; MTA, mineral trioxide aggregate; SV, saponification value; RA, ricinoleic acid; PU, polyurethane; PV, peroxide value; Y + 5R; Yellow + 5(Red).

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Author Contributions

Conceived and designed the study: VRP, GGD, and LCKV. Analyzed the data: VRP, GGD, and LCKV. Wrote the first draft of the manuscript: VRP. Contributed to the writing of the manuscript: VRP, GGD, LCKV, RM, and BJJS. Agreed with manuscript results and conclusions: VRP, GGD, LCKV, RM, and BJJS. Jointly developed the structure and arguments for the paper: VRP, GGD, LCKV, RM, and BJJS. Made critical revisions and approved the final version: VRP, GGD, LCKV, RM, and BJJS. All the authors reviewed and approved the final manuscript.

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