Castor Oil: A Vital Industrial Raw Material

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Abstract. Even though castor oil is inedible, it has for long been an article of commerce. This is in large measure due to the versatility of the oil. This review discusses the extraction of castor oil and its refining methods, while emphasis is placed on the review of the industrial applications of the oil. Since castor oil is not edible, it could be substituted in many industrial application areas where edible oils are used. An awareness of the various applications of the oil can be used to emphasize the need for an increase in its production as a vital raw material for the chemical industries.

Keywords: castor oil, raw material, industrial oil

The trade of castor oil as an item of commerce dates back to antiquity. The oil is obtained by extracting or expressing the seeds of Ricinus communis, or red castor Family Eurphorbiacae (Kirk-Othmer, 1979). It is also obtained from the seeds of another plant, R. sanguineous. Castor oil is a viscous, pale yellow, non-volatile and non-drying oil, with bland taste. It is sometimes used as a purgative. It has a slight characteristic odour while the crude oil tastes slightly acrid with a nauseating after-teste. Relative to other vegetable oils, it has a good shelf-life and it does not turn rancid unless subjected to excessive heat. The objective of this paper is to highlight the various uses of castor oil in the chemicals production industries. Being a non-edible oil, its increased use can reduce the demand of some edible oils used in the chemical industry, for its availability for human consumption.

Producing countries. Castor oil is a vegetable oil used as a major industrial raw material. The world's major producers of castor oil are India, Brazil, China and Russia. The importance of castor oil to the economy of many African countries is evident from the fact that many companies in the continent sponsor the cultivation of castor plant. Although reliable production statistics are hard to come by, it is noteworthy that a substantial amount of the oil is produced in Zimbabwe, which is expected to exceed 1000 tonnes in the near future (Chamunorwa, 1995). The total world production of seeds is estimated at 1 million tonnes and the oil expressed from these is about 500,000 tonnes. The breakdown of production is shown in Table 1 (www.ciara.com.ar/ estadize.htm).

Cultivation of castor plant. The castor plant grows in the wild in large quantities mostly in the tropical and sub-tropical countries. It is a herbaceous plant with a height between 1 m and 2 m when fully developed. Some varieties are perennials with the size of small trees, whereas some other varieties are dwarf types and are grown as annuals. Generally, the plant is able to grow on most soils, except those that are compacted, such as heavy clays. For best yields, it requires moderate soil fertility, warm conditions, and average rainfall between 600-700 mm (Weiss, 1971). However, the plant is able to tolerate varying weather conditions and it has been adapted to semi-arid conditions of Brazil, making the country to be a major producer of castor seeds. High soil fertility enables the castor plant to grow vegetatively, while humid and wet conditions may promote the development of capsule moulds. On the other hand, high temperatures affect pollination and seed set (Woodend, 1993). A disadvantage of the cultivation of castor plants is the presence of the castor bean white fly population that has the characteristics of developing into a severe pest hazard potential. Castor seeds are about the size of a bean and sometimes the seed is referred to as a bean although it is not a legume. Other informations on the agricultural production of castor oil (Woodend, 1993; Roetheli et al., 1991) and other biological aspects of the plant have been published (Weiss, 1983; 1971).

There are different varieties of the castor seeds, but on the average, they contain about 46 to 55% oil by weight (Weiss, 1983). Castor seeds are poisonous to humans and animals, because they contain ricin, ricinine and certain allergens that are lethally toxic. If a seed is ingested accidentally, it cause abdominal pain, vomiting and diarrhoea. In fact, it is claimed that as little as one milligram of ricin can kill an adult (Woodend, 1993). Mascolo *et al.* (1996) have reported that administration of castor oil at 2 ml/rat produced diarrhoea in all the rats they tested; similar effects are also expected in humans.

Extraction of castro oil. The extraction of oil from castor seeds is done by one or a combination of mechanical pressing and solvent extraction procedures. In mechanical pressing, the seeds are crushed and then adjusted to low moisture content by warming in a steam-jacketed vessel. Thereafter, the seeds are loaded into a hydraulic press and the seeds are pressed by mechanical means to extract oil. The oil obtained through the from mechanical pressing procedure has light colour and low free fatty acids (Kirk-Othmer, 1979). However, mechanical pressing removes only about 45% of the oil present and the remaining oil in the cake can only be recovered by solvent extraction. In the solvent extraction method, the crushed seeds are extracted with a solvent in a Soxhlet extractor or a commercial extractor. Solvents used for extraction include heptane, hexane and petroleum ether.

Refining of castor oil. As in other vegetable oils, it is usual to refine the crude oil obtained, either from mechanical pressing or solvent extraction. The main aim of refining is to remove impurities, such as colloidal matter, free fatty acids, colouring matter, and other undesirable constituents, thus making the oil more resistant to deterioration during storage. The general method of refining oils is also applicable to castor oil. Refining includes the following stages:

- removal of solid and colloidal matter by settling and filtration, and neutralization of the free fatty acids by alkali treatment,
- removal of colouring matter by bleaching,

• only edible oils are deodourized by treatment with steam at high temperatures and under low pressure, this step is thus redundant for castor oil.

Properties and chemistry of castor oil. Castor oil, like all other vegetable oils, has different physical and chemical properties that vary with the method of extraction. The average fatty acids composition of castor oil is, ricinoleic acid 86%, linoleic acid 3.5%, stearic acid 2%, and dihydrostearic acid 2% (Kirk-Othmer, 1979). Cold pressed castor oil has low acid value, low iodine value and a slightly higher saponification value than the solvent extracted oil, and it is lighter in colour. Also, the oil is insoluble in alcohol. Typical properties of castor oil are given in Table 2.

The chemistry of castor oil is centred on its high content of ricinoleic acid. Castor oil consists mainly of esters of 12-hydroxy-9-octadecenoic acid (ricinoleic acid), thus the presence of hydroxyl groups and double bonds makes the oil suitable for many chemical reactions and modifications (Fig. 1). The ricinoleic acid comprises over 80% of the fatty acids of the oil. Castor oil is characterized by high viscosity, although this is unusual for a natural vegetable oil, which is largely due to hydrogen bonding of its hydroxyl groups. It is a unique naturally occurring polyhydroxy compound.

Dehydration. Castor oil is classified as a non-drying oil, but it can be dehydrated to give semi-drying or drying oil. The treatment involves the removal of water from the fatty acid portion of the oil. Being a polyhydroxy compound, its hy-

Major producers	1990	1991	1992	1993	1994	1995	1996	1997	1998	1999	2000
India	192	239	232	242	271	333	344	278	304	294	324
Peoples Republic of China	77	86	93	97	97	82	73	83	80	91	105
Brazil	77	73	54	28	28	22	21	43	21	19	52
Thailand	18	18	19	18	16	14	10	9	9	7	5
European Union	20	16	14	12	14	11	9	10	7	8	8
Others	54	52	49	41	20	21	22	19	20	23	23
Total	438	484	461	438	446	483	479	442	441	442	517

 Table 1. Production volume (x000 tonne) of castor oil by major producers*

*source: www.ciara.com.ar/estadize.htm

Table 2. Characteristics of castor oil grades

Properties	Cold-pressed oil	Solvent-extracted oil	Dehydrated oil
Specific gravity (at 30 °C)	0.961-0.963	0.957-0.963	0.926-0.937
Acid value (KOH, mg/g)	3	10	6
Iodine value (Wijs)	82-88	80-88	125-145
Saponification value (KOH, mg/g)	179-185	177-182	185-188

$$\begin{array}{ccc} {\rm CH}_2{\rm -O}{\rm -C}({\rm O}){\rm -R} & {\rm CH}_2{\rm -O}{\rm -C}({\rm O}){\rm -R} \\ | & | \\ {\rm CH}{\rm -O}{\rm -C}({\rm O}){\rm -R} & + {\rm CH}{\rm -O}{\rm -C}({\rm O}){\rm -R} \\ | \\ {\rm CH}_2{\rm -O}{\rm -C}({\rm O}){\rm -R} & {\rm CH}_2{\rm -O}{\rm -C}({\rm O}){\rm -R} \end{array}$$

where:

R: - (CH₂)₇-CH=CH-CH₂-CH(OH)-(CH₂)₅-CH₃

R¹: other fatty acid derivatives

Fig. 1. Constitution of castor oil.

droxyl functionality can be reduced through dehydration or increased by interesterification with a polyhydric alcohol. The dehydration process is carried out at about 250 °C in the presence of catalysts, such as concentrated sulphuric acid, activated earth, and under an inert atmosphere or vacuum. Under this condition of dehydration, the hydroxyl group and an adjacent hydrogen atom from the C–11 or C-13 position of the ricinoleic acid portion of the molecule is removed as water (Fig. 2). This yields a mixture of two acids, each containing two double bonds, but in one case they are conjugated. The presence of an acid containing conjugated double bond results in the oil resembling tung oil in some of its properties. Thus, castor oil, which is non-drying, can be treated and converted into a semi-drying/drying oil, commonly known as dehydrated castor oil.

 $CH_{3}-(CH_{2})_{5}-CH(OH)-CH_{2}-CH=CH-(CH_{2})_{7}-COOH$ (Ricinoleic acid) $-H_{2}O$ $CH_{3}-(CH_{2})_{4}-CH=CH-CH_{2}-CH=CH-(CH_{2})_{7}-COOH$ 9:12 Octadecadienoic acid
or

CH₃-(CH₂)₅-CH=CH-CH=CH-(CH₂)₇-COOH 9:11 Octadecadienoic acid

Fig. 2. The dehydration of ricinoleic acid.

Industrial uses. Although the oil is not edible, it is widely used as a starting material for many industrial products because of its unique structure. It is one of those vegetable oils that have found usage in many chemical industries; it is a raw material for paints, coatings and a variety of other products.

Because of its hydroxyl functionality, the oil is suitable for use in isocyanate reactions to make polyurethane elastomers (Quipeng *et al.*, 1990), polyurethane millable (Kirk-Othmer, 1979), castables (Lyon and Garret, 1973; Heiss, 1960), adhesives and coatings (Yeadon *et al.*, 1959), interpenetrating polymer network from castor oil-based polyurethane (Patel and Suthar, 1988), and polyurethane foam (Ogunniyi *et al.*, 1996; Ehrlich *et al.*, 1959). Some semi-rigid foams that have potential uses in thermal insulation were produced when castor oil/polyether mixture was reacted with toluene diisocyanate (Ogunniyi *et al.*, 1996).

Sebacic acid is manufactured by heating castor oil to high temperatures (about 250 °C) with alkali. This treatment results in saponification of the castor oil to ricinoleic acid that is then cleaved to give capryl alcohol (2-octanol) and sebacic acid (Fig.3). Although the sebacic acid yields are low, this route has been found to be most competitive. Sebacic acid is used in the production of nylon-6,10. The esters of sebacic acid are also used as plasticizers for vinyl resins and in the manufacture of dioctyl sebacate, a jet lubricant and lubricant in aircooled combustion motors. Also, capryl alcohol is used in plasticizers in the form of dicapryl esters of various dibasic acids.

Castor oil + NaOH ----> Ricinoleic acid + Glycerol

Fig. 3. Production of sebacic acid and capryl alcohol from castor oil.

As shown in Fig. 4 the pyrolysis of castor oil at 700 °C under reduced pressure has been used to obtain heptaldehyde and undecylenic acid (Das *et al.*, 1989). Undecylenic acid and heptaldehyde are important intermediates in the preparation of perfume formulations. When undecylenic acid is mixed with isobutylamine, an insecticidal synergist is obtained. Heptaldehyde can be further hydrogenated to produce alcohol for use as a plasticizer. In addition, undecylenic acid is used in preparing the athlete's foot remedy.

In order to obtain ω -aminoundecanoic acid (Saunders, 1988; Brydson, 1975), the castor oil is subjected to methanolysis to yield the methyl ester of ricinoleic acid, for which the route shown in Fig. 4 is used. In the first step, the pyrolysis of methyl ricinoleate is carried out at about 500 °C to give *n*heptaldehyde and methyl undecylenate. The methyl undecylenate is hydrolysed to give undecylenic acid, which is

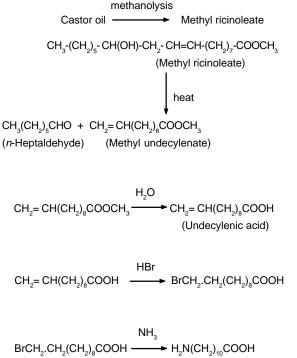


Fig. 4. Production of ω-aminoundecanoic acid from castor oil.

treated with hydrogen bromide in a non-polar solvent in the presence of peroxide. Under these conditions, reverse Markownikoff addition occurs and the main product is ω -bromoundecanoic acid. This product is then treated with ammonia to give ω -ami-noundecanoic acid, which is a crystalline solid. Amino-undecanoic acid is the starting material for nylon-11. It is claimed that a French company produces nylon-11 from this route (Kovaly, 1982).

Another characteristic of castor oil is the hydrogen bonding of its hydroxyl group. This confers high viscosity to the oil, which makes the oil useful as a component in blending lubricants and as an ingredient in fuels (Kirk-Othmer, 1979).

The castor cake is mainly used as a fertilizer. It is unsuitable as an animal feed because of the presence of toxic protein called ricin and toxic allergen, often referred to as CBA (castor bean allergen). Some methods reported for the detoxification of the cake include treatment with ammonia, caustic soda, lime and heat (Horton and Williams, 1989; Kirk-Othmer, 1979; Weiss, 1971; Gardener, 1960). When the cake is steamed, the ricin is detoxified and the allergen is inactivated. Although the use of detoxified cake as cattle feed has been reported (Woodend, 1993), extreme caution and experimentation are desirable before the cake is fed to farm animals. Interestingly, however, some people in parts

of South-Eastern Nigeria have long developed a method for treating and detoxifying the unextracted seed that is subsequently used as food seasoning (Okagbue, 1993; Weiss, 1971).

Castor oil was previously used as plasticizer for celluloid and in lacquers, however, the blown oil has been discovered to perform better. Blown or oxidized castor oil is prepared by blowing into it air or oxygen at temperatures of 80-130 °C, with or without a catalyst, to obtain oils of varying viscosity. The blown oil is used widely as plasticizer in lacquers, artificial leathers, hydraulic fluids, and adhesives (Kirk-Othmer, 1979; Weiss, 1971).

Castor oil can also be modified by reduction with hydrogen to produce hydrogenated castor oil, which is a wax like material with melting point of 86 °C. Hydrogenated castor oil is used in cosmetics, hairdressing, ointments, preparation of hydrostearic acid and its derivatives, and in certain cases as wax substitutes and for polishes. Sometimes, hydrogenated castor oil is used as a paint additive, solid lubricant, and as pressure mould release agent in the manufacturing of formed plastics and rubber goods (Kirk-Othmer, 1979; Weiss, 1971).

Another product formed from the modification of castor oil is sulphated castor oil (also known as "Turkey red oil"). Sulphated castor oil is prepared by adding concentrated sulphuric acid to castor oil at 25-30 °C, allowed to stand for several hours, followed by washing and neutralizing with sodium hydroxide solution. It is an active wetting agent. As such, it is used extensively in dyeing and in finishing of cotton and linen. The action of sulphuric acid on castor oil also produces a useful emulsifier for certain insecticidal oils (Kirk-Othmer, 1979; Weiss, 1971).

Even though a small amount is involved, about 0.7 parts per hundred of rubber of castor oil is added to latex or wet rubber to promote crumbling and thus produce the crumb rubber grade (RIMK, 1966).

Dehydrated castor oil (DCO) is used in the preparation of alkyd resins (Ogunniyi and Njikang, 2000) that are in turn used for paints, enamels, lacquers and varnishes with high gloss, good adhesion, and wetting qualities. It has advantages over tung oil because it is non-yellowing (Weiss, 1971). The vulcanization of DCO with sulphur has been reported (Botros and Meinecke, 1987), the resulting product, factice, has been found to be a rubber additive with antiozonant and good flow properties.

Other miscellaneous applications in which castor oil is used include the preparation of brake fluids, the formulation of cathartic, the formulation of contraceptive creams, the preparation of bland emollient to treat skin diseases, and for inducing labour in pregnancy. It is also used as an ingredient of soaps and polishes. Castor oil-based synthetic detergents are less prone to foaming and the disposal of the detergent is hastened since microbiological breakdown is simplified. Since DCO contains unsaturated acids, it is probable that DCO can be epoxidized (Kirk-Othmer, 1979; Weiss, 1971). If DCO is epoxidized, the product can be evaluated in polyvinyl chloride compounds as a plasticizer/stabilizer with the possibility of serving as an alternative to epoxidized soybean oil that is currently being used.

In addition, stems from castor plant can be used as fibre for making ropes while the cellulose obtained from the stem can be used for making cardboard and paper. The leaves in the growing plant are also said to be able to repel flies and mosquitoes. An assessment of the use of the castor plant in agroforestry has also been reported (Muchena, 1998).

Conclusion

The various uses of castor oil have been outlined but it must be realized that several other chemicals that can be produced from castor oil have not been mentioned. In many countries, with little or no petrochemical feedstock, castor oil can prove to be a useful renewable resource. This oil, with a variety of uses, is a suitable substitute for industrial applications where many edible oils are being used currectly. Generally, it is desirable that nonedible oils should be exploited for such purposes, as far as possible, so that edible oils can become available for human consumption. This is especially important in developing countries where food security poses a serious challenge and renewable chemical feedstocks are not available.

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