Production and Uses of Key Castor Oil Oleochemicals

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Key Castor Oil Derivatives & Oleochemicals Discussed in this Article

- Turkey Red Oil
- Ricinoleic Acid
- Hydrogenated Castor Oil
- 12-Hydroxy Stearic Acid (12-H.S.A.)
- Dehydrated Castor Oil (Commercial)
- Sebacic Acid
- Undecylenic acid

ABSTRACT

Castor oil is one of the most versatile plant oils. The various grades of the oil and its derivatives are currently used in over a dozen diverse industries. In future, with the rising environmental concerns and the need for bio-based products to replace synthetic feedstocks, castor oil and castor oil oleochemicals have the potential to be used in many newer industries,

Many derivatives and oleochemicals of castor oil require relatively simple methods for their production, while higher generation derivatives such as sebacic acid or salts of ricinoleic and undecylenic acid could require more sophisticated production methods.

This paper has a focus on the key oleochemical derivatives of castor oil, as it is felt these derivatives will have significant increases in demand in future. For instance, there has been a tremendous amount of interest worldwide in the use of castor oil for production of polyamides and other polymers such as polyurethane; this is likely to result in significant demand increases for oleochemicals such as sebacic acid, undecylenic acid and special grades of castor oil such as the low moisture grade.

This article provides more details on the production processes for the key oleochemicals derived from castor oil, and especially those that are likely to have very high future business potential. It will also provide inputs on the various current and future possible applications of these oleochemicals.

It is hoped that these details will motivate entrepreneurs and businessmen to explore the business opportunities in castor oil-based oleochemicals with greater vigour.

Manufacturing Processes of the Key Castor Oil Oleochemicals and End Uses

Introduction to Castor Oil Oleochemicals Production

The following are the generic reactions through which a range of castor oil oleochemicals are produced.

Generic Chemical Reactions of Castor Oil for Manufacture of Various Grades & Derivatives

Reaction Type	Nature of Reaction	Added Reactants	Type of Products
Ester Linkage	Hydrolysis	Acid, enzyme or Twitchell reagent catalyst	Fatty acids, glycerol
	Esterification	Monohydric alcohols	Esters
	Alcoholysis	Glycerol, glycols, pentaerythritol, and other compounds	Mono- and diglycerides, monoglycols, etc.
	Saponification	Alkalies, alkalies plus metallic salts	Soluble soaps, insoluble soaps
	Reduction	Na reduction	Alcohols
	Amidation	Alkyl amines, alkanolamines, and other compounds	Amine salts, amides
Double Bond	Oxidation, polymerization	Heat, oxygen, crosslink agent	Polymerized oils
	Hydrogenation	Hydrogen (moderate pressure)	Hydroxystearates
	Epoxidation	Hydrogen peroxide	Epoxidized oils
	Halogenation	Cl_2, Br_2, I_2	Halogenated oils
	Addition reactions	S, maleic acid	Polymerized oils, factice
	Sulphonation	H_2SO_4	Sulphonated oils
Hydroxyl Group	Dehydration, hydrolysis, distillation	Catalyst (plus heat)	Dehydrated castor oil, octadecadienoic acid
	Caustic fusion	NaOH	Sebacic acid, capryl alcohol
	Pyrolysis	High heat	Undecylenic acid, heptaldehyde
	Halogenation	PCl_5, $POCl_3$	Halogenated castor oils
	Alkoxylation	Ethylene and/or propylene oxide	Alkoxylated castor oils
	Esterification	Acetic-, phosphoric-, maleic-, phthalic anhydrides	Alkyl and alkylaryl esters, phosphate esters
	Urethane reactions	Isocyanates	Urethane polymers
	Sulphation	H_2SO_4	Sulphated castor oil (Turkey red oil)

Reference: G. R. O'Shea Company and other sources

A brief production process for each of the following oleochemicals is provided in this white paper:

- Turkey Red Oil
- Ricinoleic Acid
- Hydrogenated Castor Oil
- 12-Hydroxy Stearic Acid (12-H.S.A.)
- Dehydrated Castor Oil (Commercial)
- Sebacic Acid
- Undecylenic acid

Note 1: Non-castor Routes for the Products

It should be noted that almost all the products mentioned above are produced solely using castor oil. In some cases such as Sebacic Acid, alternative starting products are possible (Sebacic Acid can also be produced from Adipic Acid, for instance), but the primary method of production is using castor oil as the starting material.

It should also be noted that none of the above products are currently produced with petroleum as the starting product, though it is technically possible to use petroleum as the base for these. The reason most likely has to do with the economics of production. It is more economical to produce these from castor oil owing to the unique chemical structure of the oil than it is to use synthetic materials.

Note 2: Availability of Indigenous Technology for the Products

Except for Sebacic Acid, for all the products mentioned, indigenous technologies are available in India for their manufacture. The large producers of castor oil are currently producing and exploring all the derivatives except Sebacic Acid, which is produced only by one or two companies in India. China is the largest producer of Sebacic Acid in the world, with production volumes being orders of magnitude higher than those for India.

Note 3: Third Generation Castor Derivatives

Most of the derivatives noted in the list above belong to the second generation derivatives. There are derivatives that belong to the third generation. These comprise chemicals which are high specialty chemicals such as Zinc Ricinoleate. Most of the third generation derivatives are produced outside of India. These derivatives however have much smaller volumes individually than the second generation derivatives (though they command much higher prices), and as a result, these have not been included here.

Turkey Red Oil / Sulfonated Castor Oil

Sulfonated castor oil, considered the first detergent, is created by adding sulfuric acid to castor oil. It is prepared by adding concentrated sulphuric acid to castor oil at 25-30^{o}C for several hours, followed by washing and neutralizing with sodium hydroxide solution.

End Uses

- Producing synthetic detergents
- Formulating lubricants, softeners, and dyeing assistants.
- Active wetting agent, used in dyeing and in finishing of cotton and linen.
- Used in bath oil recipes along with fragrance or essential oils, or in shampoos.
- Used to emulsify essential oils

Hydrogenated Castor Oil

Hydrogenated castor oil (HCO) or castor wax is a hard, brittle wax. It is produced by adding hydrogen to castor oil in the presence of a nickel catalyst. In the hydrogenation process, the ricinoleic acid becomes fully saturated and forms a viscous wax-like product with a high melting point of 86°C. Hydrogenation may be defined as the conversion of various unsaturated radicals of fatty glycerides into more highly or completely saturated glycerides by the addition of hydrogen in the presence of a catalyst.

Hydrogenated oils are created by a controlled heat process in which the melting point is raised to change the oil into a waxy substance. The hydrogenation process improves the stability and texture of a product and is heat controlled to avoid the creation of trans-fats. The object of the hydrogenation is not only to raise the melting point but also to improve the keeping qualities, taste, and odor. As the reaction itself is exothermic, the chief energy requirements are in the production of hydrogen, warming of the oil, pumping, and filtering.

End Uses

- Used for coatings and greases.
- Utilized in the manufacture of waxes, polishes, carbon paper, candles and crayons.
- Finds use in cosmetics, hair dressing, ointments, and in preparation of hydroxyl-stearic acid.
- Used as a paint additive, pressure mould release agent in the manufacture of formed plastics and rubber goods.

12-Hydroxy Stearic Acid

12-HSA 12-HSA (12 Hydroxystearic Acid) is produced from hydrogenated castor oil. It is formed by hydrolysis of hydrogenated castor oil (HCO), during which glycerin is split off from HCO.

End Uses

- Used in grease manufacture, plastics lubrication and as raw material for synthesis of complex chemicals.
- Used as a high hydroxyl castor based wax, as a wax ingredient.
- Used for providing a hard finish for the automotive and small appliance industries.

In cosmetics

- Used for gelling liquid petroleum to produce brilliance.
- It may be incorporated into cold creams and vanishing creams to give a jelly-like feeling.

In paints

Used to produce acrylic esters to produce hard, durable thermosetting polymers used in high-quality automotive, industrial appliance and metal decorative finishes.

In rubbers

Functions as an activator and internal lubricant for natural and synthetic rubbers.

Ricinoleic Acid

Ricinoleic acid is obtained from castor oil through hydrolysis, usually carried out under basic conditions, by treating it with NaOH.

Castor Oil + NaOH (Hydrolysis) -> Ricinoleic Acid + Glycerol 12-HAS

End Uses

While known chiefly as a purgative a few decades ago, this fatty acid now affords a wide range of reactions enabling the formation of several derivatives. These chemicals are on par with petrochemical products for use in several industrial applications.

- Primary uses include coatings, plastics, inks and cosmetics.
- Used as a topical treatment for ringworm, keratoses, skin inflammation, abrasions, and fungal-infected body parts.
- Used in the production of macrolactones and polyesters.
- Has been used in contraceptive jellies
- Used in soaps, amine compounds, esters in cutting oils, industrial lubricants, emulsifiers, metal working compounds.
- Used in resins, thermosetting acrylics and non-drying plasticizing esters.
- Quaternary ammonium compounds based on ricinoleates and hydroxy stearates have been used in for cosmetics skin and hair care, personal products, germicides and textile processing agents.
- A new class of biodegradable polyanhydrides based on ricinoleic acid has been synthesized

Dehydrated Castor Oil

The dehydration process is carried out at about 250^{o}C in the presence of catalysts (e.g., concentrated sulphuric acid, activated earth) and under an inert atmosphere or vacuum. Under this condition of dehydration, the hydroxyl group and adjacent hydrogen atom from the C-11 or C-13 position of the ricinoleic acid portion of the molecule is removed as water. 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 bonds results in an 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 or drying oil known as dehydrated castor oil.

End Uses

- Used to improve the quality of house paints, enamels, caulks, sealants and inks.
- Used as primary binder for house paints, enamels, caulk sealant, and making varnishes.
- In the form of dehydrated castor fatty acid, it is used in the manufacture of alkyd resins, coatings, appliance finishes, primers and inks; alkyd resins in turn are used for paints, enamels, lacquers and varnishes with high gloss, good adhesion and wetting qualities.

Undecylenic Acid

The pyrolysis of castor oil at 700oC under reduced pressure has been used to obtain heptaldeyde and undecylenic acid. (Pyrolysis is the chemical decomposition of organic materials by heating in the absence of oxygen or any other reagents, except possibly steam.) Heptaldehyde can be further hydrogenated to produce alcohol for use as a plasticizer.

Another method is via the hydrolysis of Methyl Undecylenate. Methyl Undecylenate is hydrolysed to give Undecylenic Acid.

(CH_2=CH (CH_2)$_8$$COOCH_3$) Methyl Undecylenate → H_2O → Undecylenic Acid (CH_2=CH (CH_2)$_8$$COOH$)

End Uses

- Undecylenic acid has a long history as antifungal drug. It is used to treat many types of fungus infections.
- Undecylenic acid can be used as a surfactant in hair lotions
- Used as biocide in soaps and deodorants
- Starting material for Nylon-11

Sebacic Acid

Sebacic acid, a 10-carbon dicarboxylic acid, can be synthesized from phenols and cresols, but castor oil oxidation is considered a —greener|| process. Sebacic acid is manufactured by heating castor oil to high temperatures (about 250oC) 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.

End Uses

- One of the largest uses of sebacic acid is in the manufacture of Nylon 6-10.
- Sebacic acid and its derivatives such as Azelaic acid have a variety of industrial uses in plasticizers, lubricants, hydraulic fluids, cosmetics, candles, etc. They are used in the synthesis of polyamide and alkyd resins. An isomer, isosebacic acid, has other applications in the manufacture of extrusion plastics, adhesives, polyesters, polyurethane resins and synthetic rubber.
- Sebacic acid is also used as an intermediate for aromatics, antiseptics and painting materials. A large number of esters can be obtained from thousands of potential starting materials.
- It is used as a corrosion inhibitor in metalworking fluids and as a complexing agent in greases. When mixed with amines, sebacic acid can give a very effective water soluble corrosion inhibitor for metal working fluids.
- Lithium hydroxystearate complex greases often utilize dibasic acids such as sebacic acid for the more unusual performance parameters. These greases require the esters of sebacic acid, which were developed for specific performance criteria under varying conditions.
- The esters of sebacic acid also are used as plasticizers for vinyl resins and in the manufacture of dioctyl sebacate - a jet lubricant and lubricant in aircooled combustion motors.

Current demand-supply estimates for the select grades of castor oil derivatives

Product	Demand	Current Demand Supply Gap	Future Demand
Hydrogenated Castor Oil (HCO)	Medium	Medium	Very High
12 Hydroxy Stearic Acid (12 HSA)	Medium	Medium	Very High
Sulfated/Sulfonated Castor Oil, Turkey Red Oil	Medium	Medium	Medium-High
Dehydrated Castor Oil (DCO)	Medium-High	Medium	Very High
Undecylenic Acid	Very High[1]	Very High[1]	Very High
Ricinoleic Acid	Medium	Medium	Low-Medium
Sebacic Acid	Very High[2]	Medium-High	Low

[1] *A very large percentage of Undecylenic Acid is used by Arkema to manufacture Nylon 11*
[2] *Large percentage of Sebacic acid is used for the manufacture of Nylon 6*

Notations for Demand

Very High: 50,000 T and above per year
High: 30,000 - 50,000 T per year
Medium-High: 15,000-30,000 T per year
Medium: 5,000-15,000 T per year
Low-Medium: 1,000-5,000 T per year
Low: Less than 1,000 T per year

Notations for Demand-Supply Gap

Medium: There exists some demand over and above supply, but there has not been a significant amount of demand that has gone unmet
Medium-High: There have been some instances where a significant demand has gone unmet
High: There have been many instances where a significant demand in the market has gone unmet
Low: There have been very few instances when a significant demand has gone unmet
NA: denotes that information on demand supply gap is not available owing to the negligible demand volumes.

SUMMARY

Derivatives of castor oil find application in a number of industries and end uses. Of these derivatives, the most prominent are turkey red oil, ricinoleic acid, hydrogenated castor oil, 12-hydroxy stearic acid (12-H.S.A.), dehydrated castor oil (commercial), sebacic acid and Undecylenic acid.

An analysis of these derivatives in the context of their applications and trends in demand suggest that most of them promise significant increase in demand in future, implying attractive opportunities for businesses and entrepreneurs to invest in these derivatives. CastorOil.in recommends further research and exploration of these derivatives by the Indian and global industry.

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Profile of CastorOil.in

CastorOil.in is the leading global intelligence and information resource for the castor oil and castor derivatives industry. In addition to providing comprehensive information assistance online, the *Comprehensive Castor Oil Report* is the most comprehensive report on castor oil, providing essential inputs for businesses, entrepreneurs and investors interested in exploring the castor industry.

Comprehensive Castor Oil Report

Those interested in knowing more about the castor oil and derivatives industry will find the *Comprehensive Castor Oil Report* an indispensable guide. This report provides comprehensive details on all the segments of the castor industry value chain – from cultivation of castor crop to production of high end derivatives. It contains critical investment and production process intelligence relevant to investors and businesses, and has a detailed section on the production of second and third generation derivatives from castor oil.

Get to know more about the *Comprehensive Castor Oil Report* from here - http://www.castoroil.in/reference/report/report.html

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