Spilling the Beans About Castor Oil and its Derivatives

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It has become apparent that customers are curious about castor oil and its origin. This presentation will remind some and educate others about the why and wherefore of the castor bean, its valuable oil and its importance to the industrial markets. This is not an attempt to teach the organic chemistry of castor oil or its derivatives, but rather a discussion about its versatility, proficiency and availability. It is hoped that everyone leaves here today with some new information or a new understanding about castor oil. Let's crack open this industrial strength legume!

Castor beans grow best in hot, dry climates in sandy loam soils, like those in India or Brazil. They have deep root systems and are regarded by farmers as excellent rotation crops. The beans are both perennial and annual and require strict weed control early in their 4- month growing season. This weed control has a definite influence on the yield. The crops are harvested either by hand or mechanically, and harvesting is usually done twice each season to maximize the yield.

The seed content makes up 65-85% of the weight of the bean, and the oil content can range from 35-52%, depending on the variety of seed and environment. While the terms castor bean and castor oil are often used interchangeably, it is the oil that has commercial value. Extraction of the oil from the bean is accomplished through a critical mechanical pressing. Since castor beans can be fatal if ingested, great care must be taken when handling them. Castor residue or meal contain toxins and allergens which remain behind in the residual meal. These toxins are soluble in water, but not in castor oil. Despite these unhealthy toxins, when detoxified, they make an important by-product that is potentially beneficial in horticultural and agricultural applications. There are several studies being conducted to explore this end use, and the cost of detoxification vs. the benefits will be the determining factor for future investments.

Let's run through this bean's vital statistics:

Typical Properties of Castor Oil

Density @ 20°C	0.956-0.963g/ml
Refractive Index	1.477 -1.479
Saponification Number	177-187
Iodine Value	82-88
Unsaponifiable Matter	0.3-0.5%
Hydroxyl Number	160mm
Viscosity @ 20°C	9.5-10.0dPa.S

Unique to castor oil is that regardless of where the beans are grown, the chemical composition remains constant. It is this consistency that has allowed castor oil to be used as the absolute standard for viscosity by the Bureau of Standards.

Castor oil's chemical formula is: CH_3-$(CH_2)_5$-CH(OH)-CH_2-CH=CH-$(CH_2)_7$-COOH

It is a fatty acid with 18 carbon atoms, a double bond between the ninth and tenth carbons, and is known as Dodecahydroxyoleic Acid. No other vegetable oil contains such a diverse and high proportion of fatty hydroxyacids.

Castor oil has a molecular weight of 298, a low melting point (5°C) and a low solidification point (12°C to -18°C). It is a monounsaturated fatty acid, soluble in pure alcohol, insoluble in water and has some miscibility in petroleum aliphatic solvents. It resists heat and leaves virtually no residue. There are two grades sold, pharmaceutical and industrial, and there are first, second and third quality in the industrial grades. Pressed castor oil, extracted with no solvents, is called first quality.

Castor beans have been a relatively stable product for over 25 years. Weather has been a major factor in production fluctuations for some countries, and total world production has exceeded a million tons per year since the 1980's. The USSR was a major producer until 1990; however, today the major producing countries are India, Brazil and China. India currently produces 90% of the world's castor seeds and is responsible for 80% of the world's export product. China's production has doubled since 1970, while India's has increased four-fold. China, the EC and Japan have been major importers of castor oil.

Yields of the castor bean crop are generally poor for various reasons. Mother Nature's fickle ways are the primary influence on all crops in all countries. Farming technique in some producing countries is non-intensive and often done manually. In some third world countries the full benefits of scientific advancements in agriculture have not been fully enjoyed.

In all producing countries, castor oil is a strategic revenue generator to the governments. Farming has been and continues to be subsidized by governments for growing a castor bean crop. The relationship between these farmers and their government has a fiscal impact around the world!

More than 80% of castor oil is processed in the producing countries, which benefits the individual countries economically by retaining the added value of the oil. The United States has recently started to produce castor beans, but it is not yet a factor globally. The health and safety issues of processing the oil are the biggest concern to our government. Until about 1960, there was some processing in the U .S., but it has all gone away. Germany, Italy and France have processing plants, and France is the largest importer of castor oil in the EC.

The castor oil market has been on a vicious cycle of shortfall and surplus, depending on yields, weather, domestic consumption and economic conditions in the producing countries. Although the price has fluctuated between $500 and $1500/ton, the price of castor oil remains higher than any other vegetable oil.

This next chart shows one of the most significant aspects of this presentation -who's producing, who's not, and how much! It is worth noting that this bean is a year round

commitment for the farmer- 4- months of growing, 5 months of harvesting. Truly a financial windfall or bust, depending on Mother Nature and market demand.

World Castor Seed Production (1000 tons)

	'96 – '97	'97 – '98	'98 – '99	Main Harvest
USSR	3	3	4	July - Sept
Brazil	45	128	45	May - Sept
Paraguay	9	9	10	May - Sept
China	220	180	210	Sept - Jan
India	770	700	800	Nov - Mar
Pakistan	3	8	7	Dec - May
Thailand	18	18	15	Dec - May
Others	40	50	50	Nov - Jan
World Production	~1100 tons	~1100 tons	~1200 tons	(thousands)
Average Yield/ton	0.85	0.87	0.88	
Oil Produced (42%)	462 tons	462 tons	504 tons	

This next chart is a great comparison of the chemical make-up of some vegetable oils. The obvious standout is the high concentration of ricinoleic acid in the castor oil -90%. Again, this concentration is consistent regardless of where the castor bean is grown.

Castor Beans Oil Yield vs. **Other Vegetable Oils Yield**

	% A vg. Oil Content	Oleic Acid	Linoleic Acid	Linolenic Acid	Ricinoleic Acid
Castor	45%	3%	4.2%	0.3%	90%
Rape Seed	42%	32%	19%	7%	-0-
Linseed	38%	20%	16%	50%	-0-
Sunflower	48%	26%	62%	-0-	-0-
Soybean	18%	27%	53%	7%	-0-
Palm	52%	40%	8%	-0-	-0-

There is some work underway investigating the use of soybean oil as a lubricant. Although the preliminary results are encouraging, they are still inconclusive.

Reactions and Applications

The world's largest single use of castor oil in one product, outside the lubricants markets, is in the manufacture of polyamide 11 (Nylon 11). The process is involved and includes several reaction steps. Compared to its predecessors, Nylon 6, 6-6 and 6-10, Nylon 11 has

the lowest melting point, lowest specific gravity and the lowest moisture absorption. It also is resistance to acid and alkaline reagents or oxidizing agents. These qualities are of particular importance in high quality engineering plastics and in durable protective coatings. This application is mentioned only because of its impact on the consumption of castor oil.

As often happens, despite our advances in science, it is not the chemistries that change as much as the applications. Older chemistries are often given new life when their proven features are recognized due to economic restrictions or supply considerations. Castor oil has long been used as a lubricant; however, today, it is also a natural plasticizer. It has great compatibility with rosins, gums and resins. It allows inks, coatings and adhesives to be supple and easy to use.

Castor oil has been used in many different reactions for everything from soap to polymers to lubricants. Reactions include hydrolysis, esterification, hydrogenation, caustic fusion and sulfonation. Quite a resume for a bean!

Let's discuss a few of these reactions, but stay focused on the applications pertinent to the grease and lubricant markets.

HCO -Hydrogenated Castor Oil
Hydrogenation of castor oil accounts for the largest single use of castor oil for a standard commodity. 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, which makes HCO valuable in resin and polymer mixtures. The HCO is insoluble in water and most organic solvents, but it is soluble in hot solvents. It is this insolubility that makes HCO valuable to the lubricants markets. It is water resistant while retaining lubricity , polarity and surface wetting properties. It is perfect for metal drawing lubricants and multipurpose industrial greases. HCO made its debut in greases as a replacement for traditional soap thickeners, sodium, potassium and calcium. Today, it is the lithium soap thickeners which are dominant. The early use of HCO in greases was to improve texture and oxidative stability of greases exposed to high sheer stress with little effect on structure or consistency. The introduction of HCO opened up a whole new world of possibilities to the formulator.

12HSA -12 Hydroxystearic Acid
12HSA is formed when glycerin is split off from HCO. Both HCO and 12HSA have enjoyed popularity with the growth of lithium complex greases, which are growing to be the largest segment of the grease market. These greases have excellent heat tolerance like the sodium greases and the water resistance of calcium greases -the best of two worlds. The addition of 12HSA enhances the overall performance with better texture, improved heat stability and improved dropping points. It simplifies the grease manufacturing process because it no longer requires milling and homogenization steps that were normally used with lithium type greases.

12HSA soaps are used in mineral oil-based multipurpose greases making it possible for one grease to fill the requirements of a variety of needs in the automoti ve and truck

greases. In aviation and other high performance greases where there is a wide range of temperatures, -65C to + 180C, dibasic-acid esters of glycols or polyols are recommended.

Methyl 12HSA -Methyl 12 Hydroxystearate
Methyl 12HSA is formed by direct esterfication of the 12HSA with methanol. It is usually sold in the liquid form and is widely used in the continuous grease process. It has a lower melt point than 12HSA and is, therefore, easier to handle in the liquid form. Methyl 12 is an ester that is efficient in extending the lubrication life of a grease. Greases made with the product can be formulated to higher drop points, and they experience both less bleeding and improved oxidative stability .The development of these products was most beneficial in the grease processing area due to no more milling and homogenizing, less shearing and overall uniform consistency.

Typical Properties of HCO, 12 HSA, Methyl 12 HSA

	HCO	12 HSA	Methyl 12 HSA
Hydroxyl Value	158	178	160+
Iodine Value	3	3	3
Saponification Value	180	186	175+
Acid Value	2	180	1.2
Melting Point °C	86	76	52
Specific Gravity 25 °C	1.02	1.021	1.02

Sebacic Acid -SBA
A major commercial reaction of castor oil involves caustic fusion to yield Sebacic Acid (SBA) and a by-product, 2-octanol (capryl alcohol). There is an older domestic conversion which uses a mixture of molten caustic soda and caustic potash. The modern method, which claims higher yields, uses recinoleic acid and molten caustic. The type of reaction used affects the purity of the sebacic acid, but the modern conversion technology results in a higher purity.

China is currently the primary producer of SBA. The United States and (soon) India are also producers. Although the largest use of SBA is in the manufacture of Nylon 6-10, it is also used as a corrosion inhibitor in metalworking fluids and as a complexing agent in greases. When mixed with amines, SBA can give a very effective water soluble corrosion inhibitor for metal working fluids. Results were confirmed using the standard cast iron chip test.

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. Examples: DOS (dioctyl sebacate) is very functional in low temperature formulations, DSS (disodium sebacate) has been used to replace sodium nitrites in aluminum greases. Its fine particle size allows it to be added to the grease during the cool down period with no additional processing. DMS/DBS (dimethyl sebacate/dibutyl sebacate) are synthetic base stocks that can replace the mineral oils for environmentally friendly applications. DOS or DMS in complexed greases improve workability and low temperature properties

particularity for applications in aircraft, trucks, automobiles and equipment exposed to arctic conditions.

This is just a "scratch on the surface" of the applications for castor oil, but it shows the varied applications and the importance of these beans to our industry.

Conclusions

Castor oil is a proven competitor in the industrial chemical markets. It is a necessary commodity whose pricing issues, whether real or perceived, can have a global impact.

We are confident in saying that castor oil is a critical raw material for the industrial chemical markets. It is **practical, natural, renewable** and very **versatile,** and it has been a staple for the oleochemical markets for a very long time. Castor oil has been called on to resolve numerous formulating and processing needs because of its unique fatty acid structure. It offers consistent benefits that no other vegetable oil has been able to offer.

Jack was right, "there is magic in those beans".

Bibliography

Chemistry of Castor Oil and Its Derivatives and Their Applications International Castor Oil Association Technical Bulletin No.2, 1992

Le Ricin, Alain Bonjean, 1991

The Processing of Castor Meal for Detoxification and Deallergenation Technical Bulletin #1-1989

Castor Production Technology Guide, Elf Atochem

CasChem Technical Bulletin 100 Hampshire Commodities Ltd.