

## Unbodied Dehydrated Castor Oil from Oil of Castor Beans Cultivated in Tropical and Sub Tropical Zones of Pakistan

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**Abstract.** Commercially available castor oil was analysed for specific gravity at 25/25 °C (0.959), acid value (0.5), iodine value (85), refractive index at 25 °C (1.4769), viscosity at 25 °C (6.8), and hydroxyl value (162). Fatty acid composition, including palmitic acid (1.7%), stearic acid (1.39%), oleic acid (5.73%), linoleic acid (6.25%), and ricinoleic acid (84.2%) was estimated by means of GLC. Unbodied dehydrated castor oil (DCO-15) 93% was prepared by using sodium bisulphate and sodium bisulphite and other reaction conditions. Unbodied DCO was analysed for iodine value (139), acid value (3.6), refractive index at 25 °C (1.4820), specific gravity at 25/25 °C and 30/30 °C (0.9333&0.925) viscosity at 25 °C and 30 °C (200 cps & 1.85 poise), respectively. Fatty acid composition was also determined to ascertain the extent of dehydration due to the formation of conjugated linoleic acid (CLA, 36.9%) and non conjugated linoleic acid (NCLA, 46.8%). Ricinoleic acid was estimated as 3.83%. Unbodied DCO-15 was in good conformance with the standard specification of ASTM and other values cited in the literature.

**Keywords:** castor beans oil, gas liquid chromatography, ricinoleic acid, linoleic acid, dehydrated castor oil

### Introduction

Castor beans *Ricinus communis* L., is a rich source of industrial oil crop, which is an important industrial oil crop of the world. Castor bean is successfully cultivated in tropical and sub tropical regions of Pakistan. Castor seeds contains about 50-55% of castor oil which is composed of 81-96% of glycerides of ricinoleic acid ( $C_{18}H_{34}O_3$ ) (Castor-PARC). Ricinoleic acid (85-95%) is reported as the predominant hydroxyl fatty acids of castor oil (Raie, 2008). This hydroxyl fatty acid makes the castor oil unique vegetable oil. Dehydrated castor oil is one of these derivatives and is employed in manufacture of paint and varnish and to improve the quality of house paints, enamels, caulks, sealants and inks.

In the process of dehydration, two isomers of linoleic acids were obtained according to the position of double bond, named as 9,12-octadecadienoic acid and 9,11-octadecadienoic acid. On the basis of viscosity and iodine value dehydrated castor oil is categorised in two main types, termed as unbodied and bodied. Unbodied refers to the dehydrated castor oil (DCO) that has not been additionally heat polymerised. Bodied refers to polymerised castor oil of higher viscosity (7-100 poise) as mentioned by Krik-Othmer (1993). The aim of this

study was to investigate the most suitable reaction conditions including minimum temperature and holding time at which the polymerisation of the oil has to be maintained to produce unbodied DCO of the standard specifications (ASTM, 1995, D961-86). Present work was based on the physicochemical characterisation of castor oil, utilisation of minimum quantity of chemicals to produce unbodied DCO and its physicochemical evaluation by applying standard analytical techniques at laboratory scale. This work was initiated first time in Pakistan.

### Materials and Methods

Pure castor oil was procured from a super market in Saddar, Karachi, Pakistan. All chemicals including sodium bisulphate and sodium bisulphite, iodine monochloride, carbon tetrachloride, anhydrous sodium sulphate, sodium hydroxide, ethanol, methanol etc., pure standards of methyl esters of fatty acids were purchased from Merck, Sigma and Aldrich Co. Perkin Elmer's gas chromatograph, Clarus 500 model equipped with flame ionisation detector was used for fatty acid composition of castor and dehydrated castor oil. RTX 2330 column was installed in GC oven. Dehydration reaction assemblies (three) were designated with respect to the excess time given to each system after 2.5 h, as DCO-15, DCO-25, and DCO-35.

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**Physicochemical analysis of refined castor oil.** Acid value, iodine value, refractive index, specific gravity, viscosity and hydroxyl value of castor oil were determined by and ASTM and AOCS test methods (ASTM, 2006; AOCS, 1998).

**Fatty acid composition of castor oil.** Gas chromatographic analysis was conducted to evaluate fatty acids composition of castor oil. For this purpose fatty acid methyl esters were prepared according to the IUPAC method (IUPAC, 1987) and the GC conditions applied were same as in our previous work (Saleem *et al.*, 2007).

**Dehydration of castor oil.** Castor oil (0.250 kg) was measured into three different round bottom flasks marked as DCO-15, DCO-25, DCO-35, equipped with thermometer, condenser, and mechanical stirrer. Sodium bisulphate (1.3%) as catalyst and sodium bisulphite (0.3%) as an antipolymerising agent were added into each flask. Reaction was initiated under vacuum 23-25" Hg to pull off water into the receiver. These systems were heated on three heating mantles with continuous stirring. Temperature of heating mantles was raised gradually from ambient to 230 °C within 2.5 h (150 min). Then DCO-15, DCO-25, DCO-35 were subsequently controlled at the same temperature for 15, 25 and 35 min, respectively. Then reaction flasks were disconnected and cooled immediately and all the three products of DCO were filtered and weighed to calculate their yields.

**Physicochemical analysis of unbodied dehydrated castor oil.** DCO-15, DCO-25 and DCO-35 were analysed for acid value, hydroxyl value, refractive index, viscosity and specific gravity by using standard and ASTM and AOCS test methods (ASTM, 2006; AOCS, 1998). Iodine value was determined by using ISO (1996), this method is especially recommended for oils containing conjugated fatty acids such as tung oil and DCO.

**Fatty acid composition of unbodied DCO.** Gas chromatographic analysis was conducted to evaluate fatty acid composition of DCO and to assess the degree of dehydration by quantification of conjugated and non conjugated linoleic acid (CLA and NCLA) and ricinoleic acid. For this purpose fatty acid methyl esters were prepared according to the IUPAC method (IUPAC, 1987) and GC conditions applied were same as in our previous work (Saleem, *et al.*, 2010).

## Results and Discussion

**Physicochemical analysis and fatty acid composition of refined castor oil.** Physicochemical properties and

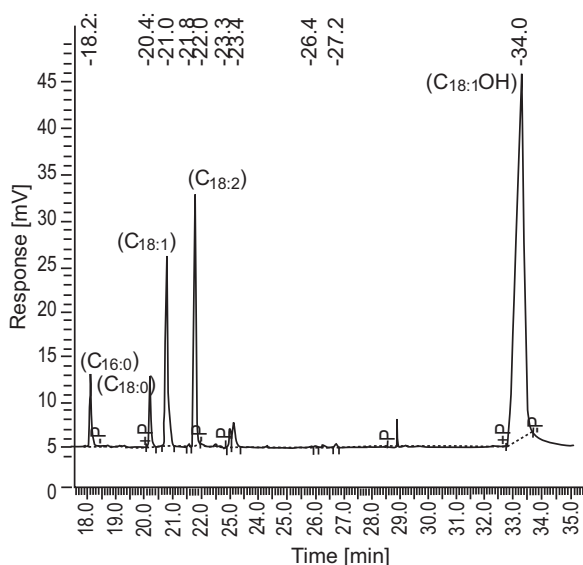
fatty acid composition of castor oil are presented in Table 1. Acid value (0.5) proved that castor oil contained minimum amount of acidity in the form of free fatty acids and the oil is of good quality. Similarly, refractive index (1.4772), viscosity (6.8), hydroxyl value (162), iodine value (85) and fatty acid composition in Table 1, show that castor oil is pure and comply with the standard specification of castor oil. The oil was found to possess much potential to produce dehydrated castor oil due to the presence of ricinoleic acid (84%) (Fig. 1).

**Dehydration of castor oil.** In three systems it was observed that water formation was initiated at 210-220 °C and transferred into the receivers at 230 °C. It was evident from experimental results that DCO-15, 25 and 35 were quantitatively obtained as 93%, 80% and 75%, respec-

**Table 1.** Physicochemical characteristics and fatty acid composition of castor oil

Characteristics	Current values	Specification <sup>a</sup>
Specific gravity @ 25/25 °C	0.959	0.957-0.961
Viscosity @ 25 °C (St) = poise	6.8	6.3-8.8
Acid value	0.5	2.0 max
Refractive index @ 25 °C	1.4769	1.4764 or 1.4772
Hydroxyl value	162	160-168
Iodine value	85	84-88
Fatty acid composition (wt%)	-	-
Palmitic acid (C <sub>16:0</sub> )	1.7	1.0
Stearic acid (C <sub>18:0</sub> )	1.39	1.0
Oleic acid (C <sub>18:1</sub> )	5.73	3.0
Linoleic acid (C <sub>18:2</sub> ) NCLA*	6.25	4.2
Ricinoleic acid (C <sub>18:1</sub> OH)	84.2	89.5

<sup>a</sup> = reference from Krik-Othmer (1993).



**Fig. 1.** Gas chromatogram of castor oil.

tively, concluding that the minimum duration to produce the unbodied DCO in maximum amount was 165 min as in the case of DCO-15.

**Physicochemical analysis of unbodied dehydrated castor oil. Specific gravity, viscosity, refractive index, iodine value.** Specific gravity and viscosity are inversely proportional to temperature. In Table 2, it is mentioned that specific gravity(0.9333, 0.9346, 0.937) and viscosity (200, 215, 220 cps) at 25 °C were higher than at 30 °C (0.925, 0.928, 0.932) and (185, 200, 210 cps) of DCO-15, 25 and 35, respectively. It was also evident from Table 2 that specific gravity and viscosity of sample DCO-15 were lower than DCO-25 and DCO-35.

As soon as the hydroxyl group and hydrogen were removed as water then viscosities were decreased, iodine value and refractive index were increased as compared to the pure castor oil. These parameters were used to

**Table 2.** Physicochemical characteristics and fatty acid composition of unbodied dehydrated castor oil

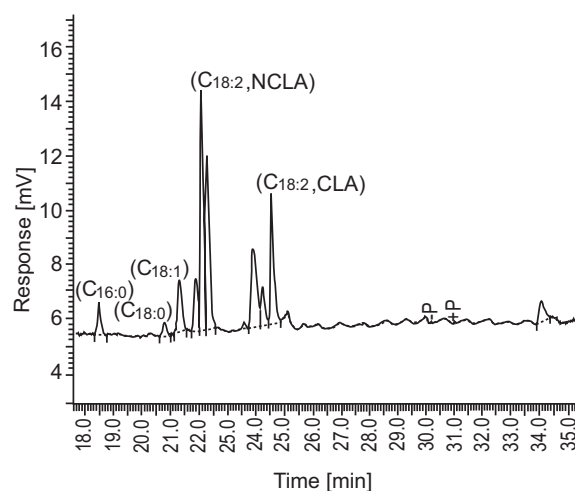
Characteristics	Current values			ASTM D445 (2006)
	DCO-15	DCO-25	DCO-35	
Specific gravity @ 25/25 °C	0.9333	0.9346	0.9370	0.926-0.937
Specific gravity @ 30/30 °C	0.925	0.928	0.932	-
Viscosity @ 25 °C (cSt) = cps	200	215	220	140-225
Viscosity @ 30 °C (poise)	1.85 = 185 cps	2.0 = 200 cps	2.10 = 210 cps	-
Acid value	3.6	6.8	7.9	6 max
Refractive index @ 25 °C	1.4820	1.4813	1.4809	1.4805-1.4825
Hydroxyl value	12.4	14.8	16.9	-
Iodine value	139	120	115	125-145
Fatty acid composition (wt %)	-	-	-	***
Palmitic acid (C <sub>16:0</sub> )	1.74	1.9	2.37	0.5 (total saturated fatty acids)
Stearic acid (C <sub>18:0</sub> )	1.58	1.42	2.79	
Oleic acid (C <sub>18:1</sub> )	5.58	5.94	6.68	7.5
Linoleic acid (C <sub>18:2</sub> )	46.8/36.98	47.62/37.6	44.99/	65/22
NCLA*/CLA**	8	6	27.4	
Ricinoleic acid (C <sub>18:1</sub> OH)	3.83	3.92	7.1	5.0

@ = Indian standard; \* = non conjugated linoleic acid; \*\* = conjugated linoleic acid; \*\*\* = Baily, A.E.1964; chapter 12, paint varnishes and related products, page no. 516.

monitor degree of dehydration and polymerisation. Iodine value of DCO-15 was higher (139) than the values for DCO-25 (120) and DCO-35(115). Iodine value of DCO 15 was maximum after a certain reaction time then decreased to a minimum (DCO-35,115) as the dehydration time was increased. Same conditions were observed by Naughton (1974), they reported that maximum iodine value was achieved near the minimum viscosity, beyond this point iodine value drops due to polymerisation.

**Acid value and hydroxyl value.** DCO-15 was found to possess the least acid value (3.6) as compared to the other two DCO-25 (6.8) and DCO-35 (7.9). This observation indicated that acid value was increased with time and higher than the prescribed limits of unbodied DCO. Similarly, hydroxyl value of three samples were also decreased from initial value i.e., 162 to 12.4,14.8 and 16.9, respectively (Table 2), which is the indication that the dehydration process had been carried out and comparatively better quality unbodied DCO (DCO-15) was prepared than DCO-25 and DCO-35.

**Fatty acid composition of unbodied DCO.** Gas chromatographic (GLC) analysis of mono,di and poly-unsaturated fatty acids of natural fats have been reported (Jabeen *et al.*, 2013; Sultana, *et al.*, 2011; Saleem, *et al.*, 2008; 2007). Fatty acid composition of three products have been mentioned in Table 2. Figure 2 shows the gas chromatogram. Initially 6.25% of NCLA was present in castor oil. Due to dehydration process major part of ricinoleic acid was converted into NCLA and CLA. In DCO-15, 25 and 35, NCLA and CLA were quantified as 46.38% and 36.98%, 47.62% and 37.6%, 44.99% and 27.4%, respectively. Ricinoleic acid was quantified as 3.83%, 3.92% and 7.17%, respectively. These results



**Fig. 2.** Gas chromatogram of unbodied DCO.

conclude that DCO-15 comply with unbodied DCO. In a previous study gas chromatographic analysis of dehydrated product showed 44% of total NCLA and 35% CLA (Achaya, 1971).

## Conclusion

Unbodied DCO of minimum viscosity and maximum iodine value was obtained by heating the reaction mixture at 230 °C further maintained for 15 min (DCO-15). This product was found to possess a low quantity of ricinoleic acid (RA) due to the conversion of major part of RA into NCLA and CLA. The other two products, DCO-25 and DCO-35, obtained by maintaining the temperature for further 25 and 35 min, respectively, were also dehydrated castor oil but their viscosities were comparatively higher and iodine value was lower than DCO-15. These products were categorised as bodied DCO. It was concluded from this study that total appropriate time for dehydration was 165 min to prepare a good quality unbodied DCO (DCO-15).

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