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Turkey Red Oil from Castor Oil using Sulphonation Process

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Abstract

Castor oil can be sulfonated directly with So_3 in commercially available continuous and batch equipment. The product has good colour, excellent water solubility and improved acid stability. The process has following advantages. it is more direct and considerably faster than the present process. It required fever man hours and therefore is more economical conditions can be varied to give a wide range of products having different solubility characteristics and combined So_3 content. Since the reaction, batch or continuous is stoichiometry, no waste product are formed, thus eliminating any pollution problem. Sulphated castor oil, also known as turkey-red oil, represents one of the earliest chemical derivatives of castor oil. The addition of conc.H_2So_4 in the castor oil by continuous agitation up to 3 hours maintaining temperature between 25-30 °C also adding very small amounts (0.1 % of that feed) of EDTA as a catalyst as a result the yield has increased rapidly.

Keywords: *Sulphonation Process, Material Balance, Kinetic Theory, Testing methods*

Introduction

Castor is cultivated around the world because of the commercial importance of its oil. **India** is the **world's largest producer** of castor seed and meets most of the global demand for castor oil. India produces 8 to 8.5 lakh tonnes of castor seed annually, and accounting for more than 60% of the entire global production.

Because of its unlimited industrial applications, castor oil enjoys tremendous demand world-wide. The current consumption of Castor Oil and its derivatives in the domestic market is estimated at about 300,000 tonnes. India is also the biggest exporter of castor oil and its derivatives at 87% share of the international trade in this commodity.

Castor is an important non-edible oilseed crop and is grown especially in arid and semi arid region. It is originated in the tropical belt of both India and Africa. It is cultivated in different countries on commercial scale, of which **India, China and Brazil** is major castor growing countries accounting for 90 per cent of the world's production.

Castor seeds contain about 48-50 percent oil by weight. The overall castor oil & derivatives manufacturing process is: Sowing > Cultivation > Harvest > Seed Dehulling& Cleaning > Oil Extraction >Oil Filtration & Purification > Oil Refining > Production of Castor Oil Grades & Derivatives. While castor oil by itself is used in diverse applications, chemical derivatives of castor oil find further uses in industrial applications and their domains of use are increasing rapidly.

Castor Oil and Its Derivatives

Vertellus supplies a variety of castor oil grades whose uses are dictated by acid value, moisture level, color and purity. Castor Oil, also known as ricinus oil, is a triglyceride of fatty acids which occurs in the seed of the castor plant.

Castor Oil is unique among all fats and oils in that:

- it is the only source of an 18-carbon hydroxylated fatty acid with one double bond
- ricinoleic acid (12-Hydroxyoleic Acid) comprises approximately 90% of the fatty acid composition
- product uniformity and consistency are relatively high for a naturally occurring material
- it is a nontoxic, biodegradable, renewable resource

The remarkably constant composition of castor oil fatty acids is shown below:

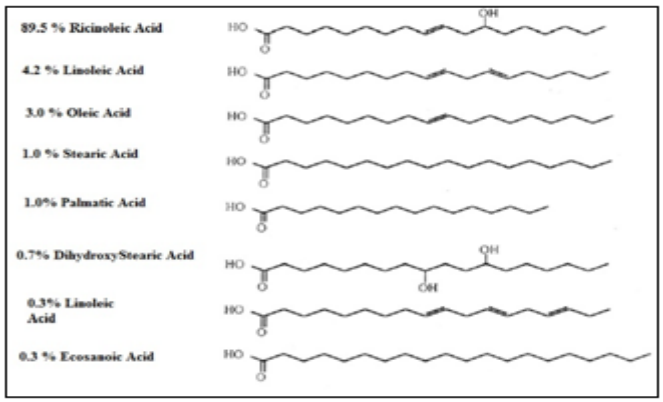

Fig. 1 Fatty acids Composition

The hydroxyl groups in castor oil account for a unique combination of physical properties:

- Relatively high viscosity and specific gravity
- Solubility in alcohols in any proportion
- Limited solubility in aliphatic petroleum solvents

The uniformity and reliability of its physical properties are demonstrated by the long-term use of castor oil as an absolute standard for viscosity. Because of its higher polar hydroxyl groups, castor oil is not only compatible with but will plasticize a wide variety of natural and synthetic resins, waxes, polymers and elastomers. Castor Oil also has excellent emollient and lubricating properties as well as a marked ability to wet and disperse dyes, pigments and fillers. In the form of its chemical derivatives, castor oil's application versatility is further enhanced.
Chemical reactions commercially used to produce a variety of derivatives are as follows:

Table 1 Chemical reactions

	Name of Reaction	Reactant	Product
Double Bound	Sulphonation	Sulphuric Acid	Sulphonated Castor Oil
Hydroxyl group	Sulphonation	Sulphuric Acid	Sulphated Castor Oil (Turkey Red Oil)

Methods
Process Diagram:
The experimental setup designed to manufacture Turkey red oil.

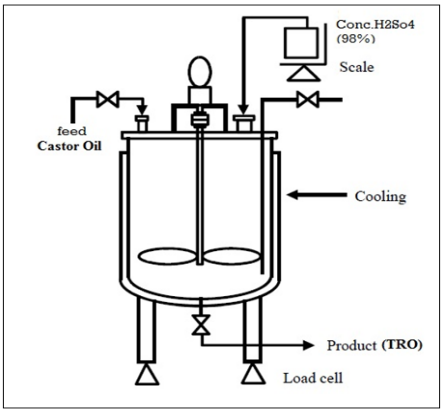

Fig. 2 Experimental Setup

Construction Details:

A Batch reactor consists of inlet for Feed(castor oil) and other one is for conc. H_2SO_4 (98 %), agitator, cooling jacket and outlet for the product. The feed inlet from the top of the reactor and at the same time, continuously adding conc. H_2SO_4 solution having purity 98%. The cooling provided through the jacket for maintaining temperature up to 25-30 °c at atmospheric conditions.

Both of the feed inlets are well mix through the agitator having speed 1000-1500 rpm. The operation carried nearly up to 3 hours.

The MOC for the reactor is stainless steel is specially used. The surrounding chilling water is provided for the cooling purpose. Because the reaction being exothermic. After sufficient time interval (Reaction time), the system is switch off to carry out next product analysis or for the next batch.

Selection of Reactants:
The following points are deduced while selection of reactants,

1) Castor oil is used as a source of vegetable oil which, on reaction with warm concentrated alkali.
2) Relatively the castor oil has high viscosity and specific gravity and it highly Soluble in alcohols in any proportion.
3) The castor oil sulphation results largely in a sulphuric acid.
4) The sulphate group acts as a hydrophile imparting in the reaction.
5) In addition to acting as retarding agent on the action of sulphuric acid, one and only this property we getting turkey red oil.

Selection of Catalyst:

1) EDTA is an animopolycarboxylic acid and colourless and water soluble solid as well as it is chelating agent to reduce the reaction temperature.
2) It prevents metal ion impurities from modifying colours of dyed products in textile industry.
3) Reduce water hardness and do not form precipitate with the action of surfactant.
4) EDTA is highly stable and having neutral-pH, this is useful property in agriculture applications.
5) It is best sequestering agent in cosmetics.

Out of these properties which are similar to the applications of
the Turkey red oil so that we choose EDTA as a catalyst for the reaction.

Reaction Methodology:

The general reaction is given by

$$A + B \longrightarrow T + W$$

This is overall reaction in which,
A= Castor oil,
B= H2So4,
T= Turkey Red Oil,
W= Spent acid
The above reaction can split into two parts:

1. $A + B \longrightarrow S + W$
2. $S + N \longrightarrow T + W$

Where, S = Sulphonated castor oil,
N= Sodium Hydroxide.
We can carry out both the reactions separately or we can replace both the reactions by a single overall reaction at room temperature with same pressure. The above reactions (1) and (2) are actually shown here and out of these two reactions, the sulphonation reaction adopted in our case.

$$\underset{\text{Castor oil}}{C_{54}H_{100}O_7} + 3\,H_2So_4 + 6\,\underset{\text{Caustic soda}}{NaOH} \xrightarrow{EDTA} \underset{\text{Turkey Red Oil}}{3\,C_{18}H_{32}Na_2O_6S} + 7H_2O + H_2\uparrow$$

Solubility of Acid in Castor Oil:

1) If the compound is insoluble in 5% HCl and 5% NaOH, add 1 drop of a liquid sample or about 25 ml of a sample to 0.5 ml of concentrated sulfuric acid

(H2SO4) in a dry test tube. Tap the tube with your finger to mix or stir gently with a glass stirring rod.

2) Record the sample as soluble or insoluble. Interpret a color change or a precipitate as soluble.
3) *If the compound is soluble in H2SO4, the sample is an alcohol.*

Table 2 Solubility data

Temperature (°c)	Solubility H_2SO_4(ml)/Castor oil(ml)
20	5.86
25	8.28
30	10.95
35	12.26
40	14.56
45	17.62

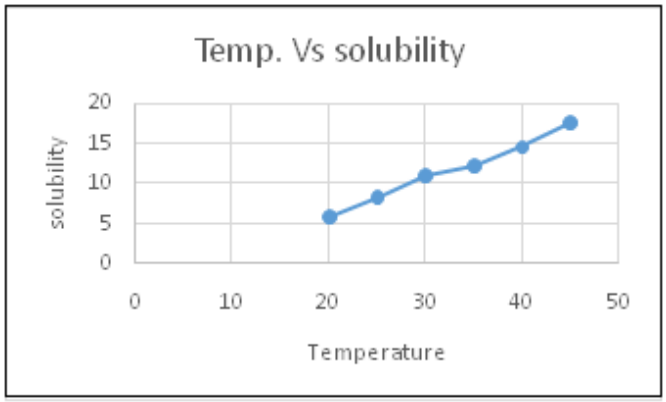

Fig. 3 Solubility Curve

Experimental Work and Procedure

Sulphonation of Castor Oil With Sulphur Trioxide

Materials-

Castor oil of purity 96%, conc.H_2So_4 of 98% pure, EDTA(Ethylene diaamine tetraacitic acid), 1 N NaOH of 60% to that of the feed, chilling water to the jacket.

Method-

The production of turkey red oil by the sulphonation method by continuous agitation process to maintaining temperature up to 25-30 °c. Also measured the Iodine value and Acid value of the product through this process.

Experimental setup-

The experimental setup as shown in fig. In which, the reactor vessel containing castor oil, inlet for conc.H_2So_4, agitator for mixing, separating funnel to separate the product. The contactor assembly was immersed in a thermostatic water bath, with temperature control.

Fig. 4 Experimental setup

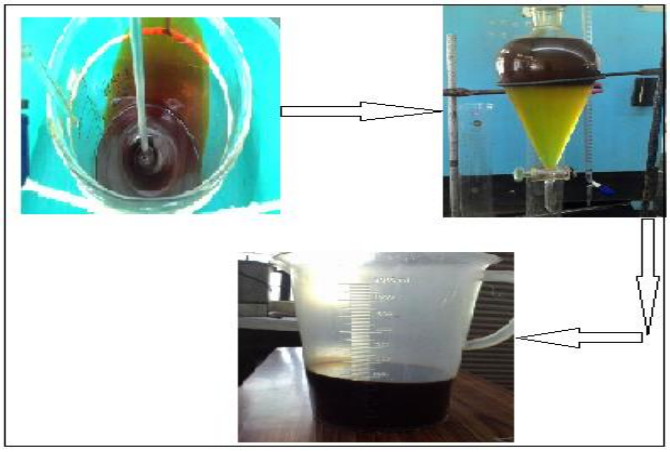

Fig. 5 Process Flow Diagram

Results and Discussion

The results getting from our experiment shows the better identification of 100% sure product quality also gets the expected effect on the yield while using the catalyst. The quantity of catalyst % adding to the mixture was found from the kinetic study of the various parameters like temperature, time and at different concentrations.

The kinetic study from the experimental data which have find comparison to that of the experimental value of equilibrium conversion factor, concentration and the % catalyst is 0.1 % to that of the feed which we have find from kinetic data.

The following results are evaluated in this project are:

Table 3 Analysis parameters

Sp. gravity	0.96
Viscosity	192 poise
pH	7.24
Acid value	0.20
Iodine value	68
Reaction time	3 hours
Reaction temperature	25-30 °C
Solubility	Miscible in water
Color of the product	Brownish Red color

The above results finds from the experiment are comparatively matched with standard specifications.
In actual experimentation, for Run1 to Run 6, we obtained readings at 38 °C, 35°C, 33°C, 30°C, 28°C and 25°C. Having the concentration increases with this temperature while the viscosity decreases with minimising the temperature. The catalyst was added up to 0.1 % of the feed we get the maximum yield of the product.

Conclusion

In this project we have tried to implement, The traditional method of preparing sulphonated castor oil i.e turkey red oil. By the continuous addition of concentrated sulphuric acid at a controlled rate to castor oil over a period of 3 hours with constant cooling and agitation of the reaction mass to maintain a temperature of 25 – 30 °C. This is very simple process to getting Turkey red oil.
The equilibrium conversion factor increases with time from kinetic study. The pH of the product is 7.24. The heat of the reaction is 10^0 C/hr. The order of the reaction is 10. The highest yield of the product is obtained when 0.1% catalyst is added. The 65% yield is getting. After that there is no change in the product.

References

[1] "Castor and beaver origin of words from bills casselmann's Canadian word of the day".
[2] "Castor Oil as a Renewable Resource for the Chemical Industry" – Mutlu -2010 – Europian Journal of Lipid Science and Technology.
[3] Auld , Dick L.; Pinkerton ,Scott D.;Rolfe, Rial ;Ghetie ,Victor and Lauterbach, Brenda F.,(1999)"selection of castor for divergent concentrations of Risin and RicinusCommunisAgglutinin and referances therein"
[4] The Chemithon Corporation, *Application of Pilot Studies to Minimizing 1,4-Dioxane Production During Sulfonation of Ethoxylated Alcohols,* 1988
[5] Marash, S.; Gubler, R.; Yagi K. *Chemical Economics Handbook*, 2001.
[6] United States Department of Agriculture: *Oilseeds: World Markets and Trade Monthly Circular*. http://www.fas.usda.gov/ oilseeds/circular/Current.asp.
[7] F. D. Gunstone, Market report, *Lipid Technol.* 2008, 20, 264. [F. D. Gunstone, *Lipid Library*, 'Oilseeds, Oils and Fats and Seed Meals' in 2007/08 http://www.lipidlibrary.co.uk / market/ofo6-07.htm]
[8] Komori ,S.; Kahara, M. O.; Okamatto, K. *J. Am. Oil Chem. Soc.*, 1960, 37, 468.
[9] Nakamura, S. *Oleochemicals*, 1997, *8*, 866-874.
[10] Davidson, A.S.; Milwidsky, B. *Synthetic Detergent*, *7th Ed. John Wiley and Sons, New York,* 1987, 36.
[11] *Kök, M. V., Iscan, A. G.* Oil shale kinetics by differential methods // J. Therm. Anal. Calorim. 2007. Vol. 88, No. 3. P. 657–661.
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