Transesterification and Reactive Extraction of Castor Oil for synthesis of Biodiesel/Biolubricant

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Abstract The use of non-edible vegetable oils as a substitute for petroleum fuel has gained popularity due to increased environmental contamination and depletion of petrochemical resources. There is high percentage of oil in castor seeds, that can be converted into biodiesel and biolubricant. Castor oil has high lubricity due to presence of higher percentage of (nearly 90%) ricinoleic acid. In comparison to other vegetable oils, ricinoleic acid having a double bond and a hydroxyl group, gives higher lubricity to the castor oil and its alkyl esters. The study comprises production of castor oil alkyl esters from castor oil using different alcohols such as methyl, ethyl, propyl and butyl alcohol. The reaction parameters are optimized to get effective yield for all the four alkyl esters. Propanol was used as both an extracting solvent and a transesterification reagent in the reactive extraction of castor seed. The physico-chemical characteristics like low cloud point, pour point, oxidation stability and lubricity of castor oil alkyl esters was determined, which suggests that methyl and ethyl esters of castor oil could be used as a sustainable biodiesel whereas higher alkyl esters such as propyl and butyl esters are suitable for biolubricant.

Keywords: Castor seed, Transesterification, Reactive extraction, Biodiesel, Biolubricant

1. Introduction

Lubricants and fuel from biological origin are gaining significant attention because of its tremendous use in the industrial world and the pollution issue prompted by the extra-dependence on petrochemical-based fuel and lubricants. Due to some inherent technological properties and their potential for biodegradability, vegetable oils are considered to be alternatives to petroleum oils for biofuel and lubricant formulations [1, 2]. Owing to environmental issues, future lubricants must be enviro-friendly and originate from a renewable resource. They have low volatility due to the triacylglycerol molecule's high molecular weight and have a limited range of temperature variations in viscosity. Because of heavy intermolecular interactions due to unsaturation and molecule linearity, vegetable oils have a high viscosity index. Polar ester groups can bind to surfaces of metal and have strong boundary lubrication properties. Plant based oils s have a high solubilizing ability for additive molecules and polar pollutants [3]. Among the different plant-based oils, castor is native to India. Castor (Ricinus communis), an oleaginous plant, is grown in almost every tropical and subtropical area. India ranks second among the world's castor seed producing countries after Brazil, with an average castor seed yield of 1.5 to 2 tonnes/ha above India. One of the centres of origin is India. Initially, Castor is a tree or shrub that can grow taller than 10 m and reach an average age of about 4 years. Cultivated varieties reach upto a height of 60–120 cm in 1 year and in perennial cultivation, several metres growth occurs. There are various types of castor seeds, but they contain an average of 46-55 % oil by weight (4). In castor oil, ricinoleic acid accounts for 80-90 % other acids are linoleic acid, oleic acid and saturated fatty acids of 1-5% (5). Owing to its enormously viscous nature it’s application as a fuel for vehicles and ignition machineries becomes hard but transesterified oil in contrast is best suited for combustion engine. Castor oil also has an unsaturated hydroxy fatty acid and inclusion of unusual functionality
gives additional stability and avoids formation of hydroperoxides [4]. In comparison to other plant-based oils, existence of ricinoleic acid having unsaturation and -OH group gives the castor oil and its derivatives improved lubricity and makes it a leading fuel additive [6, 7]. Many research have conducted on the synthesis of castor oil fatty alkyl esters by traditional transesterification in our country. Meneghetti et al transesterify castor oil using ethyl alcohol and methyl alcohol as transesterification agents in presence of traditional catalysts [8]. Several researchers have documented an alternative method of generating esters using lipases as catalysts by enzymatic reactions. Varma et al synthesised biodiesel from castor oil and linseed oil using supercritical alcohols without catalysts and supercritical CO₂ with enzymes [9]. The lubricity of various fatty compounds was researched by Gerhard Knothe and Kevin R. Steidley and compared to hydrocarbon compounds found in petrodiesel. They concluded that the lubricity of low-level blends of biodiesel (1-2%) with low-lubricity petrodiesel is mainly due to the free fatty acid and monoacylglycerol contaminants contained in biodiesel [10] Some researchers have found that castor and lesquerella oil esters increase the lubricity at lower bending levels of low sulphur petrodiesel esters than those of non-hydroxylated vegetable oils [6, 7]. The traditional method of generating biodiesel and biolubricant is transesterification but in reactive extraction method, oil extraction and transesterification occurs simultaneously. Reactive extraction (RE) could minimize the tedious pre-oil extraction, degumming, refining production method and optimize the yield of alkyl ester as this process is easy and has resulted in a higher conversion of castor oil to castor oil alkyl ester than traditional transesterification. The method for the development of green lubricant from castor seed is more convenient and environmentally friendly [11]. The current study deals with the synthesis of castor seed fatty acid alkyl esters (FAAE) using various alcohols through transesterification and reactive extraction of castor oil propyl ester. In the context of its use as biodiesel and biolubricant, the physico-chemical characterisation of fatty alkyl esters was carried out.

2. Materials and Methods

Extraction and Characterisation of Castor Oil

Soxhlet extraction method is used to determine the oil content of castor seed [12]. Three different solvents hexane, methyl alcohol and ethyl alcohol were used to extract the macerated castor seeds in soxhlet separately. The extraction is carried out for 8 hrs, then content in the flask was cooled and filtered. After filtration, the extracted material was evaporated in rotavapor, then cooled and the residual oil was weighed. Physico-chemical properties of oil were calculated following standard methods.

Fatty acid profiling by Gas Chromatography

Extracted oil was transformed into its methyl ester derivatives by reaction with transmethylating agent and analysed in GC for fatty acid profiling [13]. GC (Nucon 5765) fitted with a flame ionization detector (Nucon Engineers, Delhi, India), with fused silica capillary column BPX-70, 60m x 0.25 mm x 0.25 μm, determined the fatty acid composition of the oil (SGE, India).

Transesterification of Castor oil

Methanalysis of castor oil was carried out in a reactor equipped with a condenser and stirrer. The reaction was conducted with different oil to alcohol molar proportions of alcohol and castor oil (1:6, 1:9, 1:12, 1:18), catalyst concentrations (0.25-1.5 %), temperatures (37-65 °C) and different mixing intensities (180-600rpm). About 50g of castor oil was taken in a reactor which is immersed in a oil bath maintained at constant temperature. After that the solution of catalyst in alcohol was added to reaction mixture and heated by increasing the reaction temperature up to a certain level. The reaction was halted after 3 hours and the remaining alcohol was evaporated using a
rotavapor (Ika, Germany). During transesterification, the alcohol recovered in the rotavapor was again reused in alkyl ester synthesis. The products of transesterification were separated by centrifugation in 4000 rpm. Purification of upper alkyl ester layer was performed using heated distilled water and transferring the alkyl ester layer over anh. Na₂SO₄, the castor oil alkyl ester (COAE) was filtered and dried under a rotavapor at 80 °C. Similarly, higher alkyl ester (ethyl, propyl and butyl ester) of castor oil was prepared at 9:1, 12:1, and 15:1 alcohol to oil molar proportions, different KOH concentrations (0.8-1.8%) and varying alcohol boiling point temperatures at 600 rpm.

**Reactive Extraction of castor seed**

Propanol is used as an extracting solvent and transesterificating reagent for in-situ esterification of castor seed oil to alkyl ester. About 20 g of macerated kernel was taken in a 250 ml three necked round bottom flask fitted with reflux condenser and merged in water bath, which is kept over a magnetised stirrer fixed at 600 rpm. Freshly prepared solution of KOH–methanol was poured to the reaction flask and heated to a temperature up to the boiling point of alcohol with stirring. Hexane was used in the reaction mixture as co-solvent (15 % v/v of propanol) to significantly increase the extraction rate acting as both extraction solvent and enhances in-situ transesterification. The reaction was carried for 3 hours, then cooled and reaction mixture was centrifuged. Recovery of solvent from the supernatant was done by vacuum distillation, product alkyl ester was separated and dried using rotary evaporator.

**Characterization of Castor oil Alkyl esters**

Physicochemical properties of alkyl esters required in context of fuel and fuel additives were investigated. A Modular Compact Rheometer (Anton Parr, MCR 52 model) analysed the viscosity of various alkyl esters at 40 °C. The thermal oxidation stability of biolubricants was calculated using the instrument Rancimat 873 (Metrohm, Switzerland). High Frequency Reciprocating Rig (HFRR, PCS, UK) is used to determine the lubricity of various fatty alkyl esters according to EN ISO 12 156-1 standard. The wear scar diameter left on the ball in HFRR test is measured with a microscope and recorded.

**3. Result and Discussion**

**Extraction and Characterisation of Oil**

Due to more solubility of castor oil in alcohols, extraction in methyl alcohol yields highest amount of oil (48 % w/w) as opposed to hexane (38 % w/w). Different physico-chemical properties and fatty acid composition of oil is represented in Table 1. Low acid value and the high saponifiable matter of the oil mean that in diesel engines the transesterified oil can be used as fuel. Due to high viscosity, it can be best suited as a lubricant.

**TABLE 1: Physico-chemical Characterization of oil [11]**

| Physico-chemical Characteristics | Castor oil | Fatty Acid Composition | Amount (%) |
|----------------------------------|------------|------------------------|------------|
| Specific Gravity at 20 °C (g/cm³) | 0.96       | Ricinoleic Acid (C18:1OH) | 87.1       |
| Acid Content (mg KOH/g oil)      | 0.92       | Linoleic acid (C18:2)   | 5.1        |
| Iodine Value (g I₂/100 g oil)    | 91.0       | Oleic acid (C18:1)      | 3.2        |
| Saponification Value (mg KOH/g oil) | 186.0     | Palmitic acid (C16:0)   | 1.25       |
| Unsaponifiable matter (%. w/w)   | 0.935      | Stearic acid (C18:0)    | 1.51       |
| Viscosity (cp) at 40°C           | 240        | Linolenic acid (C18:3)  | 0.5        |
Castor oil, like other vegetable oils, consists primarily of triglycerides consisting of three fatty acids and one glycerol molecule. The oil consists predominantly of ricinoleic acid (87%), 5% linoleic acid and 3.4% oleic acid. There are small concentrations of palmitic acid (1.3 percent), stearic acid (1.5 percent) and linolenic acid (0.6 percent)\[^{[11]}\]. The findings obtained are comparable to those of other researchers. Since the oil has tremendously high viscosity, its use is not recommended for fuel but transesterified oil is best suited as fuel. In contrast to other vegetable oils, ricinoleic acid gives the castor oil and its derivatives improved lubricity and makes it a promising additive of diesel fuel\[^{[6, 7]}\].

**HPLC Analysis of Alkyl ester of Castor oil**

The yield of the reaction is monitored by HPLC (Waters 600 HPLC system) equipped with reverse phase C\(_{18}\) column (Waters Spherisorb column, 250mm x 4mm i.d. with 5µm particle size), Refractive index detector (Waters 2414), Waters 600 HPLC quaternary pump, Waters inline degasser and empower software. HPLC grade methanol was used as a carrier solvent with isocratic solvent run having flow rate 1ml/min. The product was diluted up to 20 times with HPLC grade methanol and filtered through 0.45µm Nylon syringe filter before HPLC analysis. FAME standards procured from Sigma Aldrich and standard sample preparation was also done with HPLC methanol. 20µl of both standard and sample was injected into HPLC. The peaks were identified by co-elution of standard alkyl ester samples and analyzed in the same HPLC conditions. The chromatogram of castor oil propyl ester (COPE) and castor oil butyl ester (COBE) was given in Fig.1.

![HPLC chromatogram of Castor oil Alkyl esters (I) COPE (II) COBE](image-url)
The yield of the reaction of different FAAEs is obtained by analyzing the reaction product in HPLC. The optimized reaction conditions for different alcohols are given in Table 2.

| Reaction Parameter       | Methanol | Ethanol | Propanol | Butanol |
|--------------------------|----------|---------|----------|---------|
| Catalyst Conc.           | 1% KOH   | 1% KOH  | 1% KOH   | 1% KOH  |
| Oil/Alcohol Molar Ratio  | 1:6      | 1:9     | 1:12     | 1:15    |
| Temperature (°C)         | 55       | 75      | 95       | 110     |
| Stirring Speed (rpm)     | 600      | 600     | 600      | 600     |
| % Yield of FAAE          | 93       | 90      | 87       | 85      |

Physico-chemical characterization of Castor oil Alkyl esters

Physico-chemical properties of COAEs is show in Table 3. The order COME< COEE<COPE<COBE is applicable to physical and chemical properties such as lubricity, viscosity and stability of alkyl esters.

| Properties                  | COME     | COEE    | COPE    | COBE    | Method        |
|-----------------------------|----------|---------|---------|---------|---------------|
| Kinematic viscosity (mm²/s) | 15.94    | 18.25   | 22.87   | 25.8    | ASTM D445    |
| Pour point (°C)             | -45      | -37     | -37     | -31     | ASTM D97     |
| Cloud Point (°C)            | -22      | -20     | -18     | -17     | ASTM D2500   |
| Lubricity HFRR wear (µm)    | 268      | 255     | 247     | 232     | ASTM D6079   |
| Flash point (°C)            | 189      | 193     | 197     | 205     | ASTM D93     |
| Rancimat Stability (h)      | 4.5      | 13.3    | 18.5    | 24.6    | ASTM D2440   |

As the chain length of alcohol increases, the lubricity of alkyl esters is observed to increase. Therefore, because of better lubricity, higher fatty alkyl esters derived from castor oil can be employed as biolubricant and methyl ester of castor oil can be used as biodiesel. With an increase in the chain length of the alkoxy group, the wear scar diameter of castor oil esters decreases, meaning that the lubricity of COAEs increases as fatty acid ester chain length increases. Higher COAEs can thus be employed as an additive to low lubricating fluids [14]. It can therefore be decided that reactive extraction for the production of renewable biolubricant is a quick, high-yielding and economical process.

4. Conclusion

Castor seed is rich in oil, which can be used for biodiesel and biolubricant production. The yield of COAEs decreases as the alcohol chain length increases. Physico chemical properties such as lubricity, viscosity and
stability of alkyl esters follow the order COME< COEE<COPE<COBE. Reactive extraction eliminates the lengthy production process like pre-extraction of oil and maximizes the yield of alkyl ester and reduces the cost of biodiesel production. The reactive extraction yield of COAEs decreases as the length of the alcohol chain increases. It was calculated that the biolubricant price obtained from castor seed was $3.71/gal, which is lower than traditional synthetic lubricants. The properties of COAES lead to an conclusion that lower castor oil alkyl esters can be used as benign biodiesel for the environment and higher esters as biolubricant.

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