International Journal of Engineering and Allied Sciences (IJEAS)
||Volume 2|| ||Issue 2|| ||2016||
ISSN: 2455-2054

Reactive extraction of Sustainable Biolubricant from Wild Castor Seed

Subhalaxmi Pradhan[a,b]* , Lalit Prasad[a], Gitanjali Pradhan[c] , S.N. Naik[b]

[a]*School of Basic and Applied Sciences, Galgotias University, Greater Noida, Uttar Pradesh, India*
[b]*Centre for Rural Development and Technology, Indian Institute of Technology, Delhi, India*
[c]*School of Basic and Applied Sciences, Indraprastha University, New Delhi, India*
**Email: subhalaxmipradhan@gmail.com*

----------ABSTRACT----------

About 12 million tonnes of lubricants per annum are disposed to the environment through leakages, exhausted gas, and water-oil emulsions and so on. Some are resistant to biodegradation, having bad environmental effect. To overcome this situation, mineral oil based lubricant can be replaced by plant oil based biodegradable lubricant. Fatty alkyl esters of vegetable oils are excellent substitute of mineral oil. Use of non-edible oils for lubricant production is adaptable as India is the importer of edible oils. Castor oil alkyl esters are promising lubricant due to presence of 90% ricinoleic acid, which is a hydroxy fatty acid, imparts better lubricity to the oil. The present study focus on production of castor oil ethyl ester (COEE) by reactive extraction (RE) of wild castor seed to reduce the cost and time associated with conventional method. The reaction parameters oil to alcohol molar ratio, catalyst concentration, temperature and mixing intensity were optimized to get 93% yield of COEE. Different physico-chemical properties such as viscosity, lubricity, oxidation stability, cloud point and pour point of COEE was determined. Lubricity study of COEE represents that COEE can be used as a biolubricant and fuel additive to ultra-low sulphur diesel fuels.

Keywords- *Wild Castor seed, Reactive extraction, Alkyl esters, Lubricity, Biolubricant*

I. INTRODUCTION

The vast utilization of non-biodegradable resources, scarcity in near future and its disadvantages is the major incentive for the use of biodegradable resources. The ever increasing use of petrochemical based lubricants has bad environmental impact. The environmental pollution is highly concern for the use of excessive petroleum based lubricants and their disposal especially in lost lubrication, military applications and in outdoor activities such as forestry, mining, fishing and agriculture hydraulic systems. Vegetable oils are preferred over synthetic lubricants because they are renewable resources, cheaper and eco-friendly biodegradable and non-toxic [1, 2]. They have low volatility due to high molecular weight of the triacylglycerol molecule and have a narrow range of viscosity changes with temperature. Vegetable oils have high viscosity index due to the strong intermolecular interactions because of the double bonds and the molecule linearity. Polar ester groups are able to adhere to metal surfaces and therefore, possess good boundary lubrication properties. Vegetable oils have high solubilizing power for polar contaminants and additive molecules [3]. Among various vegetable oils castor is indeginous to India. India occupies the second position among castor seed producing countries in the world following Brazil and average yield of castor seed over India is 1.5 to 2 tonnes/ha (Bussiness line, 5th December 2012). There are different varieties of castor seeds but on the average, they contain about 46–55% oil by weight [4]. The fatty acids of this oil consist of approximately 80-90% ricinoleic acid, 3-6% linoleic acid, 2-4% oleic acid and 1-5% saturated fatty acids [5]. Its use as fuel for internal combustion engines, however, can become complicated because of its extremely high viscosity and high water content but transesterified oil is better adapted as fuel and lubricant. Castor oil also possesses a hydroxyl functionality that is rare in vegetable oils and the presence of such a functional group adds extra stability to the oil and its derivatives by preventing the

formation of hydroperoxides [4]. The presence of ricinoleic acid, containing both a double bond and a hydroxyl group, impart increased lubricity to the castor oil and its derivatives as compared to other vegetable oils and makes of it a prime candidate as an additive for diesel fuel [6,7]. Transesterification is the conventional method for producing biodiesel from vegetable oil but reactive extraction (in situ transesterification) is the simultaneous oil extraction and transesterification of the raw oil bearing materials with alcohol. It could reduce the long production system associated with pre-extracted oil and maximize the alkyl ester yield. The alkyl ester of castor oil can be used as a biolubricant due to it's high viscosity and better lubricity. Reactive extraction of castor oil alkyl ester directly from seed reduces production cost of biolubricant. Few reports are available on production of biolubricant from castor seed and optimization of biolubricant production from castor seed is yet to be studied. The aim of the present study is optimization of reaction conditions such as alcohol to oil molar ratio, catalyst concentration, rotation speed and temperature to get higher yield of biolubricant.

II. MATERIALS AND METHODS

2.1. Reagents and materials

Wild Castor seeds were collected from waste lands nearer to micro model complex of IIT Delhi. Reagents like analytical grade ethanol, KOH (≥ 85%) was procured from Merck and was used without purification. Pure ethyl ester such as ethyl ricinolate was purchased from Sigma Aldrich (USA).

2.2 Oil Content and Physico-chemical characterization of oil

The oil content was determined by solvent extraction [8]. For oil content determination, the macerated castor seeds were extracted in Soxhlet apparatus using three different solvents, hexane, methanol and ethanol separately. The extraction was continued for 8hrs. After eight hours the micelle in the round bottom flask was cooled and filtered. The extract was concentrated in Rotary evaporator (Laborata 4000-Efficient, Heidolph Instruments, Germany), the residual oil was cooled and weighed. The materials remain after extraction of oil is cake. The % oil yield with different solvents was measured. The physico-chemical properties such as density, viscosity, acid value, iodine value, saponification value and unsaponifiable matter of the oil were determined by using IS 548 test methods. The fatty acid composition of the castor oil was determined by gas chromatography.

2.3. Reactive Extraction

Reactive extraction (RE) was carried out taking kernel (without husk) using ethanol both as an extraction solvent and transesterification reagent. The kernels (20 g) were macerated and transferred into a 250 ml three necked round bottom flask equipped with reflux condensor. The round bottom flask was merged in water bath placed on the plate of magnetic stirrer set at 600 rpm. The potassium hydroxide–alcohol solution was prepared freshly in order to maintain the catalytic activity and to prevent moisture absorbance. The reaction flask with macerated sample was heated to a reaction temperature and freshly prepared potassium hydroxide–alcohol solution was added under mechanical stirring. Then hexane was used as co-solvent (15 % v/v of ethanol) in reaction mixture to improve the rate of extraction significantly which plays the role of both extraction solvent and reaction promoter in the process and accelerates the in situ transesterification. The reaction was carried out for 3 h at desired temperature with stirring. After 3 h of reaction time the reaction mixture was cooled and centrifuged at 4000 rpm. The solvent was recovered from the supernatant by vacuum distillation. The product was transferred into the separating funnel and allowed to separate gravitationally. The upper ester layer was purified by washing with hot distilled water. The moisture was removed from castor oil alkyl ester by drying at 80 °C under vacuum rotary evaporator and passing the ester layer over

anhydrous sodium sulphate. The reaction was carried out at varied oil to alcohol molar ratio (1:50 to 1:400), catalytic concentration (0.5-1.5%), different rotations (180-600 rev.per min), temperature (55-85 °C) and the reaction conditions were optimized to get higher conversion. The purity of the product is cheked and quantified by HPLC.

2.4 Physico-chemical Characterization of Castor oil ethyl ester

The physico-chemical properties such as viscosity, lubricity, density, acid value, pour point, cloud point and oxidation stability were determined. The lubricity of the COEE was evaluated by using High Frequency Reciprocating Rig (HFRR), PCS, UK Instrument according to the standard EN ISO 12 156-1. The HFRR test involves a steel ball and a static steel disk submerged in a tested fuel at a temperature of 60 °C. The test ball oscillates against the disk with a constant frequency of 50 Hz for 75 min. The ball is removed from the vibrator arm and the wear scar diameter left on the ball is measured by means of a microscope and is reported as the HFRR test result.

Thermal oxidation stability of COEE was determined with a Rancimat 873 instrument (Metrohm, Switzerland). In this experiment sample was heated at a constant temperature with an excess airflow, which passed through a conductivity cell filled with distilled water. During this oxidation process volatile acids are formed and due to which conductivity increases at end. The period upto this point is called "Induction period". The oxidation period measurement was performed at air flow 10L/h with the heating block set at temperature 110 ^{0}C. The experiments conducted in duplicate and the mean value of the induction period was measured.

III. RESULTS AND DISCUSSION

3.1 Oil Content and Physico-chemical characterization of oil

Extraction of castor seeds in alcohol gives the maximum oil yield as compared to hexane, as castor oil is soluble in alcohols. In hexane oil yield is 34% whereas in ethanol improved oil yield (44%) is obtained.

Physico-chemical properties of castor oil are shown in Table 1. The oil content of castor seed and acid value of the oil are important parameters to carry out in situ transesterification. The physico-chemical properties obtained for the oil is comparable with the results obtained by other researchers [5, 9].

Table 1: Characteristics of Castor oil and Fatty acid Composition

Properties	Castor oil	Fatty Acid	Amount (%)
Specific Gravity 20°C (g/cm^3)	0.9584	Ricinoleic Acid	82.0
Acid Value (mg KOH/g oil)	0.83	Linoleic Acid	7.4
Iodine Value (Wij) (g I_2/100 g oil)	84	Oleic Acid	4.5
Saponification Value (mg KOH/g oil)	188	Palmitic Acid	1.6
Unsaponification Matter (%, wt/wt)	0.87	Stearic Acid	2.1
Viscosity (cp, 40°C)	235.6	Linoleinic Acid	0.7

The fatty acid composition of wild castor oil is represented in Table 1. Ricinoleic acid is the major fatty acid in castor oil which is depicted in Fig. 1.

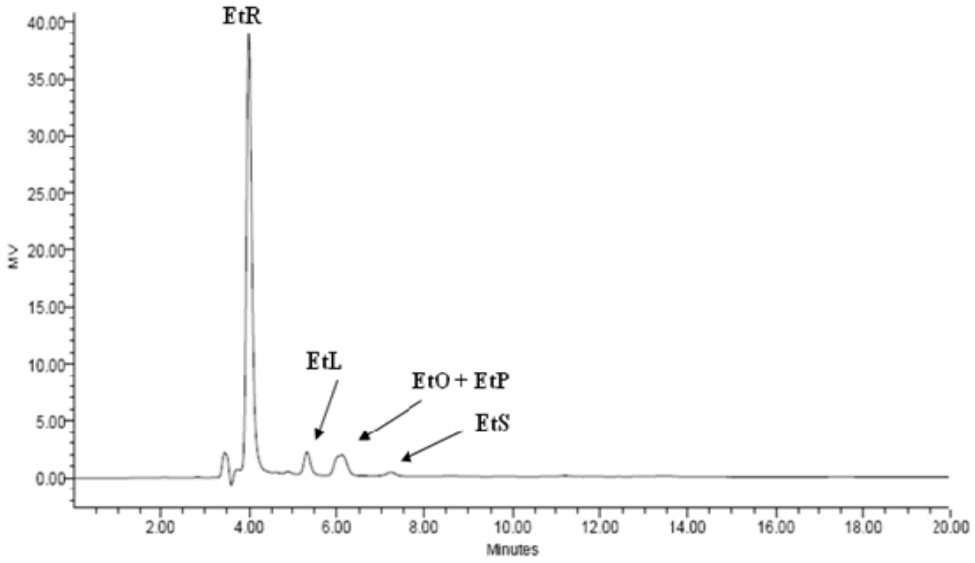

Fig.1 HPLC chromatogram of Castor oil ethyl ester

The seed oil has more amount of ricinoleic acid (82%) and the percentage of other fatty acids (Linoleic, Oleic, Palmitic, Stearic and Linolenic acid) are very less in comparison to ricinoleic acid. Low acid value of the oil suggests that the oil is suitable for fatty alkyl ester production in single step alkali catalyzed transesterification. Other researchers also reported 80–90% ricinoleic acid, 3–6% linoleic acid, 2–4% oleic acid, and 1–5% saturated fatty acids present in castor oil [9, 10].

3.2 Optimization of Reactive Extraction of COEE

3.2.1 Influence of catalyst concentration:

Reactive extraction of seed kernel was carried out with alkaline catalyst KOH at a concentration of 0.5-1.5% of oil at 75 °C with ethanol-oil molar ratio of 300:1 and stirring speed of 600 rpm. The yield of ethyl esters versus time at different catalytic concentrations are shown in Fig.2. The lower catalytic concentration i.e.0.5% of KOH is insufficient for completion of the reaction after 3h. At 1% KOH concentration the yield of the reaction is 93% after 3h and the reaction was completed to 87% after 1h. So 1% KOH concentration is the optimal reaction condition giving higher yield of COEE after 3h. There is decrease in the yield of COEE by increasing catalyst concentration to 1.5 %. Catalyst concentration plays major role during reactive extraction. Other researchers have optimized biodiesel from castor seed by reactive extraction conventionally and by ultrasound method using Response Surface methodology and during that optimization method catalyst concentration is predominant over other factors [11]. In presence of excess amount of catalyst during reactive extraction, the yield of COEE decreases as saponification predominates transesterification.

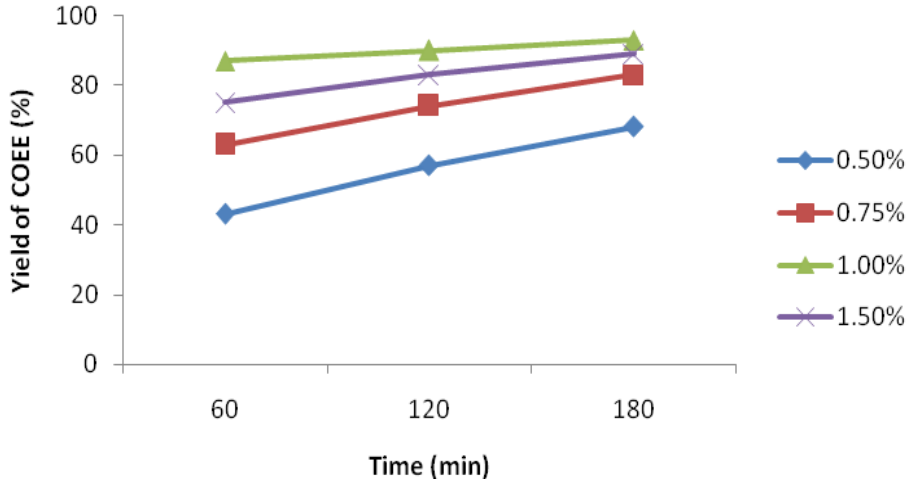

Fig.2. Influence of KOH concentration during reactive extraction of Castor seed
Other parameters: alcohol to oil molar ratio= 300:1, temperature = 75 °C, mixing speed = 600 rpm

3.2.2 Influence of oil to ethanol molar ratio

The reactive extraction was carried out with varied oil to methanol molar ratio such as, 1:50, 1:100, 1:200, 1:300 and 1:400. The yield of ethyl esters vs. time at different molar ratio of oil to ethanol are shown in Fig 3. The yield of ethyl esters for oil/ethanol molar ratio of 1:300 after a reaction time of 3 hr is 93 %, when the reaction conducted with 1% catalyst concentration at reaction temperature 75 °C and stirring at 600 rpm. The yield of reactive extraction is more for higher molar ratio of ethanol to oil but considering the cost of the product high molar ratio of alcohol is not acceptable but the alcohol is recovered from the product by vacuum distillation. The rate of reactive extraction is slower with lower molar ratio of ethanol because the solvent is not sufficient to penetrate into the seeds for carrying out extraction and alcoholysis reaction.

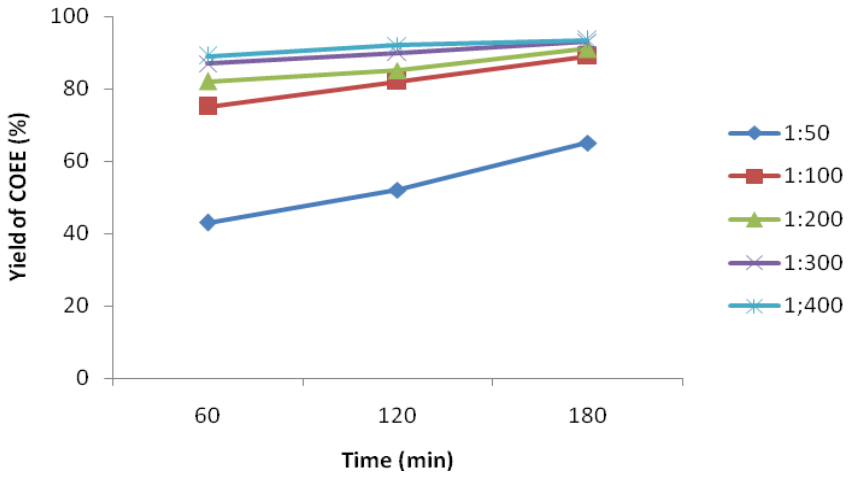

Fig.3. Influence of oil to alcohol molar ratio during reactive extraction of Castor seed; Other parameters: Catalyst concentration = 1%, temperature = 75 °C, mixing speed = 600 rpm

3.2.3 Influence of reaction temperature

The reactive extraction was carried out at different temperatures such as 55, 65, 75 and 85 °C with 1 % KOH as catalyst and ethanol/oil molar ratio 300:1 at a stirring rate of 600 rpm. The yield of COEE versus temperature at different time intervals is depicted in Fig. 4. Temperature has positive influence during reactive extraction of biolubricant from castor seed kernel. At 75 °C the yield of ethyl ester is higher because at high temperature the rate of extraction of castor oil in ethanol is faster as compared to low temperature. Thus the rate of transesterification increases resulting improved yield of COEE at high temperature in comparison to low temperature. The temperature above boiling point of alcohol is avoided because extraction will not be completed due to loss of ethanol. At high reaction temperature saponification of triglycerides facilitated by the alkali catalyst before completion of alcoholysis.

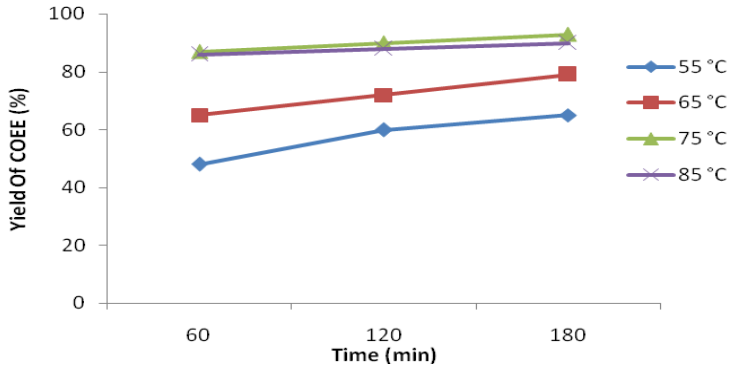

Fig.4. Effect of temperature during reactive extraction of Castor seed: Other parameters: alcohol to oil molar ratio= 300:1, catalyst concentration = 1%, mixing speed = 600 rpm

3.2.4 Influence of Mixing Intensity

The yield of ethyl esters vs. time at different rates of mixing such as 180, 360 and 600 rpm is shown in Fig.5. The reaction was incomplete with 180rpm and the rate of mixing was insignificant for extraction of oil and transesterification. At lower mixing speed, distribution of seeds are not uniform as at higher mixing speeds. The yield of ethyl esters at 600 rpm is more (93 %) after 3hrs due to uniform distribution of seeds, which increases extraction efficiency and rate of the transesterification of oil and aliphatic alcohols.

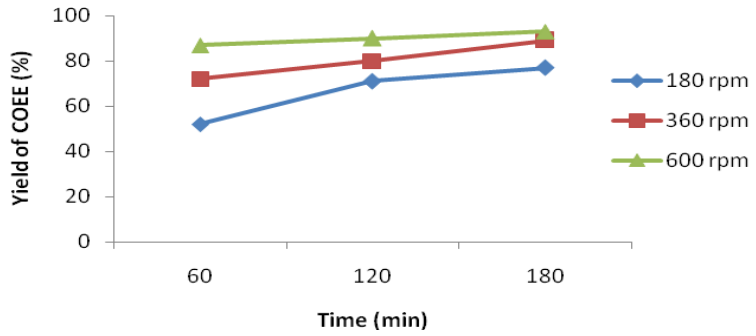

Fig.5. Effect of agitation speed during reactive extraction of Castor seed

3.3 Characterization of Castor oil ethyl ester as a biolubricant

The physico-chemical properties of COEE are given in Table.2. Castor oil ethyl ester has high viscosity compared to alkyl esters obtained from Jatropha oil and Karanja oil [12]. The physico-chemical properties of COEE are close to the physico-chemical properties of castor oil methyl ester prepared by our core research group [13]. Amdebrhan et al., (2015) have prepared biolubricant from castor oil by conventional transesterification and the physico chemical properties of biolubricant prepared by reactive extraction is comparable to that by conventional transesterification [14] Due to presence of ricinoleic acid, which is a hydroxy fatty acid, COEE has high viscosity. So it can be used as fuel additive other fuels. The wear scar diameter of COEE is 255 μm, which is obtained from the lubricity study by HFRR. The wear scar diameter of castor oil ethyl ester is very less in comparison to other oil alkyl esters. So castor oil ethyl ester can be used as a biolubricant to other diesel fuels. The biolubricants prepared from renewable resources i.e. castor oil have a potential of replacing 90% of mineral oil based lubricants in upcoming years. The use of COEE as additives in diesel fuel possesses good antiwear and lubricity properties studied on HFRR.

Table 2: Physico-chemical characterization of COEE

Properties	COEE	Method
Kinematic viscosity (mm^2/s)	18.25	ASTM D445
Acid value (mg KOH/g oil)	0.689	ASTM D664
Pour point (°C)	-37	ASTM D97
Cloud Point (°C)	-20	ASTM D2500
Lubricity HFRR wear (μm)	255	ASTM D6079
Flash point (°C)	193	ASTM D93
Rancimat Stability (h)	13.3	ASTM D2440

COEE has shown the improvement in low temperature fluidity as well as an effective antifriction and antiwear additive in terms of lubrication. Thus due to its high viscosity and enhanced cold flow properties; it can be used as potential biolubricant.

IV. CONCLUSION

RE of castor seed was carried out using ethanol. RE of castor seed using alkaline catalyst is feasible for lower chain alcohols but not for higher alcohols like propanol and butanol because in higher alcohols the oil extraction efficiency is very low. The effect of various parameters of reactive extraction was studied for ethanol. It is found that the optimum reaction condition for production of COEE is oil:ethanol molar ratio of 1:300, 1% catalyst concentration at reaction temperature 75 °C and stirring speed of 600 rpm. At optimum reaction condition the product yield is 93%. This is a very convenient method because the extraction and reaction occurs in a single step, which eliminates the

high cost associated with solvent extraction and oil cleanup. Thus it can be concluded that reactive extraction is a simple, high yielding and cost effective process for the production of alkyl esters, which can be used as biolubricant. Lower wear scar diameter associated with lower friction co-efficient and higher film formation indicates that COEE can be used as an additive (biolubricant) to low lubricating fluids.

REFERENCES

[1] Adhvaryu, A. Z. Liu, and S.Z.Erhan, Synthesis of Novel Alkoxylated Triacylglycerols and their Lubricant Base Oil Properties, *Industrial Crops and Products,* 21 (2005) 113-119.

[2] S.F. Thames, and H. Yu, Cationic UV-Cured Coatings of Epoxide-Containing Vegetables Oils, *Surface Coating Technology*, 115 (1999) 2-3.

[3] S. Dinda, A.V. Patwardhan, V.V Goyd and N.C. Pradhan, Epoxidation of cottonseed oil by aqueous hydrogen peroxide catalyzed by liquid inorganic solids, *Bioresource Technology*, 99 (2008) 3737-3744.

[4] D. S. Ogunniyi, Castor oil: A vital industrial raw material, *Bioresource Technology*, 97 (2006) 1086–1091.

[5] V. Scholz, J. S. da Nogueira, Prospects and Risks of the Use of Castor Oil as a Fuel, *Biomass Bioenergy*, 32 (2008) 95-100

[6] J. W. Goodrum, and D. P. Geller, Influence of Fatty Acid Methyl Ester from hydroxylated Vegetable Oils on Diesel Fuel Lubricity, *Bioresource Technology*, 96 (2005) 851-855.

[7] D. C. Drown, K. Harper and E. Frame, Screening Vegetable Oil Alcohol Esters as Fuel Lubricity Enhancers, *Journal of American Oil Chemical Society*, 78 (2001) 579.

[8] AOAC, Official methods of Analysis, 14th ed, Washington DC, Association of Official Analytical Chemists, 1984.

[9] S.M. P. Meneghetti, M. R. Meneghetti, C. R. Wolf, E. C. Silva, G. E.S. Lima, L.L. Silva, Biodiesel from castor oil: a comparison of ethanolysis versus methanolysis*, Energy Fuels,* 20 (2006) 2262-65.

[10] L. Canoira, J. García Galeán, R. Alcántara, M. Lapuerta, R. García-Contreras, fatty acid methyl esters (FAMEs) from castor oil: production process assessment and synergistic effects in its properties, *Renewable Energy*, 35 (2010) 208–217.

[11] N. N El-Ebiari, S.A. Abo El-Enin, A.G. Gadalla, O. El-Ardi and G.I. El-Diwani, International Journal of Innovative Science, Engineering and Technology,1 (2014) 300-311.

[12] L. Prasad, S. Pradhan, C.S. Madankar, L.M. Das and S.N. Naik, Comparative study of performance and emissions characteristics of a diesel engine fuelled with jatropha and karanja biodiesel, *Journal of Scientific and Industrial Rese*arch, 70 (2011) 694-698.

[13] S. Pradhan, C. S. Madankar, P. Mohanty, S.N. Naik, Optimization of Reactive extraction of Castor Seed to produce Biodiesel using Response surface methodology, *Fuel*, 97 (2012) 848-855.

[14] B. T. Amdebrhan, L. Damtew, D. Tesfay, H. Endris and G. Tekeste, *International Journal of Engineering Innovation and Research,* 4 (2015) 737-741.