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TRANS ESTERIFICATION STUDIES ON CASTOR OIL AS A FIRST STEP TOWARDS ITS USE IN BIO DIESEL PRODUCTION

MOHAMMED H. CHAKRABARTI[*] AND RAFIQ AHMAD[**]

[*]*Department of Environmental Engineering, NED University of Engineering and Technology, Karachi-75270, Pakistan.*
[**]*Department of Botany, Faculty of Science, University of Karachi, Karachi-75270, Pakistan.*

Abstract

Castor (*Ricinus communis* L.) is a fast growing plant of marginal and moderately saline land widely spread throughout tropical regions. It is cultivated at arid coastal sandy belt and inland waste land of Pakistan for obtaining oil from its seeds, which being of medicinal importance is an economical commodity. Facing a great shortage of mineral diesel, scientists are nowadays actively working for converting oil obtained from wild/less commercially important plants into bio diesel for economic purposes. Non-edible oil yielding plants including castor bean, which cannot compete with edible oil yielding plants of commercial importance, are considered good candidates for such research work. The work presented herein deals with the transesterification of oil extracted from castor bean as a step towards possibility of converting it into bio diesel.

Introduction

The castor bean plant (*Ricinus communis* L.) belonging to the family Euphorbiaceae family, probably indigenous of Eastern Africa, is nowadays growing on a wide scale on marginal and wastelands of South Asia. It is widely grown as a commercial crop in Ethiopia for its oil, which is a medicinal commodity. It is a non hardy fast growing suckering perennial shrub which can reach a height of 12 m. However it is cultivated in the Indo-Pakistan region as an annual crop on marginal lands and coastal sandy belts under warm climates where it reaches a height of 2-3 m and can stand moderate arid/saline environments. Its fruits are produced in typical clusters, each pod containing well developed seeds bearing sufficient oil (47-49%).

Castor oil is a colourless to very pale yellow liquid with mild or no odour or taste. Its boiling point is 313°C (595°F) and has a density of 961 kg/m^3. It is a triglyceride in which approximately 90% of fatty acid chains are ricinoleic acid. Oleic and linoleic acids are the other significant components. Ricinoleic acid, a monounstaturated, 18-carbon fatty acid, is unusual in that it has a hydroxyl functional group on the twelfth carbon. This functional group causes ricinoleic acid (and castor oil) to be unusually polar. It is the hydroxyl group which makes castor oil and ricinoleic acid valuable as chemical feedstocks.

Like any other vegetable oil it can be converted to bio diesel as described by Schuchardt *et al.*, (1998). Some extensive research activities are being carried out in India and Brazil (Conceicao *et al.*, 2007a; Conceicao *et al.*, 2007b). Bio diesel (also known as methyl esters of fatty acids) is non-toxic, biodegradable and an excellent substitute for petroleum based diesel fuel (Harun *et al.*, 2006). The energy content, cetane number and viscosity of bio diesel are similar to those of petroleum based diesel fuel (Wang *et al.*, 2007). Moreover, engines operating on bio diesel have been reported to

have a significantly lower impact upon the environment than those operating on petroleum diesel.

Several reasons for converting oils and fats into bio diesel have been discussed by Ma & Hanna (1999). Some of the main problems with oils and fats are high viscosity and low volatility that causes the formation of deposits in engines due to incomplete combustion and incorrect vaporization characteristics. The unsaturated fatty acids present in oils and fats tend to polymerize at high temperatures causing large agglomerations to be formed, which eventually result in gumming (Freedman *et al.*, 1984). Fats and oils are primarily composed of triglycerides, esters of glycerol (mono- and di-glycerides) and fatty acids (carboxylic acids). The term mono-glyceride or di-glyceride refers to the number of fatty acids that are attached to the glycerol backbone (Khan, 2002). Investigations on converting castor bean oil into bio diesel are undertaken by means of transesterification as a first step towards reducing its viscosity and improving its fuel quality for applications in the compression-ignition (diesel) engine.

One of the most common vegetable oil, that of rapeseed (and its other variety, canola oil) has been converted successfully into methyl esters (bio diesel) and tested in diesel engines several times (Nwafor, 2004; Labeckahs *et al.*, 2006; Leung & Guo, 2006; Tsolakis *et al.*, 2007; Kulkarni *et al.*, 2007; Chakrabarti & Ali, 2008). The procedures adopted by these researchers as well as those reported by Marchetti *et al.*, (2007), were adapted in this work for preparing castor oil bio diesel.

Material and Methods

Castor oil was extracted from its seeds using an oil expeller in Liaqat Abad, Karachi, Pakistan and was refined in NED University Laboratories following the procedures described by O'Brien *et al.*, (2000). The refined oil was converted to methyl esters in several different ways (single-stage reaction) following the procedures gives in the literature (Schuchardt *et al.*, 1998; Conceicao *et al.*, 2007a; Conceicao *et al.*, 2007b).

Castor oil 250 ml was reacted with a solution of KOH (potassium hydroxide) dissolved in an appropriate quantity of methanol at various temperatures. Stirring was continued for various times (for assisting the reaction of oil into methyl esters) and the product was placed in a separating funnel and left overnight to settle. Glycerine settled to the bottom of the funnel and was removed in a measuring cylinder in order to measure its volume. The impure methyl ester was washed with 2.5% (w/w) sulphuric acid (98%, Merck) and distilled water, prior to drying at 150°C for 2 h.

In addition, a separate experimental investigation involved the castor oil being made to undergo acid esterification followed by normal transesterification. This procedure was reported by Marchetti *et al.*, (2007). Acid esterification was carried out for approximately one hour (at 50°C), followed by transesterification using potassium hydroxide as catalyst (at 70°C).

Results

The results obtained by converting 250 ml castor oil into methyl esters using different amounts of reagent (methanol) and catalyst (potassium hydroxide) at different temperatures and times of reaction is given in Table 1.

Table 1. Results from transesterification of Castor oil under various reaction conditions.

Sample No.	Methanol (ml)	KOH (g)	Temperature (°C)	Time (min)	Glycerine removed (ml)	Ester content (%)
1.	200	2.4	30	30	0	8
2.	100	2.4	30	30	15	10.5
3.	70	2.4	30	30	25	10
4.	60	2.4	30	30	25-30	7.5
5.	50	2.4	30	30	16	9
6.	65	2.1	30	30	15	9
7.	65	2.7	30	30	16	10
8.	65	3.0	30	30	20-25	10
9.	65	2.4	40	30	20-25	12
10.	65	2.4	50	30	30	15
11.	65	2.4	60	30	20-25	18
12.	65	2.4	70	30	35	22
13.	65	2.4	70	60	40	35
14.	65	2.4	70	90	42	38
15.	65	2.4	70	180	47	41
16.	65	2.4	70	300	50	45
17.	65	2.4	70	360	52	48

Looking at data presented in Table 1 it appears that reaction mixture containing 65 ml of methanol alongwith 2.4 g of catalyst (KOH) took a good start in half an hour at 30°C. In this reaction, amount of glycerine removed as well as ester content produced was considerably increased with rise in temperature of mixture upto 70°C by extending time period (180-360 minutes). The removal of glycerine increased by two and half times and ester content by four times, respectively.

When castor oil was subjected to acid esterification, prior to transesterification (a separate investigation), it was found that ester contents up to 85% could be obtained. It may be possible to increase ester contents (as well as glycerine removal) by extending the reaction times for the transesterification process in further investigations.

Discussion

Castor oil is an unusual oil in that it is predominantly composed of ricinoleic acid (Conceicao *et al.*, 2007a). Other oil varieties have mixed quantities of different fatty acids and are usually insoluble in alcohol at room temperatures. However, castor oil is unusually soluble in alcohol at room temperatures purely due to the high content of ricinoleic acid (which is polar in nature). Also, ricinoleic acid has an effect on the viscosity of castor oil (being higher than conventional edible oil varieties). Table 2 has been constructed to show fatty acid composition of some conventional edible oils (as reported by Khan, 2002) and that of castor bean (as presented by Conceicao *et al*., 2007a) for the purpose of comparison.

In the transesterification of vegetable oils, a triglyceride reacts with an alcohol in the presence of a strong acid or base, producing a mixture of fatty acids alkyl esters and glycerol (Schuchardt *et al*., 1998). The overall process is a sequence of three consecutive and reversible reactions, in which di- and mono-glycerides are formed as intermediates. The stoichiometric reaction requires 1 mol of a triglyceride and 3 mol of the alcohol. However, an excess of the alcohol is used to increase the yields of the alkyl esters and to

allow its phase separation from the glycerol formed. The alcohol/vegetable oil molar ratio is one of the main factors that influence the transesterification. An excess of the alcohol favours the formation of the products. On the other hand, an excessive amount of alcohol makes the recovery of the glycerol difficult, so that the ideal alcohol/oil ratio has to be established empirically, considering each individual process (Schuchardt *et al.*, 1998).

The physical-chemical properties of castor oil, comparison of its bio diesel and mineral diesel as reported by Conceicao *et al*., (2007a), are being reproduced in Table 3 to show great difference in the values of viscosity and flash point in the bio diesel produced from castor oil with those of mineral diesel for the purpose of discussion.

This work is well in correlation with the observations reported by Meneghetti *et al*., (2006). It appears that castor oil may not prove to be a good raw material for the production of bio diesel. It is quite problematic and energy intensive to convert to bio diesel mainly due to requirement of greater quantity of alcohol, high temperatures and expensive catalysts (such as sodium methoxide). Even if high yields of bio diesel are obtained, the viscosity would cause a problem for most practical diesel engines. As a result, other non-edible vegetable oils of lower viscosity from plants that can be grown at marginal land in Pakistan would be an alternative feedstock for bio diesel production in the country.

However, in case research work for lowering viscosity of castor bean oil by some cheap enzymatic method meets success, the castor bean would rate among the most important plants being capable of growing at marginal land and providing greater quantity of oil.

Table 2. Fatty acid composition of some typical vegetable oils against those of castor oil.

Vegetable oil	Fatty acid composition (% w/w)						
	Palmitic C16:0	Stearic C18:0	Oleic C18:1	Ricinoleic C18:1 variety	Linoleic C18:2	Linolenic C18:3	Arachidic C20:0
Corn	11.67	1.85	25.16	0	60.6	0.48	0.24
Canola	3.49	0.85	64.4	0	22.3	8.23	0.00
Soybean	11.75	3.15	23.26	0	55.53	6.31	0.00
Sunflower	6.08	3.26	16.93	0	73.73	0.00	0.00
Castor	0.7	0.9	2.8	90.2	4.4	0.2	0

Table 3. Physical-chemical properties of mineral diesel, castor oil and castor oil bio diesel (Conceicao *et al.*, 2007a).

Parameters	ASTM test method	ASTM limits	Castor oil	Castor bio diesel	Mineral diesel
Viscosity (mm^2/s)	ASTM D445	1.9-6.0	239.39	13.75	3.2
Sulfur (%)	ASTM D5453	0.0015, Max	0	0.0001	0.20
Density 15°C (g/cm^3)	ASTM D 1298	0.875-0.9	0.9573	0.9279	0.8503
Density 20°C (g/cm^3)	ASTM D 1298	0.86	0.9584	0.9245	0.8465
Flash point (°C)	ASTM D93	93°C(266°F), Min	310	120	37
Copper corrosion	ASTM D130	No. 3, Max	1	1	1
Cetane index	ASTM D613	47, Min	43	50	45
Water and sediment (vol. %)	ASTM D2709	0.050, Max	Nil	0.05	Nil

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