

METHANOLYSIS OF CASTOR OIL USING POTASSIUM CARBONATE IN AMMONIUM HYDROXIDE AS A CATALYST

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Abstract

In the present work methyl esters (Biodiesel) of Castor oil was synthesized by refluxing oil with methanol and Potassium carbonate in ammonium hydroxide (NH₄OH) catalyst. The reaction conditions were optimized. Maximum yield of 97.6% methyl esters was obtained under the reaction conditions of 10:1 methanol to oil molar ratio at 50°C for a refluxing period of 3hrs using 1.8g of Potassium carbonate in conc. ammonium hydroxide(1:2.5 catalyst to NH₄OH molar ratio) as a catalyst.¹HNMR spectral characterization of methyl esters was carried out. Physicochemical properties of biodiesel was tested and compared with ASTM standards. All the values are within the range of ASTM standards.

Key words: Ammonium hydroxide, Biodiesel, Castor oil, Methanolysis, Potassium carbonate

1. Introduction

Ever increasing population and urbanization has resulted in the over consumption of conventional petroleum fuels[1]. That intern causing energy crisis and environmental depletion[2]. Production of sustainable, renewable and eco-friendly fuel will effectively resolve the global energy demand and ecological imbalance[3].

Biodiesel is one of the renewable and biodegradable liquid fuel obtained from bio-lipids containing sources like vegetable oils or animal fats[4]. More than 95% of commercial biodiesel is produced from edible oils such as ground nut oil, coconut oil, sunflower oil, soybean oil, Rape seed oil and palm oil[5]. Production of biodiesel from edible oils creates a serious problem between energy crisis and food security [6]. Above issue can be solved by shifting the focus towards non-edible oils such as Pongamia, Mahua, Neem and Castor oil because of its high oil content and availability [7][8]. Castor oil is selected as a feed stock in the present work.

Methanolysis of non-edible oils using direct NaOH or KOH catalytic method will lead to more soap formation and their by reduces the yield [9]. This is due to the formation of more amount of water as an intermediate in the methoxide formation reaction [1]. Such challenges can be prevailed by using K₂CO₃ catalyst, as it does not produce water molecules during the reaction[10]. But, methanolysis of triglycerides

using direct (unsupported) K_2CO_3 as a catalyst is experimentally unfavorable, because potassium carbonate is a mild base and hardly soluble in methanol[11].

Above mentioned problems can be easily solved by treating K_2CO_3 with known amount of NH_4OH (2.5 moles of NH_4OH with 1 mole of catalyst). The addition of small amount of ammonium hydroxide to K_2CO_3 increases the basic strength (basicity) and solubility of the catalyst and their by increases the activity of the catalyst in the synthesis of biodiesel[12]. At the same time presence of ammonium and carbonate ions in the reaction mixture, significantly reduces the hydrolysis of esters and soap formation.

2. Materials and Methods

Castor oil is purchased from Gauribidanur Town Karnataka state, India. Chemicals such as K_2CO_3 , liquor ammonia, Methanol, Isopropanol, H_2SO_4 are of analytical grade.

2.1 Methodology

The knowledge of free fatty acid content in oil is essential to carry out transesterification process. FFA content in the castor oil is found to be greater than 2%, therefore to avoid soap formation it is necessary to carry out acid catalyzed esterification prior to base catalyzed transesterification[13].

2.2 Acid catalyzed esterification of Castor oil

100 ml of oil was filtered and heated to $100^\circ C$ to remove suspended impurities and moisture content. Oil was cooled to room temperature and transferred to three necked round bottom flask. 30ml of methanol and 1% H_2SO_4 (Vol % of oil) was added, the reaction mixture was refluxed for 2 hrs with continues stirring speed of 600 rpm at $60^\circ C$. Products were decanted into separating funnel and allowed to settle for 3 hrs. Excess methanol, H_2SO_4 and residual impurities were suspended at the top layer and the esterified product was settled at the bottom layer. Esterified product was separated and heated to $100^\circ C$ to remove water content. As water is produced as an intermediate during esterification process (equation 1).

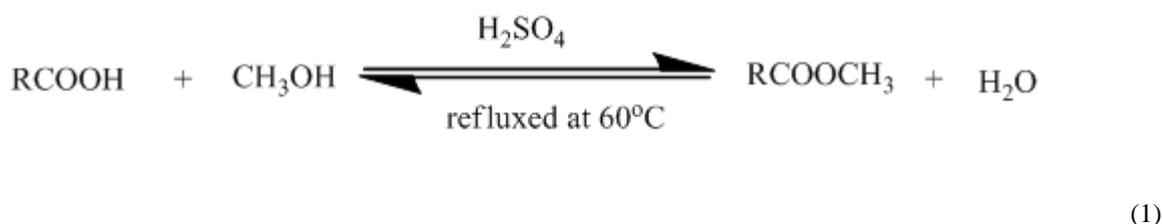
2.3. Base catalyzed Transesterification

Prior to transesterification, K_2CO_3 was first treated with 2.5 moles of Conc. NH_4OH (1:2.5 catalyst to NH_4OH molar ratio) and then added to methanol for methoxide formation, to this esterified product was added and refluxed at $50^\circ C$ for 3hrs at stirring speed of 600rpm .Obtained product was transferred into separating funnel and allowed to stand for overnight for the separation of biodiesel and glycerol phase. Separated biodiesel was subjected to hot water wash for the removal of water soluble impurities. After water wash, biodiesel is heated to $100^\circ C$ to remove water content. The completion of the transesterification reaction is confirmed through methanol test (preliminary test)[14]. Maximum yield of 97.6% biodiesel was obtained.

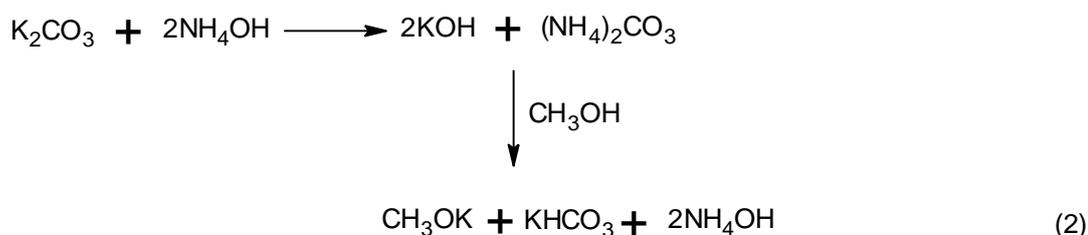
$$Yield = \frac{Volume\ of\ Biodiesel\ Obtained}{Volume\ of\ oil\ taken} \times 100$$

Reactions:

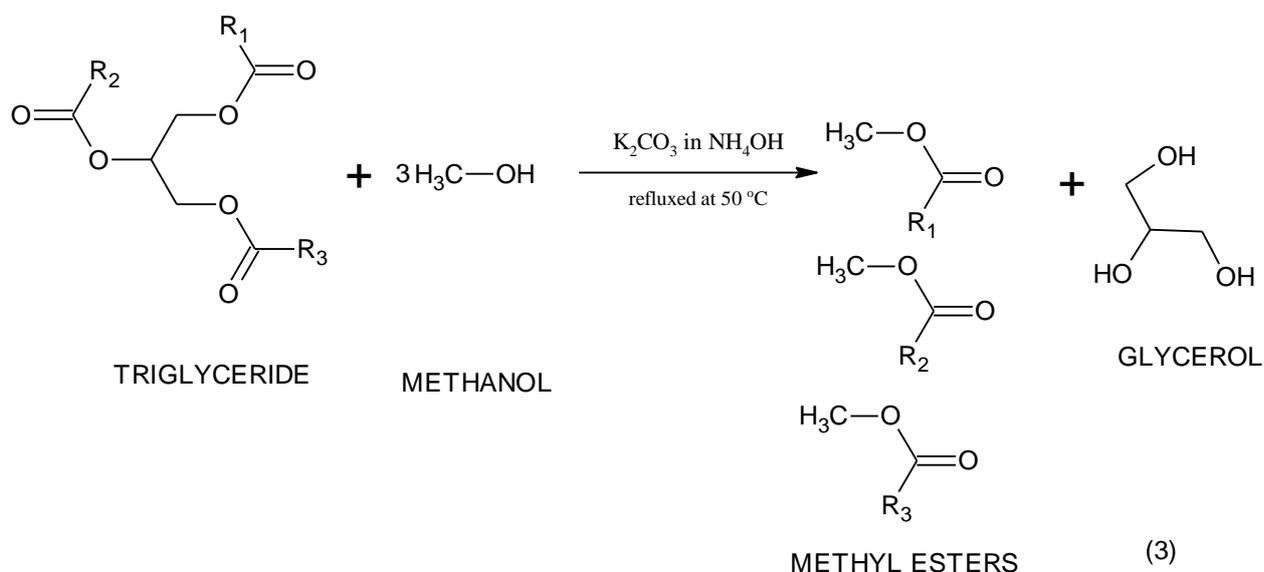
1. Acid catalyzed Esterification Reaction



2. Reaction of Potassium carbonate with NH₄OH followed by methoxide formation with methanol



3. Methanolysis of Triglycerides



Where: R₁, R₂ and R₃ represent alkyl groups

3. Results and Discussions

3.1. Role of Ammonium hydroxide in the Biodiesel production

Methanolysis of castor oil by direct treating of K_2CO_3 with methanol has not produced any methyl esters. This is mainly because, K_2CO_3 is a weak base[15] and hence it has not produced significant amount of methoxide for methanolysis reaction. But, prior treating of K_2CO_3 with concentrated ammonium hydroxide resulted in the formation of in-situ KOH and $(NH_4)_2CO_3$. On treating this mixture with methanol produced methoxide, potassium bicarbonate and ammonium hydroxide without forming free water molecules (Eq.2.2). In-situ KOH helped in effective methoxide formation and at the same time presence of ammonium and carbonate ions inhibited the formation of free water molecules during the reaction and their by reduced excess soap formation and increased methyl ester yield compared to direct K_2CO_3 and conventional KOH methods.

Separate methanolysis experiments were carried out by using conventional KOH, Direct K_2CO_3 and K_2CO_3 in NH_4OH as a catalyst. Experimental observation proved that use of K_2CO_3 in NH_4OH as a catalyst gave maximum biodiesel yield compared to direct K_2CO_3 and KOH catalytic methods.

Table:1 Comparison of castor oil biodiesel yield obtained from Conventional KOH ,Direct K_2CO_3 and K_2CO_3 in NH_4OH catalytic methods.(Optimized reaction Conditions)

Catalyst	Catalyst (Optimized amount in g)	Methanol to Oil molar ratio	Temperature	Reaction Time	Yield in %
KOH	1.2g	6:1	60°C	2hrs	86.3%
Direct K_2CO_3	1.8g	10:1	50°C	3 hrs	0% (No yield obtained)
K_2CO_3 in 2.5 moles of NH_4OH	1.8g	10:1	50°C	3 hrs	97.6%

3.2. Effect of catalyst amount on the yield of biodiesel

Catalyst optimization experiments were carried out first by using 1g of K_2CO_3 in NH_4OH . Experimental observation proved that there was no complete conversion of methyl esters (confirmed through methanol test) for 1g of catalyst. On further raise in the catalyst amount in an increment of 0.2g has increased the yield of biodiesel up to 1.8g, further rise has decreased the yield. Variation in the biodiesel yield with respect to catalyst amount is graphically represented in the Fig.1

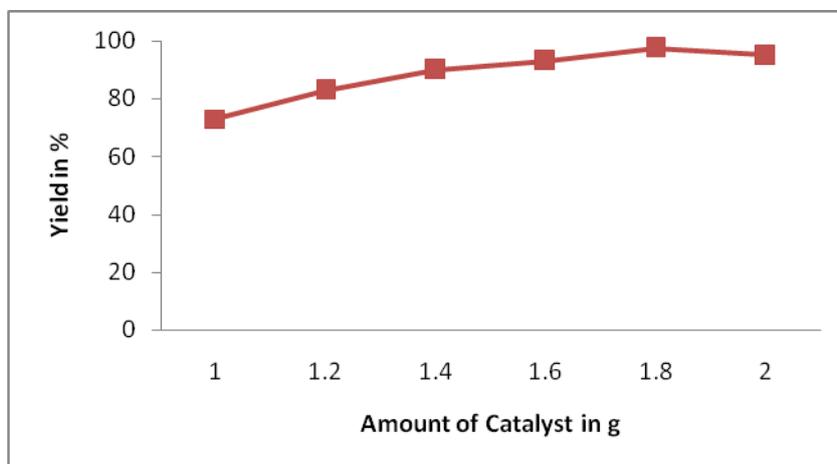


Figure 1: Graphical representation of effect of catalyst amount on the biodiesel yield

3.3. Effect of Methanol to Oil molar ratio on the yield of biodiesel

Methanol to oil molar ratios is optimized by keeping other experimental conditions constant. Experimental observation reveals that theoretical Stoichiometric molar ratio of 3:1 is insufficient to carry out transesterification, as it is a reversible reaction[16]. On increasing the methanol to oil molar ratios from 6:1 to 10:1, has increased the biodiesel yield. Further rise in methanol to oil molar ratio has reduced yield. Variation in the yield of biodiesel against methanol to oil molar ratio is graphically represented in the Fig.2

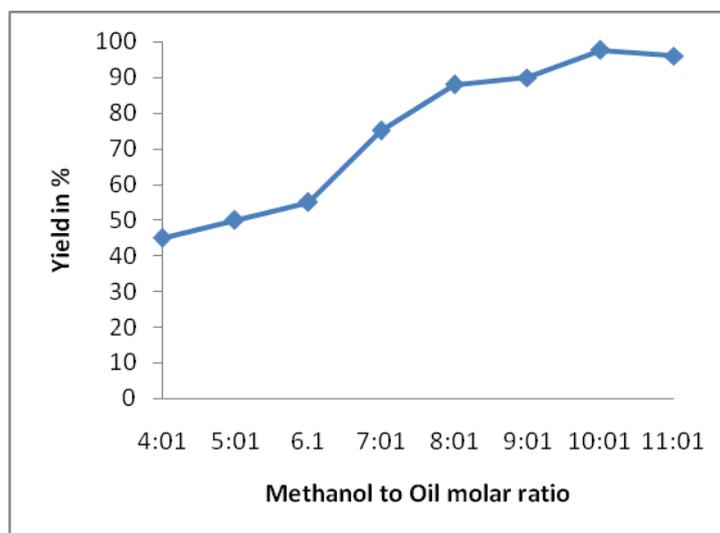


Figure 2: Graphical representation of effect of methanol to oil molar ratio on the biodiesel yield.

3.4. Effect of reaction temperature on the yield of biodiesel

Three different experiments were carried out by rising the temperature from 40-60 deg C in an increment of 10 deg C. As the temperature increases yield of biodiesel also increased up to 50 deg C, Further rise in the temperature to 60 deg C, there was no appreciable change in the yield. Hence optimum temperature of 50 deg C is fixed for the reaction. Variation in the yield of biodiesel against temperature is graphically represented in the Fig.3

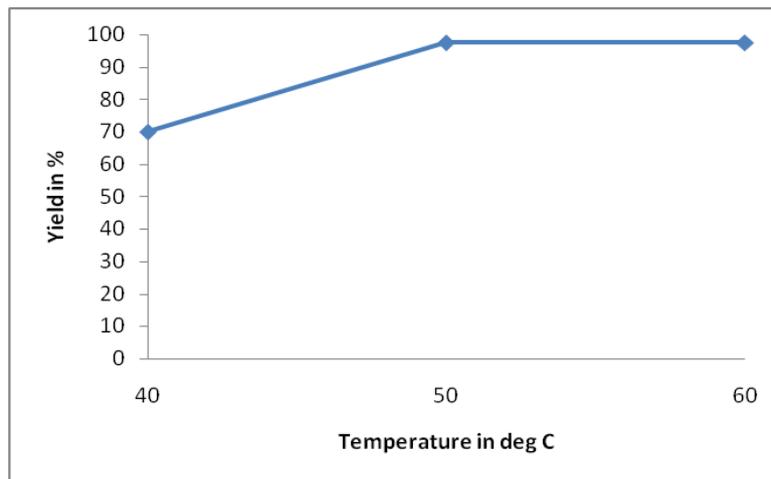


Figure 3: Graphical representation of effect of Temperature on the biodiesel yield

3.5 Effect of reaction time on the yield of biodiesel

Deviation in the biodiesel yield (%) with respect to reaction time is studied by keeping other experimental conditions constant .It is observed that the yield of biodiesel is increased with increase in reaction time up to 3 hrs. Prolonging the reaction time up to 4hrs has reduced the yield of biodiesel; this may be due to prolonged reaction time will utilize more temperature that leads to glycerin solubility in the reaction mass and favors the back word reaction, which consequently lowered the overall biodiesel yield[17]. Variation in the yield of biodiesel against reaction time is graphically represented in the Fig.4

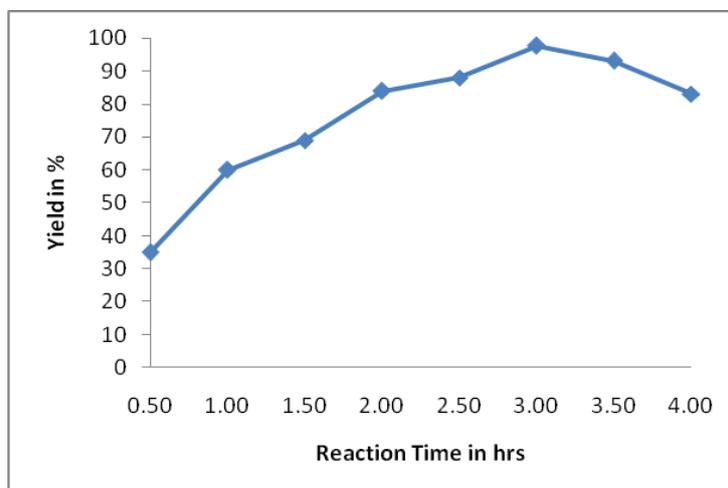


Figure 4: Graphical representation of effect of Reaction time on the biodiesel yield.

3.6 Characterization of Biodiesel by Proton Nuclear magnetic resonance spectroscopic method

¹H-NMR spectroscopy is a resourceful technique to confirm the conversion of triglycerides to methyl esters (Biodiesel). ¹H NMR spectrum of the obtained biodiesel is represented in the Fig.5. In the spectrum the sharp intense peak is observed at 3.631ppm, it clearly indicates the presence of methyl ester group[18]. The triplet at 2.286 ppm represents the presence of carbonyl carbon. The peaks around 0.866ppm is confirmed the presence of terminal methyl group[19]. The presence of α -methylene groups and α -methine groups were evident by the peaks observed at 1.2-1.7ppm. The less intense peaks at 5.3 to 5.5 ppm are due to the presence of vinylic proton in the biodiesel[20].

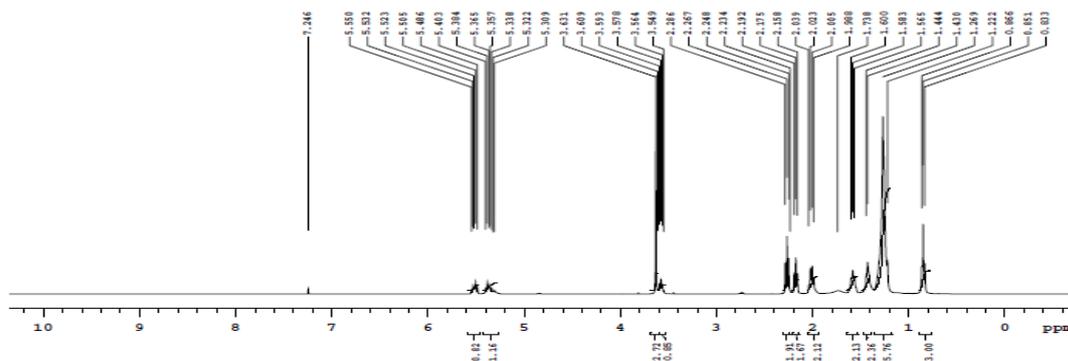


Figure 5: ¹H NMR spectrum of Castor oil Biodiesel

3.7. Physiochemical properties of Castor oil and its Biodiesel

Table: 2 Physiochemical properties of castor oil and its Biodiesel

Property	Units	Castor oil	Castor Biodiesel	ASTM D6751-07a
Density	g/ml	0.962g/cc	0.880@15°C	0.86-0.9
Kinematic viscosity at 40deg C	mm ² /s	43	5.1	1.9-6
Flash point (Open Cup)	deg C	235	195	130 Min
Fire Point	deg C	249	211	-
Calorific value	MJ/kg	41	39	-
Cloud Point	deg C	15	11	Report

Ash	% mass	-	Nil	-
Sulfur Content	% mass	-	0.001	0.05 Max
Carbon residue	% mass	-	Nil	0.05 Max
Iodine Value	83	67.7	Report
Phosphorous content	% mass	-	0.000119	0.001
Water content	% volume	-	Nil	0.05 Max
Total acid number	mg KOH/g	5.322	0.44	0.5 Max
Copper Strip Corrosion for 3h at 100°C	deg C	-	Not worse than No.1	No.3 Max
Potassium content	ppm	-	1.2	5 Max
Sediment	% volume	-	0.031	0.05 Max
Methanol Content	% volume	Nil	0.05	0.2 Max

4. Conclusion

Castor oil is one of the promising Non-edible oil feed stock for the synthesis of biodiesel. Castor oil biodiesel yield can be easily increased by using K_2CO_3 in NH_4OH as a catalyst rather than direct K_2CO_3 and Conventional KOH methods.

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