AMMONIUM HYDROXIDE-CASTROIL METHANOLYSIS USING POTASSIUM CARBONATE AS A CATALYST

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Abstract

Using an ammonium hydroxide (NH4OH) catalyst, oil was refluxed together with methanol and potassium carbonate to create methyl esters, or biodiesel, of castor oil. The settings for the reaction were tuned. A maximum yield of 97.6% methyl esters was produced employing 1.8g of potassium carbonate in conc. ammonium hydroxide (1:2.5 catalyst to NH4OH molar ratio) as a catalyst in a reaction with a 10:1 methanol to oil molar ratio at 50oC for a refluxing time of 3 hours.Methyl esters were characterized spectrally using 1HNMR. Biodiesel's physiochemical characteristics were examined and contrasted with ASTM standards. Every value falls within the ASTM standard range.

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

1. Introduction

The overuse of conventional petroleum fuels is a result of growing urbanization and population[1]. The intern is to blame for the environmental degradation and energy crisis[2]. The world's energy demand and ecological imbalance may be efficiently resolved by producing fuel that is sustainable, renewable, and environmentally friendly[3].

One type of liquid fuel that is renewable and biodegradable is biodiesel, which is made from sources that include bio-lipids, such as vegetable or animal fats[4]. Edible oils such as groundnut oil, coconut oil, sunflower oil, soybean oil, rapeseed oil, and palm oil are used to make more than 95% of commercial biodiesel[5]. The production of biodiesel from edible oils poses a significant risk to food security and the energy crises [6]. Because of their high oil content and accessibility, non-edible oils including castor, pongamia, mahua, and neem can help resolve the aforementioned problem [7][8]. In this work, castor oil is used as the feed supply.

When non-edible oils are methanolyzed using the direct NaOH or KOH catalytic technique, more soap is formed, which lowers the yield [9]. This results from the methoxide creation reaction's increased production of water as an intermediary [1]. Since K2CO3 catalyst doesn't create water molecules during the reaction, it can overcome such difficulties[10]. However, potassium carbonate is a weak base that is rarely soluble in methanol, making it experimentally disadvantageous to utilize direct (unsupported) K2CO3 as a catalyst for methanolysis of triglycerides[11].

By treating K2CO3 with a known quantity of NH4OH (2.5 moles of NH4OH with 1 mole of catalyst), the aforementioned issues may be readily resolved. The basic strength (basicity) and solubility of the catalyst are increased when a tiny quantity of ammonium hydroxide is added to K2CO3, which in turn boosts the catalyst's activity in the production of biodiesel[12]. Simultaneously, the presence of carbonate and ammonium ions in the reaction mixture greatly inhibits the synthesis of soap and the hydrolysis of esters.

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 100ºC 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 60ºC. 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 100ºC to remove water content. As water is produced as an intermediate during esterification process (equation 1).

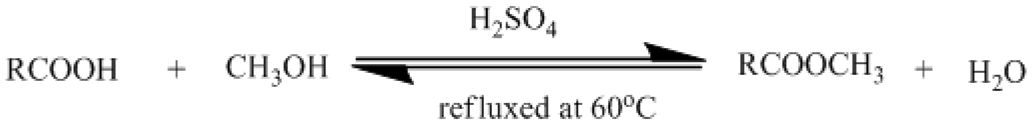
2.3. Base catalyzed Transesterification

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 50ºC 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 100ºC 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.

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

Reactions:

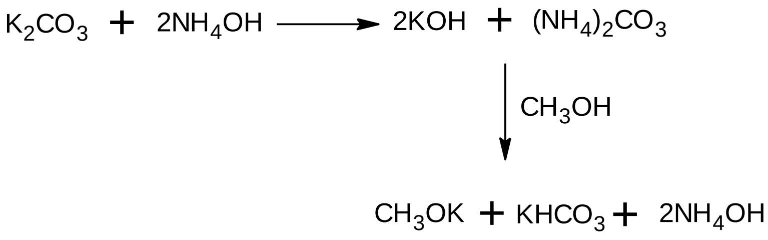
1. Acid catalyzed Esterification Reaction



$$RCOOH + CH_3OH \xrightleftharpoons[\text{refluxed at 60°C}]{H_2SO_4} RCOOCH_3 + H_2O$$

(1)

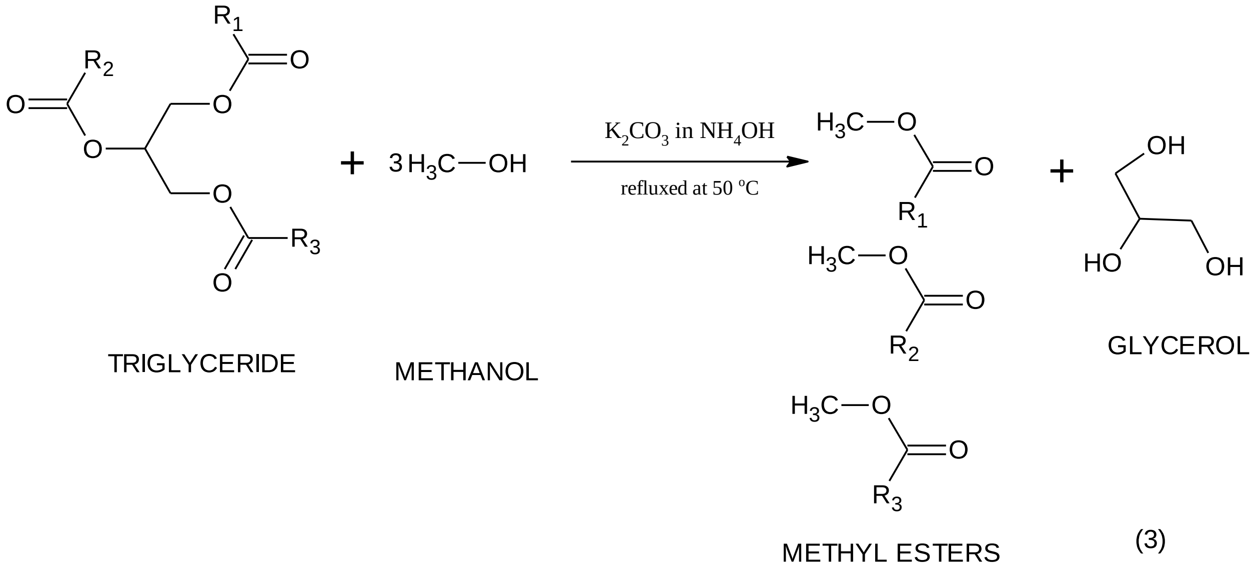
2. Reaction of Potassium carbonate with NH₄OH followed by methoxide formation with methanol



$$K_2CO_3 + 2NH_4OH \longrightarrow 2KOH + (NH_4)_2CO_3$$
$$\xrightarrow{CH_3OH} CH_3OK + KHCO_3 + 2NH_4OH$$

(2)

3. Methanolysis of Triglycerides



(3)

Where: R1, R_2 and R_3 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.

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

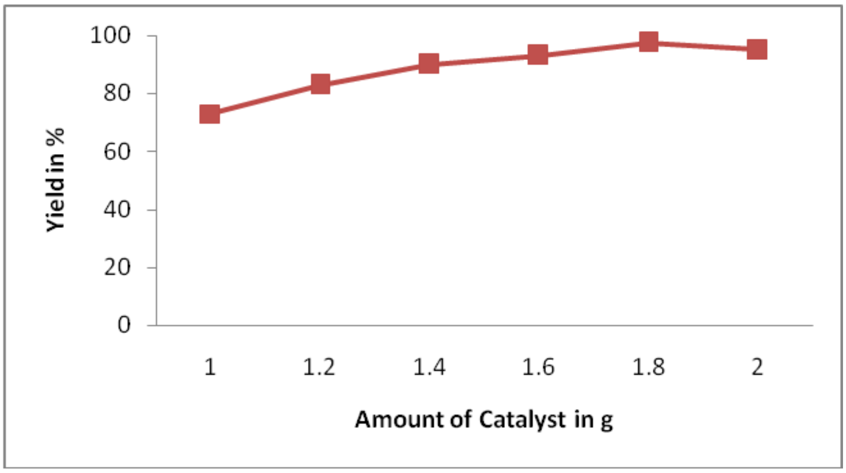


Figure 1: Graphical representation of effect of catalyst amount on the biodiesel yield

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].

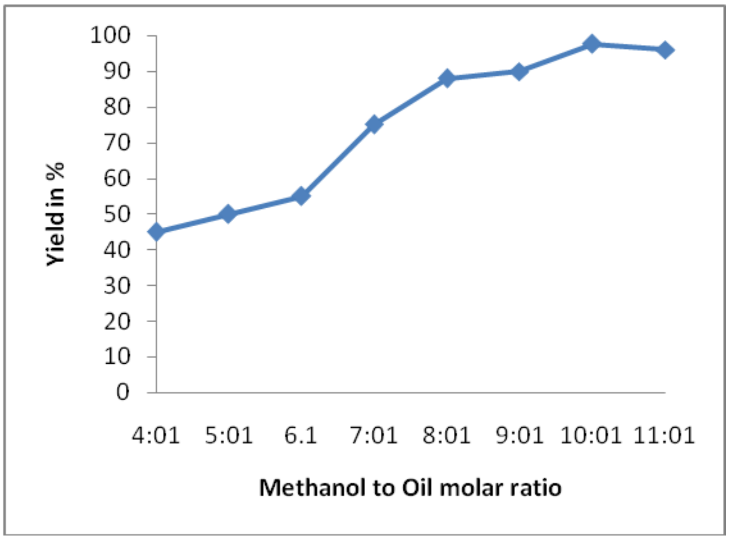


Figure 2: Graphical representation of effect of methanol to oil molar ratio on the biodiesel yield.

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

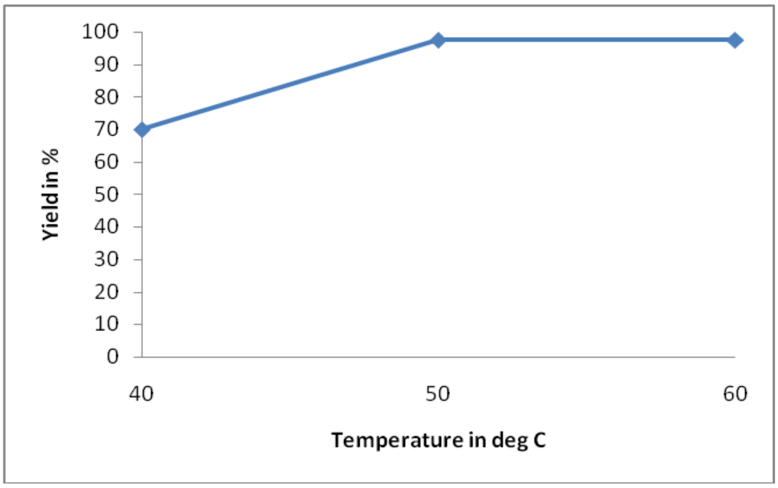


Figure 3: Graphical representation of effect of Temperature on the biodiesel yield

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].

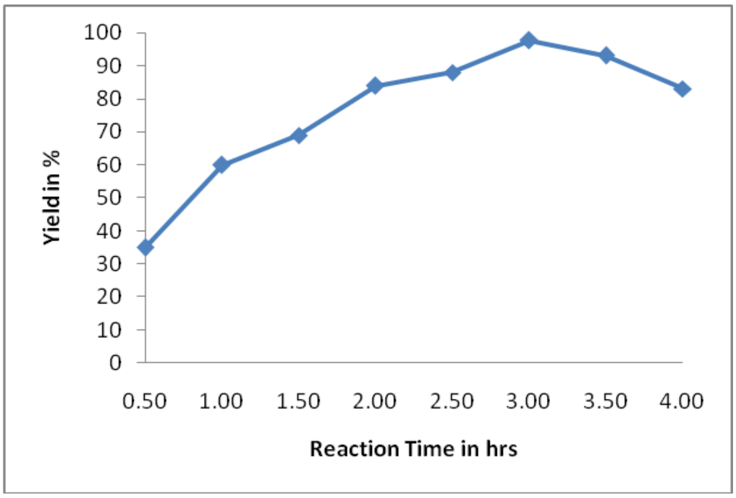


Figure 4: Graphical representation of effect of Reaction time on the biodiesel yield.

3.6 Characterization of Biodiesel by Proton Nuclear magnetic resonance spectroscopic method

^{1}H-NMR spectroscopy is a resourceful technique to confirm the conversion of triglycerides to methyl esters (Biodiesel). ^{1}H 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].

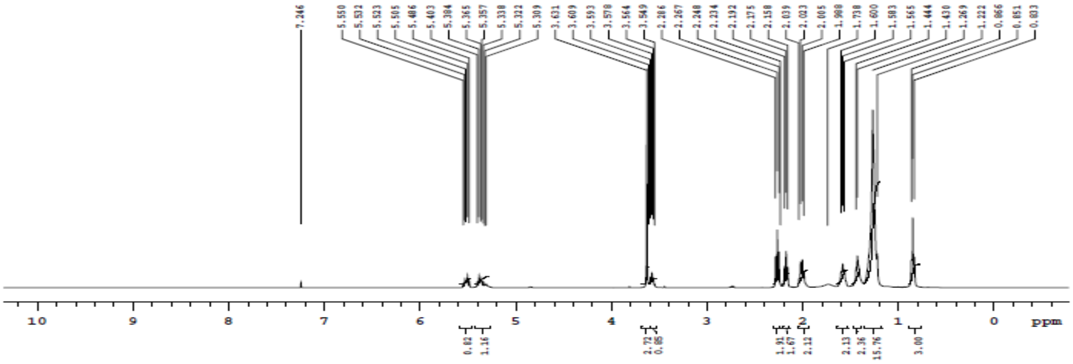


Figure 5: ^{1}H NMR spectrum of Castor oil Biodiesel

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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^{o}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^{o}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

One of the most promising non-edible oil feedstocks for the production of biodiesel is castor oil. Using K2CO3 in NH4OH as a catalyst instead of direct K2CO3 and conventional KOH techniques makes it simple to boost the production of castor oil biodiesel.

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