



# Comparative Study of Acid-Base Homogeneous Catalyst used in Biodiesel Production from Soybean WCO via trans-esterification Reaction

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## Abstract

*The present study analyses the combination of the two factors which include the determination of the best catalyst to obtained maximum conversion of yield in the production of biodiesel from soybean waste cooking oil and the second factor is to determine the best catalyst giving out maximum characteristics/properties compared to pure diesel using Gas Chromatography analysis. We compare acid/base homogeneous catalysts notably, H<sub>2</sub>SO<sub>4</sub>/HCl and NaOH/KOH respectively. Using acid catalysts, there was separation in both the samples of H<sub>2</sub>SO<sub>4</sub> and HCl. The H<sub>2</sub>SO<sub>4</sub> gave 87% yield while HCl gave 81% yield with low production of glycerol amount to 10ml and 6ml respectively. The base catalyzed trans-esterification showed that the NaOH and KOH gave 97% and 94% of biodiesel yield and glycerol as byproduct amount to 10ml and 9ml respectively. From the GC analysis, the base catalyze biodiesel (NaOH and KOH) have higher number of peaks containing Hydrocarbons from C10 to C21 which are similar to those obtained in a pure diesel.*

**Keywords:** Biodiesel, Soybean Waste Cooking Oil (WCO), Homogeneous Catalyst, Trans-esterification, Gas Chromatography (GC).

## 1. Introduction

Biodiesel which is considered as mutually exclusive substitute to fossil base fuel has immensely contribute in the reduction of serious emissions of hydrocarbons, particulates, SO<sub>2</sub> and CO<sub>2</sub> in comparison to conventional diesel. This is mainly due to its biodegradable nature, nontoxic, renewable and environmentally friendly (Oladipo *et al.*, 2018). The properties of biodiesel enable it to be used as conventional diesel since its properties are very much similar to that of conventional/petroleum-based diesel. Such properties include an elevated flash point, proper viscosity, high octane number and zero modification is needed (Colombo *et al.*, 2017). The production of biodiesel takes place via a process called trans-esterification reaction; a reaction in which alcohol reacts with either vegetable oil or fats in the presence of a catalyst to produce alkyl esters as the major and glycerol as by-products (Colombo *et al.*, 2017). This process enhances the breakdown of the chemical structure of glycerides in oil through substitution and modification of alkyl groups between alcohol and ester (Boro *et al.*, 2011). This process demands high quality and functional raw material to evade saponification and unwanted side reactions or pre-treatment in essence to get rid of initial free fatty acids as a result of the difficulty in conversion to esters through trans-esterification in the presence of free fatty acid (Chen *et al.*, 2009; Suppes *et al.*, 2001).

With the advent to the threat of food security in global market, many organizations including NGO are against the use of food source (edible oil) for biodiesel production. However, the used of waste cooking oil (WCO) could equally reduce the problem and many other such as blockages of water drainages system which consequently causes water especially in a Cosmopolitan city (Chen *et al.*, 2009). Many other environmental



problems cause by WCO include pipe drains obstructing and creation odors which consequently increase the cost of waste water treatment, it also lead to increase in organic pollutants on many water bodies that are known in altering the aquatic ecosystem there by creating layers on the water surface that prevent the passage of oxygen. It was revealed that a liter of oil can pollute 500 litres of water (Carlos *et al.*, 2014). This WCO can be collected using a special recycle bin from restaurants and houses. Though, many researches proved that state of biodiesel production using WCO is less profitable compared to the use of other fossil fuels (Yaakoob *et al.*, 2013). Many non – edible and edible oils has been tested such as mustard oil, soybean oil, rapeseed oil, rubber seed oil, neem oil, jatropha seed oil, silk cotton tree oil, micro algae oil, sunflower oil, palm oil and their waste one (WCO), in the trans-esterification process for biodiesel production (Zheng *et al.*, 2003; Demirbus *et al.*, 2009)

As other edible and non-edible oil, the trans-esterification of biodiesel from WCO takes place in the presence of alcohol. However, methanol and ethanol are interchangeably used as primary alcohols with a sting of 1-8 carbons (Cujia and Bula, 2010). Many researches however revealed that the trans-esterification method is catalysed using a homogeneous or heterogeneous acid/base catalyst (Dizge *et al.*, 2009). Another finding revealed that acid base trans-esterification process consumes less time and have lower cost compared to enzymes catalyst. The frequent notable homogeneous catalyst for the trans-esterification process in biodiesel production are sulphuric acid ( $H_2SO_4$ ), hydrochloric acid (HCl) or sodium hydroxide (NaOH), potassium hydroxide (KOH), acid/base respectively (Yaakoob *et al.*, 2013).

Researchers around the globe are working round the clock to address the major challenges in biodiesel production. Selection of reliable feedstock/raw-materials, methodology and use of suitable catalyst for the production of biodiesel are among the current existing challenges. The primary focus of this research is the selection of suitable catalyst for biodiesel production to give out maximum conversion of yield and secondly to analyse the similarities in properties of biodiesel produced in comparison with pure/conventional diesel using Gas Chromatography.

## 2. Materials and Methods

Potassium hydroxide (KOH), sodium hydroxide (KOH), methanol ( $CH_3OH$ ), hydrochloric acid (HCl), and tetraoxosulphate (vi) acid ( $H_2SO_4$ ) were obtained from Sigma Aldrich are of analytical grade, used as received. Four samples of Soybean WCO was obtained from a local restaurant of Noida sector sixteen market (Delhi NCR) India, the samples were stored in a covered plastic and taken to the laboratory for analysis. The sample was then pretreated before the analysis (Yaakoob *et al.*, 2013). The trans-esterification reaction was all carried out in a 500ml conical flask while magnetic stirrer was used to stir the mixture. Microwave was used for heating and all the product were separated using separation funnel.

### 2.1 Preparation of Reagent

According to (Hossain and Mazem, 2010) modified method, 400g of the KOH and NaOH pallet was separately weight and put into clean and dry 500ml beaker respectively, about 400ml of distilled water was added and stir to dissolve the pallets in a cold-water bath. The solution was then transferred into 1000ml volumetric flask and allowed to cool for 1 hour as all the reaction is exothermic, distilled water was then added to the mark  $0.5dm^3$  of both KOH and NaOH was formed. The same procedure was applied in the preparation of acids catalyst in which  $0.5dm^3$  was formed for both  $H_2SO_4$  and HCl.

#### 2.1.1 Base – Catalyzed trans-Esterification (NaOH and KOH)

The method of (Hossain and Mazem, 2010) was used, the methoxide was prepared with mixture of methanol and alkaline (KOH and NaOH) for biodiesel production. 0.8gm alkaline (KOH and NaOH) were taken and dissolved in 20ml methanol each to form methoxide. 100 ml of soyabean oil was taken in a conical flask, the flask was heated for

5 mins at 100°C. Then cooled at 70°C and 15ml of potassium methoxide/sodium methoxide was added in two different samples of 100ml soya bean oil. The flask was then incubated at 50°C for 4-5hrs, after 4-5, the whole mixture was transferred into the separation funnel at room temperature and left over night. Two layers were formed after 24hrs, the upper layer composed of biodiesel while the lower layer consisted of the byproduct (crude glycerol).

### 2.1.2 Acid- Catalyzed trans- Esterification ( $H_2SO_4$ and HCl)

Modified (Morshed *et al.*, 2011) method was used, 100ml of Soybean oil was taken in a conical flask, the flask was heated for 5 mins at 100°C. 18ml methoxide was prepared with methanol & sulphuric acid / Hydrochloric acid in 6:1 ratio separately. Flask was incubated at 50°C in case of sulphuric acid and 80°C in case of hydrochloric acid for 4-5hrs. The whole mixture was then transferred into the separation funnel at room temperature and left over night. Two layers were formed after 24hrs, the upper layer composed of biodiesel while the lower layer consisted of the byproduct (crude glycerol).

### 2.2 Gas Chromatography Analysis:

The sample of the conventional (pure) diesel purchased from filling station was first injected onto the head of the Gas - Chromatography column, the temperature was then raised in between 50 – 300°C volatilizations. The percentage of individual peaks of Hydrocarbons defining each biodiesel formed was obtained. All the four samples of biodiesel formed was subjected to the same procedure in the GC machine, the hydrocarbon peaks obtained from pure diesel which was accepted as the standard was compared with those obtained from biodiesel GC result, the method of (Yahaya *et al.*, 2013) was adopted for this work.

### 3.0 Result

After the separation of biodiesel and glycerol, the yield was measured to ascertain the quantity produced. Using acid catalysts, there was separation in both the samples of  $H_2SO_4$  and HCl, the  $H_2SO_4$  gave 87% yield while HCl gave 81% yield with low production of glycerol amount to 10ml and 6ml respectively. The other results (base catalyzed trans-esterification reaction) showed that the NaOH and KOH gave 97% and 94% of biodiesel yield and glycerol as byproduct amount to 10ml and 9ml respectively.



Fig 1: Separation of biodiesel in separating funnels using base catalyst

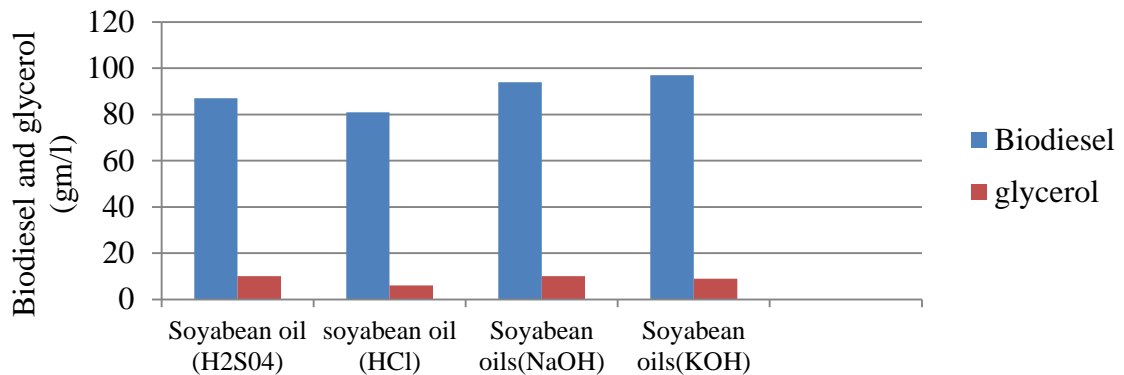


Fig 2: Volume of biodiesel produced using four different catalysts.

### 3.1 Gas Chromatography Analysis

The sample of standard conventional/pure diesel were first run for GC analysis, this is to ascertain a clear picture and the number of hydrocarbons that are present in a pure diesel. The retention time and the peak were compared and the following result was obtained.

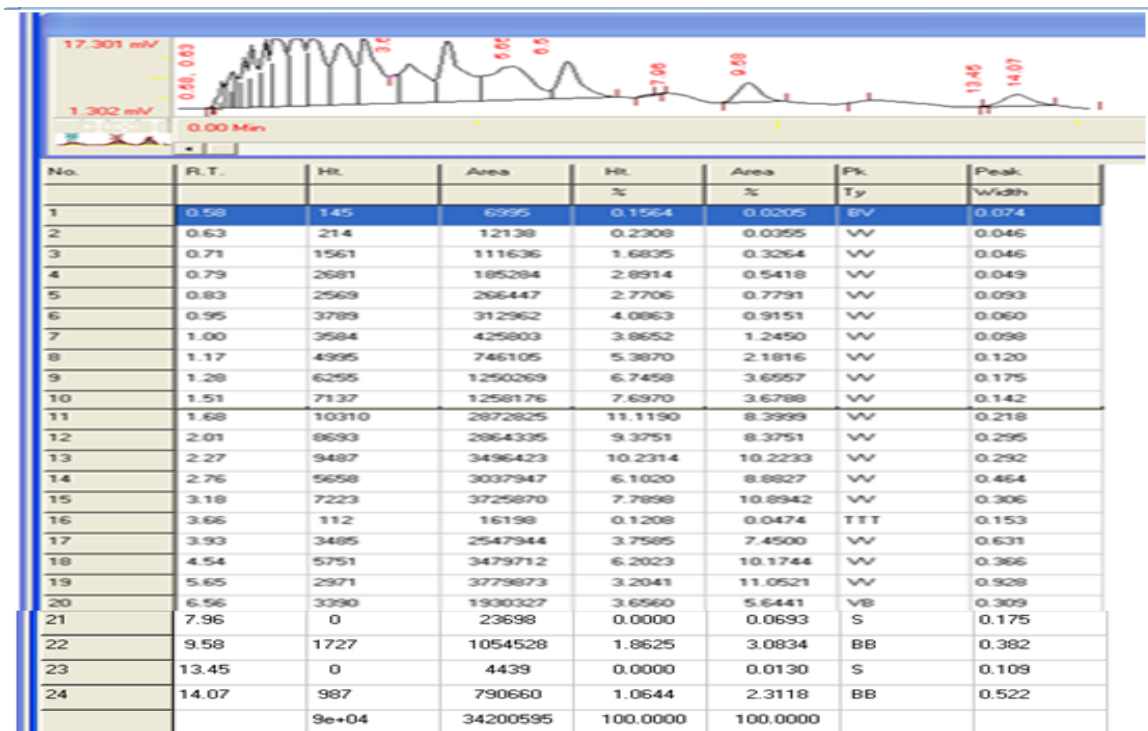


Fig 3: GC results of Standard Hydrocarbons found in Diesel

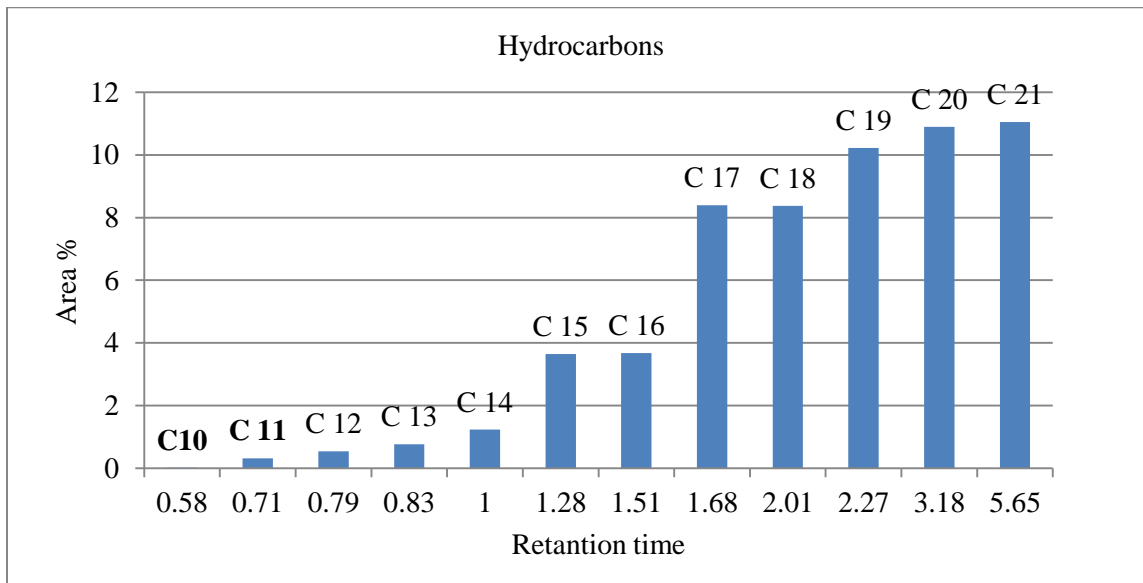


Fig 4: Standard hydrocarbons presents in pure diesel

Fours samples of the produced biodiesel were subjected to the same GC analysis and the following results was obtained.

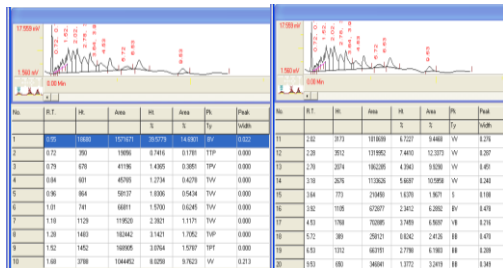


Fig 5: GC result of biodiesel from soybean wco using KOH Catalyst

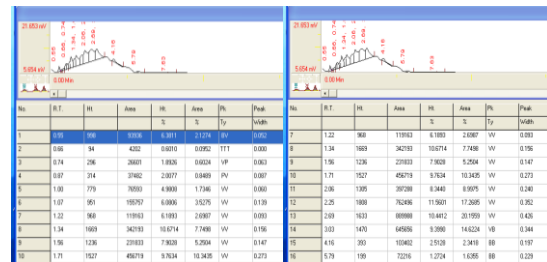


Fig 6: GC result of biodiesel from soybean wco using NaOH catalyst

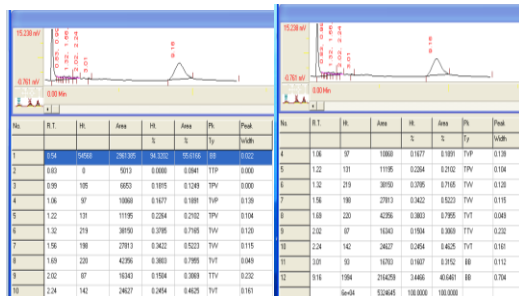


Fig 7: GC result of biodiesel from soybean wco using HCl Catalyst

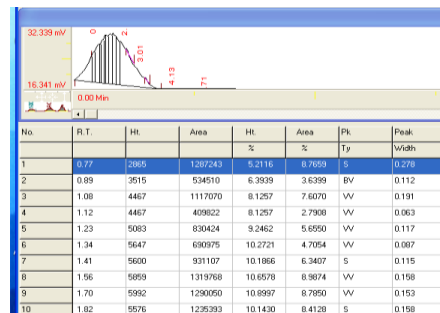


Fig 8: GC result of biodiesel from soybean wco using H<sub>2</sub>SO<sub>4</sub> catalyst

Table 1: Standard hydrocarbons presents in biodiesel samples

Soyabean oil /KOH		Soyabean oil /NaOH		Soyabean oil /HCl		Soyabean oil /H <sub>2</sub> SO <sub>4</sub>	
Retention Time	Hydrocarbon	Retention Time	Hydrocarbon	Retention Time	Hydrocarbon	Retention Time	Hydrocarbon
0.55	C 10	0.55	C10	0.54	C10	0.62	C10
0.72	C 11	0.74	C11	0.83	C13	0.73	C11
0.79	C 12	0.87	C13	0.99	C14	0.74	C12
0.84	C 13	1.00	C14	1.56	C16	0.81	C13
1.01	C 14	1.25	C15	1.69	C17	1.29	C15
1.28	C 15	1.56	C16	2.02	C18	1.61	C17
1.52	C 16	1.71	C17	2.24	C19	2.02	C18
1.68	C 17	2.01	C18	3.15	C20	2.24	C19
2.02	C 18	2.25	C19	5.67	C21	3.21	C20
2.28	C 19	3.17	C20				
3.18	C 20	5.57	C21				
5.72	C 21						

By analyzing the result, it clearly indicates that many of the hydrocarbons peak found in synthesized biodiesel are similar to that obtained from conventional/pure diesel. However, the biodiesel formed from NaOH and KOH have higher number of peaks which are much similar in comparison to conventional/pure diesel.

#### 4.0 Discussion

Wang *et al.*, 2006 in a similar researched identified inorganic acid such as HCl and H<sub>2</sub>SO<sub>4</sub> as a potential catalyst in biodiesel production obtaining high yield, he reported that HCl catalyst produced 61% yields while H<sub>2</sub>SO<sub>4</sub> produced 80% yield which correspond to our current findings. In another research by (Dinesh *et al.*, 2016) revealed that H<sub>2</sub>SO<sub>4</sub> produce yield up to 99.009% with low glycerin formation compared to HCl which gives 81% with low glycerin formation as well which is in line with ARM fuel requirements. . (A. Gnanaprakasam *et al.*, 2013) also report that H<sub>2</sub>SO<sub>4</sub> and HCl are good catalyst in the production of biodiesel however requires high reaction kinetics and reactions conditions, this similar to the present study report. Another research reported by (Hossein *et al.*, 2010) revealed that the acid catalyzed trans-esterification reactions are more tolerant to free fatty acids. NaOH gave out a high yield when compared to KOH among the base catalyst, it was also revealed that NaOH gave a better fatty ester yield, NaOH and KOH are the best alkali catalyst giving high yield in accordance with ARM. In a similar research by (Saleh *et al.*, 2014) NaOH is the best among the base catalyst as it gives greater conversion and yield compared to KOH catalyst. In a similar research by (Cheng *et al.*, 2009), NaOH produced a yield of 85% at a 1% concentration. Also reported by (Thirumarimurugan *et al.*, 2012) that 80% and above yield can be obtained using NaOH catalyst from WCO with methanol ratio of 6:1. In a similar research reported by (Wanodya and Arief, 2013), KOH gave a maximum yield of 93% with methanol ratio of 6:1 All the above results showed much correspondences with the present study.

By analyzing the GC result, it was found that the quality of biodiesel produced from base catalysis is better than the other forms of catalyst as it is seen in Table 1. (i.e. all the Hydrocarbons from C10 to C21 are present in the Biodiesel obtained from KOH catalyst). Our research in a similar way correspond to many findings as reported by (Villa *et al.*, 2010) that the retention time of Peaks for different hydrocarbons obtained in biodiesel production from soybean oils by different catalysts used for the GC analysis was based on the hydrocarbons shown to be present in older references where in GC and GCMS of Diesel was carried out, he reported that base



catalyst have similar hydrocarbons similar to that of pure diesel. Also reported by (Leung and Guo, 2006; Dias *et al.*, 2008) methyl esters of fatty acids have similar carbon chain length, this is assumed to have same volatility and response factor which allowed making a clear comparison of the peak areas to indicate the sample composition. The base catalyst always has similar carbon chain to pure diesel then the acid catalyst. According to (Carlos *et al.*, 2014) acid catalyst accelerate the reaction rate compared to base catalyst, he also reported that the major disadvantage of base catalyst is the production of soap due to the presence of high fatty acids and water. In a research reported by (Mohammed and Ghargavi, 2015) NaOH and KOH have a better advantage as known with moderate reaction conditions and less time however, high FFA may lead to the formation of soap and that reduced the overall yield.

## 5.0 Conclusion

The present study identifies the best catalyst in the production of biodiesel from soybean waste cooking oil. This study reveals that homogeneous catalyst (acid/base) can all be used in biodiesel production as the results showed higher levels of biodiesel formation from both acid and base homogeneous catalyst. However, base catalyst is identified as the best catalyst producing high yield of biodiesel. To further prove the best catalyst in biodiesel production, the GC result showed that base catalyst produces the best version of biodiesel via transesterification reaction having the same hydrocarbon peaks with pure diesel. The study finally concluded that base catalyst was more preferable in the production of biodiesel. However, both the acid and base catalyst can all be used in the production of biodiesel in larger scale from soybeans waste cooking oil and the quality of the biodiesel formed is also comparable to that of conventional (pure) diesel. It was also learnt that Recovery of the catalyst from the final product is one of the major problem associated with the used of homogeneous catalyst via transesterification reaction.

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