

Production of Biodeisel by Transesterification of Waste Cooking Oil Using Prepared Heterogeneous Catalysts

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ABSTRACT

*Heterogeneous catalysts were formulated from the ash of roots, stems and leaves of *Crotalaria pallida* Aiton plant. The catalysts were chemically activated by impregnation with kaolin. Different weights of the activated catalysts were prepared via the wet impregnation method. The esterification was done with methanol at 100-200°C. The influence of the reaction temperature, methanol-oil molar ratio, catalyst loading and reaction time on the methyl ester content was studied. The conversion of the waste cooking oil into biodiesel was revealed to increase with increase in catalyst loading, methanol to oil ratio, reaction temperature, and reaction time. The catalyst loaded with 15% kaolin at a reaction temperature of 160°C exhibited maximum biodiesel yield of 89.5%. The physico-chemical properties of the biodiesel produced was favourably compared with ASTM biodiesel standard.*

Keywords: Biodiesel. Stability, reusability, molar ratio, wastes cooking oil, catalyst loading and transesterification.

1.0 INTRODUCTION

The price of petroleum has risen as a result of depletion of fossil fuels and the pollution caused by vehicles is of environmental concern. This necessitated the need for alternative energy like biodiesel. Biodiesel is biodegradable, non-harmful and renewable (Mikael and Tang, 2013). Over 90% of global energy production comes from fossil fuels but their main drawback is causing air pollution. Industrial activities and increased motorized transport are the cause of air pollution in our modern cities. Each year, one million people were estimated to die prematurely as a result of air pollution (Douglas, 1991).

The process used to convert oils to biodiesel is called transesterification, Transesterification in biofuel production and other catalyst applications such as in the production of hydrocarbons such as olefins and processing engineering such as production of drugs in pharmaceutical industry their studies are crucial because the gradual depletion of the world petroleum reserves and the problem of environmental pollution as a result of using fossil fuels, the world attention have been shifted towards a source of renewable energy or sources which will serve as an alternative to fossil fuels (Tasneem and Abbasi, 2010).

Bio-fuels derived from vegetable oils are important alternative because it emits less carbon dioxide and other pollutants compared to fossil fuels in combustion engines and therefore environmentally friendly. People can grow their own fuel as it can be obtained renewable sources and engine modification is not needed as it has similar properties compared to diesel fuel. Diesel engines even perform better on biodiesel due to its high cetane number and high purity of biodiesel would eliminate the use of lubricants. Bio-fuel would make an area become independent of its need for energy as it can easily be produced locally (Chiroma *et al.*, 2016).

Biofuel is similar to conventional fuel. Biofuel can be obtained by the conversion waste cooking oil. A good catalyst is required to produce bio-fuel of high quality or other product while eliminating unwanted waste. The interest taken in the last few decades in the reactions of selective oxidation of organic compounds, in particular of hydrocarbons, on oxide catalysts cannot be overemphasized. These reactions are the basis of numerous industrial

processes yielding organic oxides, aldehydes, organic acids and their anhydrides (Barbara, 2000). Some particular catalyst tasks for certain reaction, it may not also be appropriate for another reaction. An impregnated catalyst has been shown to bring about completely different reactions for the same substance (Bahl *et al.*, 2000).

Oxidation reactions of hydrocarbons provide a realm for fundamental academic studies on a crucial problem in heterogeneous catalysis of selectivity, and on the relations of this parameter to the nature, structure, and properties of catalysts. Indeed, it is an intriguing question as to which properties of a catalyst determine the orientation of the reaction towards a particular product, one of many possible products differing by a number of oxygen atoms in a molecule. In this context we shall explore the use of heterogeneous catalyst in the transesterification of oil (Taufiq-Yap *et al.*, 2014).

2.0 MATERIALS AND METHODS

2.1 Materials Required

Crotalaria pallida Aiton plant was collected around the roadsides of Federal Teaching Hospital and Federal Low Cost Housing Estate in Gombe, Gombe State. The plant was identified by the Biological Science Department of Gombe State University. The root, stem and leaves of the plant were ashed separately and were used separately to carry out the catalytic reaction on a kaolin support that was obtained along Bauchi road. Waste cooking oil was also obtained from local women in Gombe State that was used for transesterification (Buhari *et al.*, 2014).

2.2 Transesterification Reaction

The procedure by Suryadi *et al.*, (2010) was adopted. Waste oil was obtained from some local women in Gombe State and used without any further refinement. Its viscosity and acid value were determined. Influence of atmospheric pressure and other several factors were studied and recorded.

2.3 Analysis of Biodiesel Produced from Transesterification process

2.3.1 Viscosity Measurements

Viscosity is one of the basic parameter reflecting the extent at which the reaction goes. The viscosity of the waste cooking oil and the obtained biodiesel were determined using viscometer. One replicate for each sample were done as to test for accuracy. Conversion value was determined by making small calculations the following equation:

Oil Conversion = $(\text{Viscosity of triglyceride} - \text{Viscosity of methyl ester} \times 100 / \text{Viscosity of triglyceride})$ (Omotola *et al.*, 2010).

Viscosity is the resistance to flow. 20ml of oil sample was added to a capillary tube and the flow was recorded. The flow time multiplied by the factor on the glass calibrated viscometer gave us the viscosity (Buhari *et al.*, 2014).

2.3.2 Acid Value of Oil and Biodiesel

Acid value is defined as the number of KOH, in mg, necessary to neutralize the free fatty acids in 1 gram of sample. The reagents used in the present study include 0.1N standard potassium hydroxide solution, solvent mixture consisting of 95% ethanol and diethyl ester at the volume ratio of 1:2, and the phenolphthalein indicator solution

consisting of 1% phenolphthalein in 95% ethanol. The acid value (AV) equals the volume of titration used times the normality of standard KOH solution and the molecular weight of KOH, which is 56.1 gram per mol, and then divides the mass of the oil sample (Suryadi *et al.*, 2010).

2.3.3 Determination of Flash Point

The flash point is a ability of a sample to produce an inflammable mixture with an ignition source. 15 ml of the biodiesel poured into a 250 ml conical flask was heated and passed over the surface of the liquid. The temperature, at which the vapour ignited, was recorded as the flash point temperature. Three determinations were obtained. (Siddharth *et al.*,2011).

2.3.4 Determination of the Cloud Point

Upon cooling a liquid at a certain temperature, a cloud of wax crystals appears. Such is regarded as a cloud point. To a test tube, 15ml of the biodiesel was added and placed in a refrigerator sometime. The sample was observed and the temperature at which the cloud first formed was recorded (Buhari *et al.*, 2014).

2.3.5 Determination of Pour Point

The minimum temperature at which a fuel sample will flow is regarded as pour point. Immediately when the sample was removed from the refrigerator, it was scrutinized at 5°C for it to flow, the minimu temperature which the biodiesel was able to flow was recorded as it pour point (Suryadi *et al.*, 2010).

2.3.6 Effect of Catalyst Loading

The influence of percentage of catalyst used to convert the waste cooking oil to biodiesel was investigated as the % loading of catalyst per to oil. 5 to 20% wt /wt variation were used while all other reaction factors remain identical (Barbara, 2000).

2.3.7 Effect of Reaction Time

Analyses were carried out at 2, 5, 8, 12 and 24 hours to determine the effect of reaction time over the oil conversion (Hilary, 2013).

2. 3.8 Effect of Reaction Temperature

Transesterification can be done at various temperatures depending on the oil used. Temperature is very important factor that affects the rate and the yield of reaction. To determine the effect of temperature over oil conversion we conducted analyses at 100, 120, 160, and 200°C temperatures (Chiroma *et al.*, 2016).

2.3.9 Effect of Molar Ratio of Methanol to Oil

The influence of the molar ratio of methanol over oil conversion was determined by varying the amount of methanol while amount of waste oil remain constant (20g) at 160°C. Methanol - Oil ratios of 6:1, 9:1, 12:1, 15:1 were adopted (Suryadi *et al.*, 2010).

3.0 RESULTS AND DISCUSSION

3.1 Effect of Catalyst Loading

Figure 1 shows the result of the preparation of heterogeneous catalyst for transesterification of waste cooking oil from *Crotalaria pallida* (Aiton) Plant. It was revealed that the leave sample catalyst has the highest percentage biodiesel production of 87.5%. The influence of the % catalyst loading used for the conversion varied from 5 to 20% wt/wt while all the reaction factors remain identical. The yield appeared to increase with concentrations above 5 wt%. This effect could be attributed to more diffusion with an increase in catalyst amount as a result of the increase of active sites of the catalyst. The maximum biodiesel yield of 89% was obtained at 20 wt% catalyst loading. Considering the reaction kinetics, we can now say that a greater % of catalyst contributed to a higher yield over shorter reaction time.

3.2 Effect of Reaction Time

The effect of reaction time was carried out and the dependence of the biodiesel yield on the reaction time was studied. As demonstrated in figure 5.

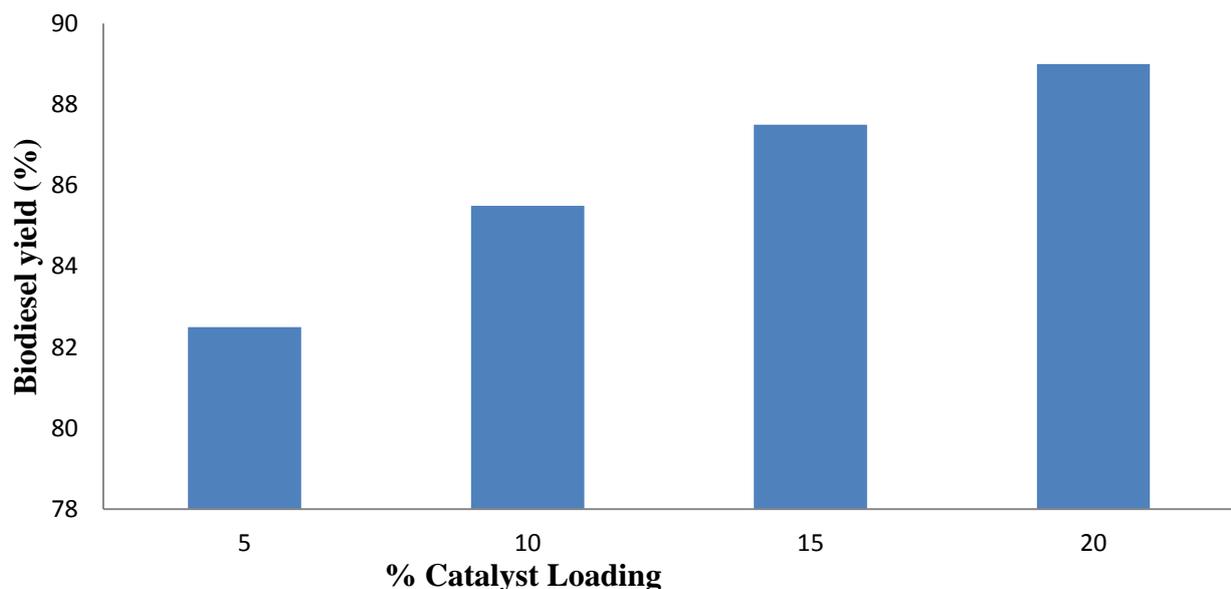


Figure 1: Effect of catalyst loading on the biodiesel yield (%) at the temperature of 160°C for 24 hours for leave sample

3.3 Effect of Reaction Temperature

The effect of reaction temperature was also observed as shown in figure 3. The activity profile showed that increase in reaction temperature also increases the conversion at the temperatures of 100°C to 120°C. Thereafter, there was no significant increase in the biodiesel production. From the graph it can also be observed that the highest biodiesel yield of 89.5% was obtained at temperatures of 200°C from the leave sample compared to that of the root and stem sample.

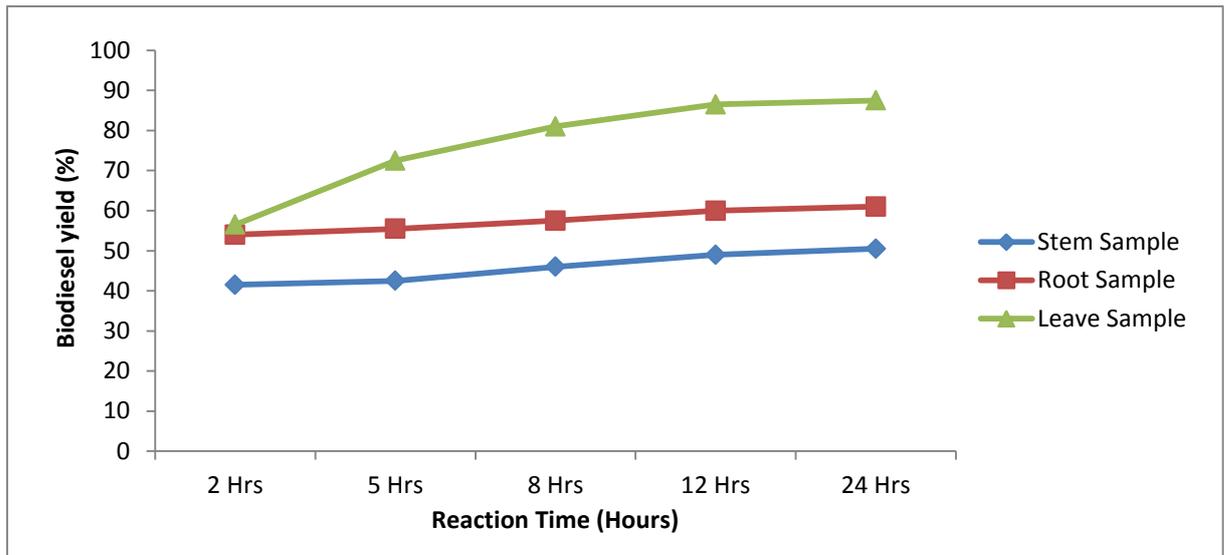


Figure 2: Effect of reaction time on biodiesel yield (%) at 160°C and catalyst C

3.4 Effect of Molar Ratio of Methanol to Oil

Figure 4 shows the effect of molar ratio of methanol to waste cooking oil. The transesterification was evaluated with a methanol -to- waste cooking oil ratio of 6:1, 9:1, 12:1 and 15:1 at 160°C with 15 wt% catalyst (with respect to the weight of oil). The results showed that the methanol molar ratio greatly affected the biodiesel conversion yield. When the methanol molar ratio increases from 6 to 15, the methyl ester conversion yield increased remarkably from 84.5% to 89.5% for the leave sample compared to that of the root and stem sample. It is worthy to note that the highest waste cooking oil conversion of 89.5% was observed at a methanol - oil molar ratio of 15:1 for the leave sample. Further addition of methanol above 9:1 to the reaction phase does not lead to any increase in the conversion.

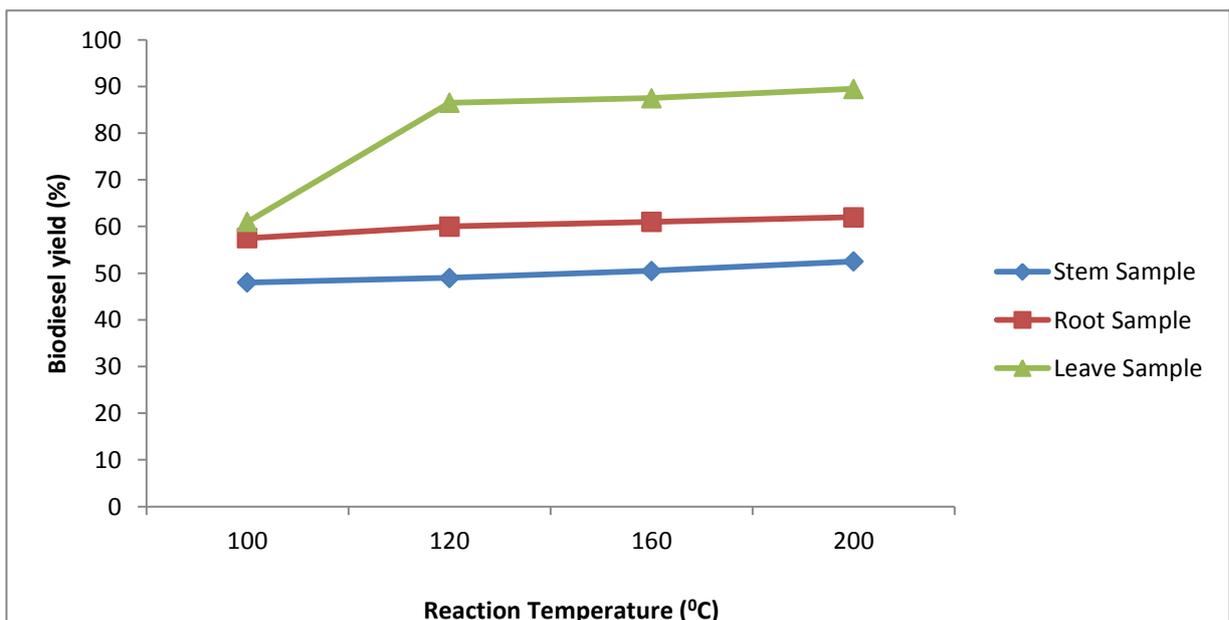


Figure 3: Effect of reaction temperature on biodiesel yield (%) with catalyst C for 24 hours

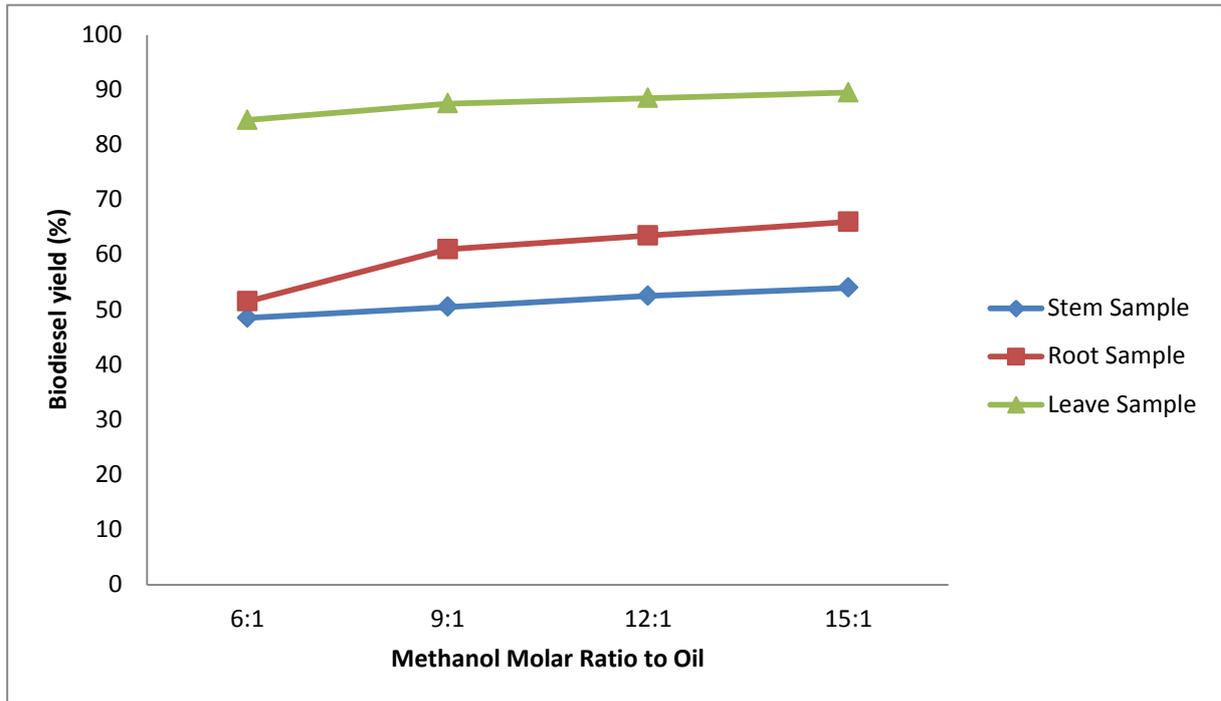


Figure 4: Effect of molar ratio of methanol to waste cooking oil for biodiesel production with catalyst C at 160°C for 24 hours

3.5 Catalyst Stability and Reusability Test

Catalyst stability and reusability test was also carried out as shown in figure 5 where 1, 2, and 3 stands for the number of runs where the waste cooking oil conversion values of 87.5%, 75.5% and 51.5% were observed respectively for the leave sample compared to that of the root and stem sample.

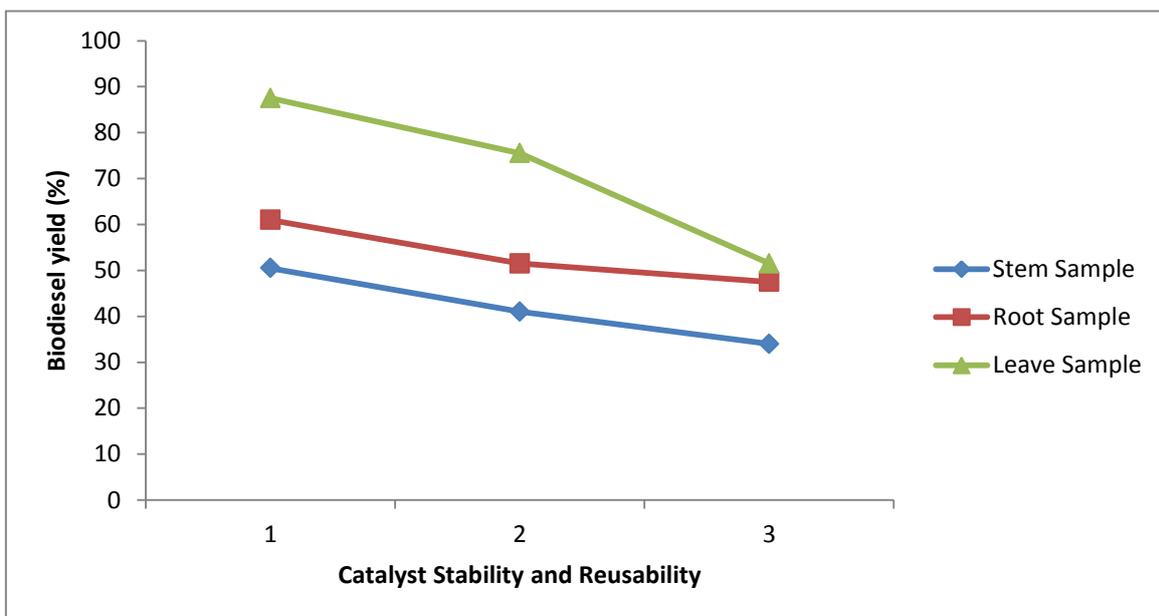


Figure 5: Catalyst stability and reusability test on biodiesel yield (%) at 160°C for 24 hours

The waste cooking oil conversion values decreased slowly from 87.5% to 51.5% when the process was repeated 1–3 times. On the other hand, a significant loss of catalytic performance was observed in the 3rd run, which

indicated a significant reduction of the number of catalyst's active sites after numerous washing and purification processes (Taufiq-Yap *et al.*, 2014). The two possible reasons behind catalyst deactivation are surface poisoning and structural collapse (Taufiq-Yap *et al.*, 2014). The surface poisoning might be due to the surface bound glycerides, i.e. triglycerides (TG), diglycerides (DG) and monoglycerides (MG) on the catalyst, which cannot be removed with the less polar solvent (Taufiq-Yap *et al.*, 2014). Therefore, the results of reusability and regeneration studies definitely indicated that the kaolin/ash catalyst is very stable and durable during the transesterification reaction, which is better than that reported by Thitsartarn and Kawi (2011). The percentage ash content for leave, root and stem sample are 30.33%, 27.66% and 29.69% respectively. The kinematic viscosity at 40⁰C and acid value (mg KOH/g) for the waste cooking oil is 55mm²/s and 3.37

Table 1: Comparison of the properties of biodiesel produced from catalyst C of stem, root and leave sample of *Crotalaria pallida* Aiton plant. 20cm³ of waste cooking oil, 9:1 of methanol to oil were used at a temperature of 160⁰C for 24 hours.

Properties	Stem biodiesel	Root biodiesel	Leave biodiesel	Biodiesel ASTM D6751
Volume of biodiesel obtained(Cm ³)	10.1	12.2	17.5	-----
Biodiesel yield (%)	50.5	61	87.5	-----
Kinematic viscosity at 40 ⁰ C (cSt)	7.6	6.3	5.2	1.9-6.0
Acid value(mg KOH/g)	0.78	0.56	0.36	< 0.50
Cloud point (⁰ C)	20	19	11	-3-12
Pour point (⁰ C)	12	8	3	-3-16
Flash point (⁰ C)	190	170	155	100-170

4.0 CONCLUSION

A large variety of raw materials have been investigated for biodiesel production in the world, therefore, heterogeneous catalyst for biodiesel production is a promising sustainable source which has received increasing interest from researchers worldwide. Easy availability and less expensive of Waste Cooking Oil (WCO) makes it a reliable source of biodiesel for sustainable energy generation and thereby reduces biodiesel production cost. *Crotalaria pallida* Aiton leaves used for the development of heterogeneous catalyst system in this study contains a reasonable ash content of 30.33% which was used for kaolin/ash catalyst impregnation. The use of kaolin/ash catalyst from the leaves is better than that of the root and the stem for biodiesel production and glycerol was found suitable in this research work and the biodiesel produced was within the limit set by ASTM D6751.

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