

Biodiesel Production from Mustard Oil, Coal Ash Using as Catalyst

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Abstract: In this study, mustard oil was used to synthesize Bio-Diesel. The transesterification was performed in the presence of coal ash as catalyst. The coal ash was characterized using SEM, XRD, Surface area and EDX analyses. The result showed that the catalyst mostly contain Al and Si and some traces of Na, Ca, Ti, Fe, Cu and Zn. The XRD study categorized the catalyst as amorphous silica. The transesterification was performed for different time duration i.e. 1h, 2h and 3h. The effect of ratio of ethanol to oil on transesterification was also studied. Mixtures 30ml and Oil 70 ml was transesterified. The transesterified products were characterized using physicochemical and instrumental methods. The result showed that mustard oil can be transesterified to get Bio-Diesel. The optimum ratio and time for the reaction were ethanol 50ml and Oil 70ml for 3h with coal ash as catalyst. The FTIR and UV analyses of transesterified oil showed that the coal ash has catalyzed the reaction.

Key words: Biodiesel • Catalyst • Coal Ash • Mustard Oil and Ethanol

INTRODUCTION

World energy sector depends on the petroleum, coal and natural gas reservoirs to fulfill the energy requirements. The demand for energy is rising day by day [1, 2]. This extensive and vigorous use of fossil fuel leads to the diminishing of fossil fuel resources and as a result it made a great impact on local and international prices of petroleum and its products [3, 4]. The use of petroleum in the vehicle and industries has great detrimental effect on the environment [4]. The burning of fossil fuel releases many harmful and toxic gases like CO, CO₂, SO_x and NO_x, along with unburned hydrocarbon and particulate matters which are carcinogenic in nature [5, 6]. Now considering all these factors and to reduce dependence on the use of fossil fuel [4], scientists are working to develop an alternative renewable energy sources which are easily available, cheap, less toxic and eco-friendly. One of such alternative source is biodiesel [2, 7, 8].

In production of biodiesel transesterification is an important step. This is a slow step and various attempts

have been made to speed up the reaction. In the transesterification of rapeseed oil with Methanol CaO/MgO was used as catalyst [9] but it contaminates very easily with the gases like CO₂, O₂ and H₂O in air. So, thermal treatment was required to activate the catalyst before reaction. In the transesterification of cottonseed oil with methanol KF/ ~ -Al₂O₃ was used as heterogeneous catalysts [10]. However the basic sites of medium strength require higher temperature to promote the reaction. Soybean oil has also been used for the production of biodiesel in presence of various types of catalysts. For example, transesterification of soybean oil to biodiesel with methanol and ethanol using calcium ethoxide as a catalyst, a 91.8 % biodiesel yield was obtained [11]. Transesterification of soybean oil with methanol Zn/1₂ was found to be a practical and effective catalyst for the conversion of soybean oil to biodiesel with ethanol [12]. Transesterification of soybean oil with methanol can also be carried out in presence of MgO and calcined hydrotalcites as catalysts. In the Transesterification of soybean oil with methanol at 60, 120 and 150°C in the

presence of a series NaX faujasite Zeolite, ETS-10 Zeolite and metal used as catalysts [13]. However the same problem reported for cottonseed oil i.e. the basic sites of medium strength require higher temperature to promote the same reaction, persists. Ultimately, all the tested catalysts are resistant to the presence of moisture in the reaction environment [14]. Subcritical and supercritical concentration of the solvent plays a key role in the production of biodiesel. Transesterification of rapeseed oil was made in subcritical and supercritical methanol under different reaction conditions of temperatures and reaction times without using any catalyst has been performed. However in presence of catalyst, the conversion rate of rapeseed oil to its methyl esters was found to increase dramatically [15]. In the transesterification of sunflower oil in supercritical methanol and supercritical ethanol at various temperatures (200-400°C) and 200 bar pressure nearly complete conversions were obtained for the thermal reaction in supercritical methanol and ethanol [16].

The temperature, stirring speed, the use of co-solvent, the oil to methanol ratio and the amount of catalyst, are the important parameters in the production of biodiesel [17]. In this study biodiesel was produced from mustard oil and ethanol in presence of coal ash as catalyst. To get maximum yield, the process was carried out at different temperature. To determine the subcritical and supercritical concentration of the ethanol, the ethanol to oil ratio was varied.

MATERIALS AND METHODS

The original mustard oil was obtained from a local store. Ethanol was obtained from Merck Chemical Company. The chemical used need no further purification. Coal obtained from Abbottabad was ashed according to ASTM method D3174.

Analysis of the Catalyst: Coal ash was analyzed by Siefert 3003PTS Diffractometer using Cu K α radiation (0.15406 nm). Scanning Electron Microscope (SEM) of a coal ash was performed on machine from Jeol Company Japan (model 5910). Energy-dispersive X-ray spectroscopy (EDX) study was performed on instrument from Oxford Company England (model Inca 200). Surface Area and pore size were determined using NOVA 2200e, Quanta Chrome USA.

Instrumental Analysis: FTIR spectra of the samples were collected on a Bruker (Tensor 27) instrument

using KBr pellet technique in the range of 4000-400 cm⁻¹ (5 mg sample with 100 mg KBr) under the atmospheric condition. Samples were also characterized by UV spectrophotometer 160A Shimadzu, Japan.

Transesterification: Three samples of mustard oil and ethanol of different ratio were prepared. The 1st mixture contains 30ml oil and 70 ml ethanol, the 2nd one has 50 ml oil and 50 ml ethanol and 3rd mixture contain 70 ml oil and 30 ml ethanol. Samples were taken in 250 ml flask of three necks, heated at 100°C for 1, 2 and 3 hours. The resulting product was separated into two layers by centrifugation. The upper layer was of solvent and biodiesel, while the lower layer was of unconverted oil and glycerin. The upper layer was then decanted to another container. This decanted blend was transferred to a rotary evaporator to remove the solvent (ethanol) at 70°C. The biodiesel was collected and stored for further analysis. The same procedure was followed to study the effect of time and catalyst concentration on transesterification.

RESULTS AND DISCUSSION

Characterization of Catalyst: The various physical parameters of the catalyst are given in table.3. The surface area of catalyst is an important parameter in synthesis of biodiesel. From data in the table it is evident that the catalyst has the required surface area needed for the production of bio-diesel. The surface area, pore volume and diameter of the catalyst are shown graphically in figure1 and 2.

The elemental analysis of the catalyst used is provided in table 2. It can be seen that the catalyst under study contain Al and Si as major elements. Other element like Na, Mg, K, Ca, Ti, Fe, Cu and Zn are also present in trace quantities. The presence of Al and Si in the catalyst in large quantity shows that the catalyst is acidic in nature. The EDX and XRD profile are also provided in Figure 3 and 4. From XRD analysis it is evident that the catalyst is amorphous in nature.

The SEM of the catalyst is also provided in Figure 5. The SEM of catalyst shows that there are several fractures in the catalyst in the form of drills, pores, cavities and kernels which indicate the porosity of the catalyst.

UV Spectroscopic Analysis of Bio-Diesel: In the literature, it is explained that bio-diesel show UV absorption in the range of 245-305 nm [18]. The blends of Ethanol/oil were analyzed on the UV spectrophotometer.

Table1: Properties of the coal ash

PROPERTIES	LEVEL
Size (µm)	212
Surface area (m ² /g)	70.16
Pore Volume (cc/g)	1.54
Pore Diameter (Å)	130.53

Table 2: Elemental analysis of the coal ash

Elements	Weight %	Atomic %
Na	0.21	0.19
Mg	0.56	0.48
Al	12.96	9.94
Si	21.45	15.81
K	3.16	1.67
Ca	0.14	0.07
Ti	2.18	0.94
Fe	2.97	1.10
Cu	2.05	0.67
Zn	1.19	0.38
Total	100.00	---

It was found that the blends show absorption in the range of 245-305 nm. The original mustard oil UV spectrum is shown in figure 5. Only one peak comes in the range of bio-diesel i.e. 259 nm. The various peaks shown by mustard oil are listed in Table 3.

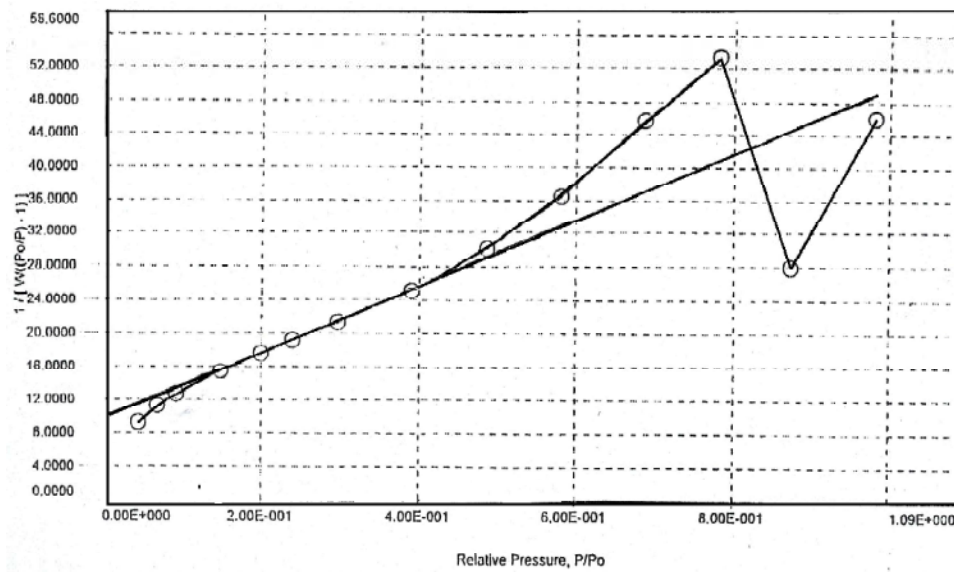


Fig. 1: Nitrogen Adsorption Desorption Curve of Coal Ash (Surface Area)

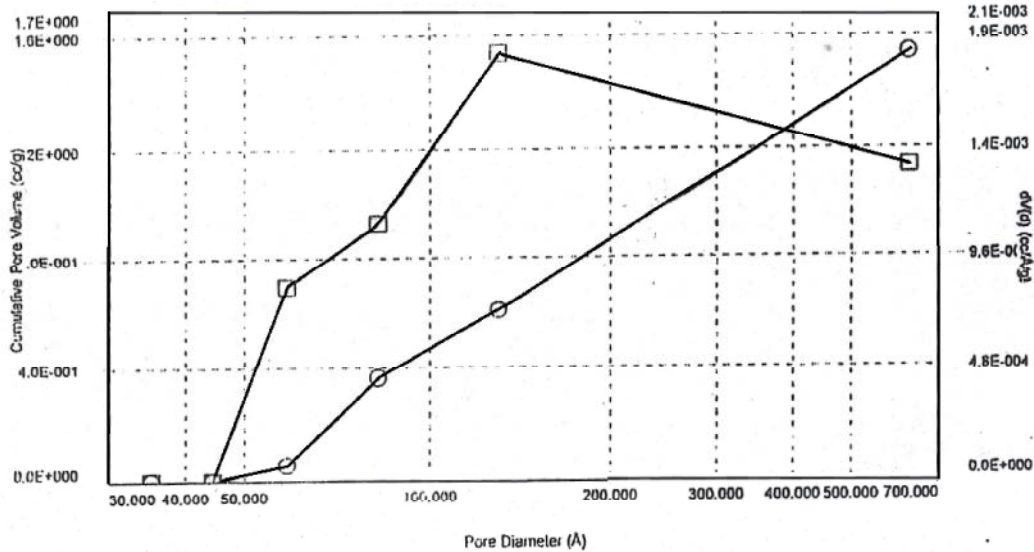


Fig. 2: Nitrogen Adsorption Desorption Curve of Coal Ash (Pore Volume and Pore Diameter)

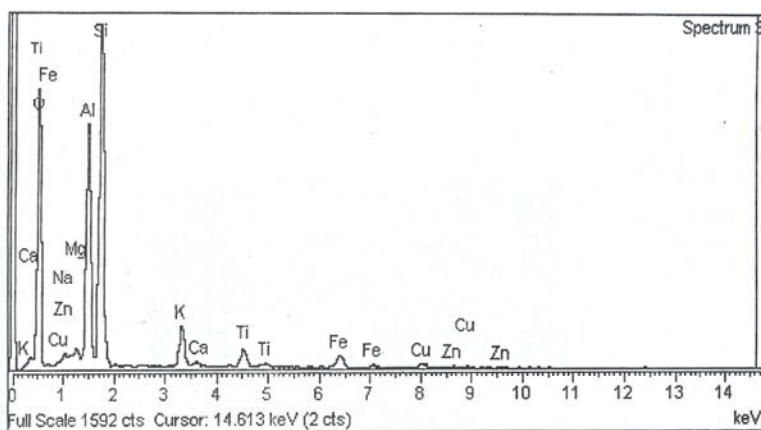


Fig. 3: EDX Profile of Coal Ash.

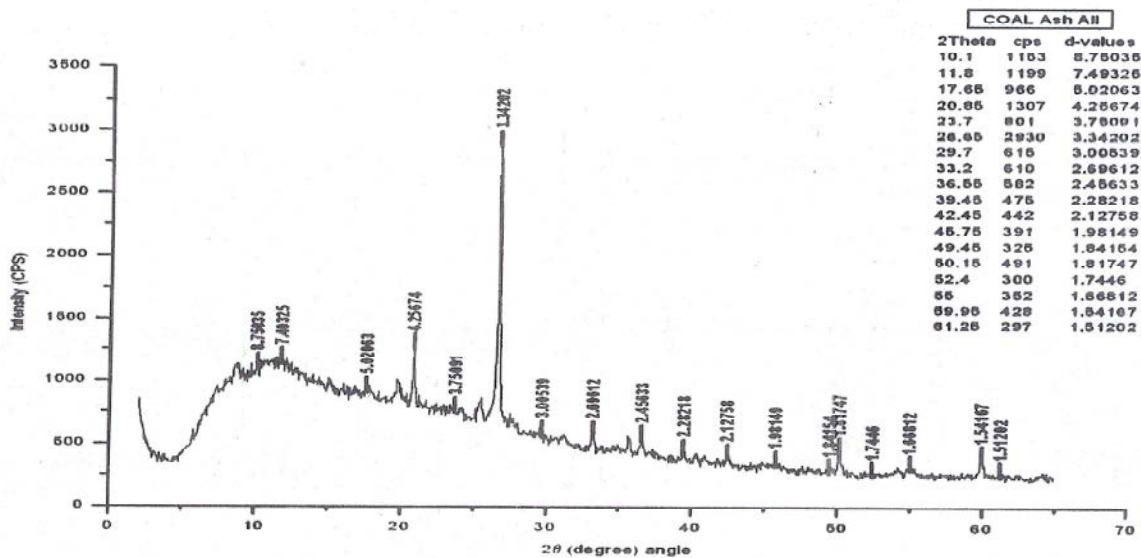


Fig. 4: XRD Profile of Coal Ash.

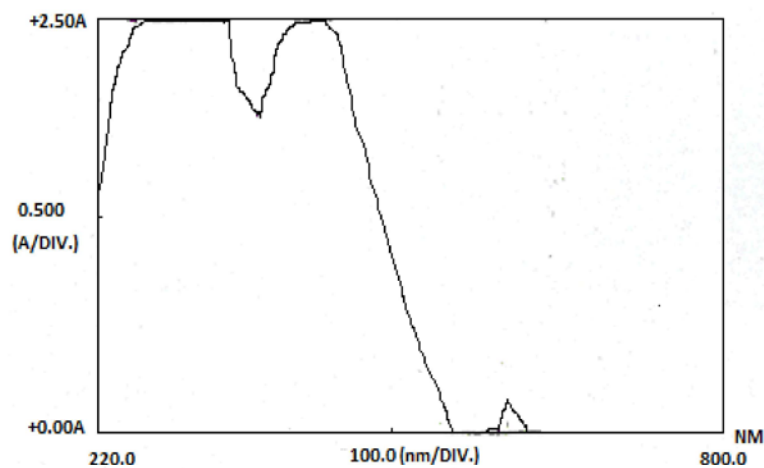


Fig. 5: UV Spectrum of Original Mustard Oil.

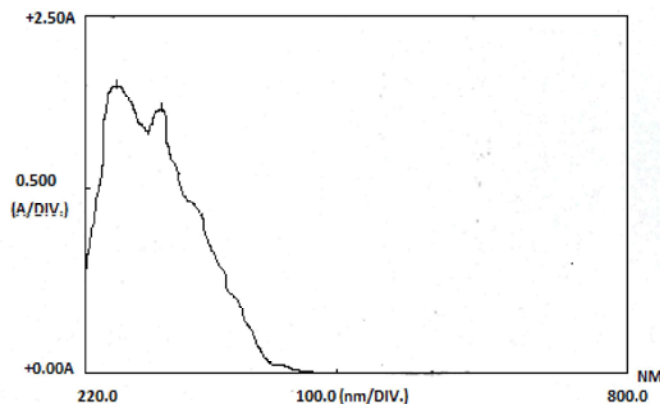


Fig. 6: UV Spectrum of Blend (Ethanol 50 ml and Oil 50 ml +Catalyst +Heated for 2h)

Table 3: UV Spectrum of Original Mustard Oil.

Peaks (λ -nm)									
259	368	492	590	609	631	670	740	764	

Table 4: UV Spectrum of Blend (Ethanol 50 ml and Oil 50 ml +Catalyst +Heated for 2h)

Peaks (λ -nm)					
241	262	270	430	444	595

Table 5: UV Spectrum of Blend (Ethanol 50ml and Oil 50ml +Catalyst + Heated for 3h)

Peaks (λ -nm)							
245	386	421	432	444	464	471	591

Table 6: UV Spectrum of Blend (Ethanol 30 ml and Oil and 70 ml + Catalyst +Heated for 1h)

Peaks (λ -nm)									
244	387	398	405	421	434	443	464	471	595

Table 7: UV Spectrum of Blend (Ethanol 30 ml and Oil 70 ml + Catalyst + Heated for 2h)

Peaks (λ -nm)					
244	258	266	434	443	622

Table 8: UV Spectrum of Blend (Ethanol 30ml and Oil 70 ml + Catalyst +Heated for 3h)

Peaks (λ -nm)					
242	261	269	434	443	625

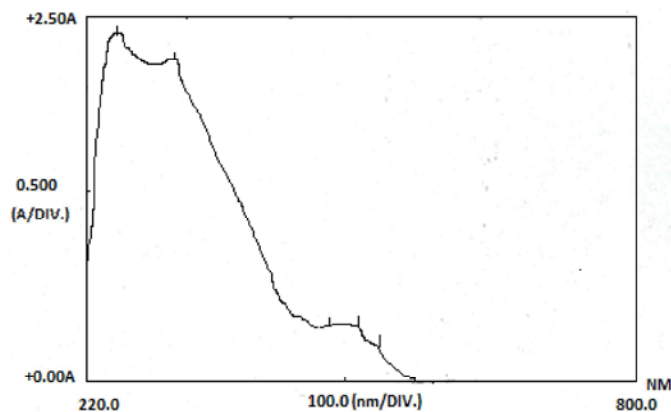


Fig. 7: UV Spectrum of Blend (Ethanol 50ml and Oil 50ml + Catalyst +Heated for 3h)

The sample of ethanol 50ml and oil 50ml in presence of catalyst heated for 2h showed three absorption peaks at 241, 262 and 270 nm. The UV spectrum of the sample is shown in the figure 6 and the characteristic peaks are listed in Table 4.

The sample containing ethanol 50ml and oil 50ml heated for 3h in presence of catalyst when analyzed on UV spectrophotometer showed only one peak in the bio-diesel range 245 nm which is shown in figure 7 and the characteristic UV absorption peaks of the sample are given in Table 5.

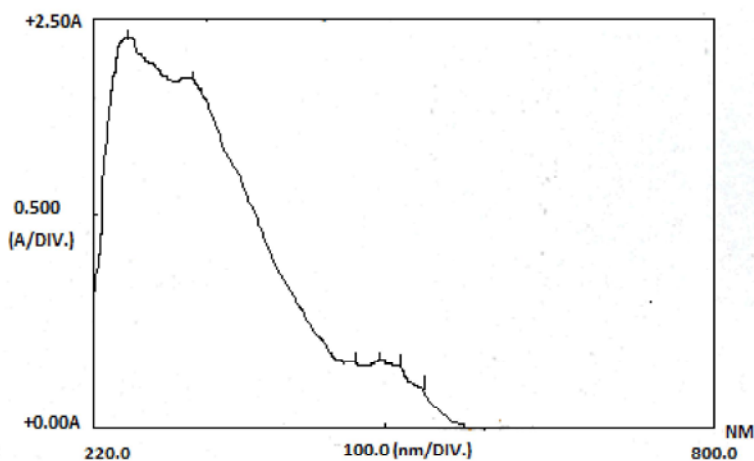


Fig. 8: UV Spectrum of Blend (Ethanol 30ml and Oil 70 ml+ Catalyst+ Heated for 1h)

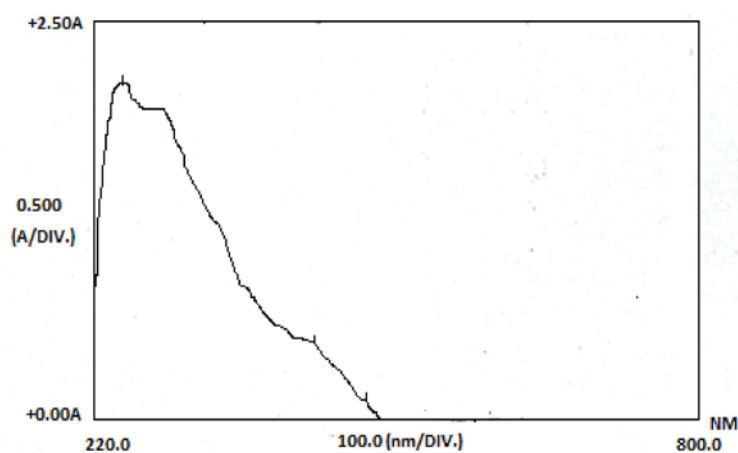


Fig. 9: UV Spectrum of Blend (Ethanol 30 ml and 70 ml +Catalyst + Heated for 2h)

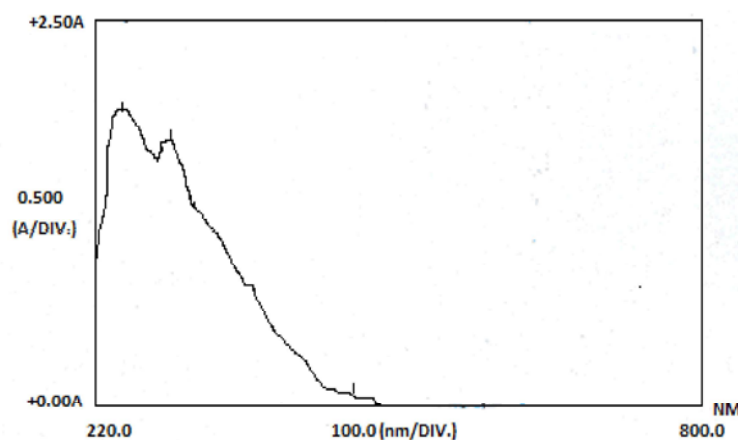


Fig. 10: UV Spectrum of Blend (Ethanol 30ml and Oil 70ml + Catalyst + Heated for 3h)

The blend containing ethanol 30ml and oil 70ml heated for 1h in presence of catalyst after UV analysis showed only one peak 244nm in

the bio-diesel range, shown in figure 8 and various absorption peaks exhibited by the blend are provided in Table 6.

Blend containing ethanol 30ml, oil 70ml and catalyst heated for 2h on analysis by UV spectrophotometer showed three absorption peaks in the range of bio-diesel i.e. 244, 258 and 266nm. The UV spectrum of the sample is shown in the figure 9 and the characteristic peaks are listed in Table 7.

The sample (Ethanol 30ml and oil 70ml + Catalyst + Heated for 3h) when analyzed on the UV spectrophotometer showed three absorption peaks in the bio-diesel range i.e. 242, 261 and 269nm, shown in figure 10 and Table 8.

CONCLUSIONS

In past, the vegetable oil fuels were not acceptable as they were expensive in comparison to petroleum fuels. With recent increases in petroleum prices and uncertainties concerning petroleum availability, there is renewed interest in vegetable oil fuels for diesel engines.

From the experimental results, it can be seen that coal Ash has excellent catalytic abilities as a solid acid catalyst. It has a moderate surface area, a relatively broader particle size distribution and no solubility in ethanol. When it catalyzes the transesterification of mustard oil to biodiesel with ethanol, the optimal condition are 1/1 and 3/7 molar ratio of ethanol to oil, the the addition of 1.0% coal ash as a catalyst 100°C reaction temperature and about 2h and 3h of reaction time.

The result can be made better by using 10g of coal ash as catalyst and using oil and ethanol in large quantity to collect enough Bio-Diesel for analyses.

REFERENCES

1. Meher, L.C., S.D. Vidya and S.N. Naik, 2006. Technical aspects of biodiesel production by transesterification- a review. *Renew Sustain Energy Rev.*, 10: 248-68.
2. Ma, F. and M.A. Hanna, 1999. *Bioresour Technol.*, 70: 1.
3. Clark, S.J., L. Wagner and M.D. Schrock, 1984. *J. Am. Chem. Soc.*, 61: 1632-1638.
4. Komers, K., R. Stloukal, J. Macheck, F., Skopal and A. Komersova, 1998. Biodiesel fuel from rapeseed oil, methanol and KOH. Analytical methods in research and production. *Fett/Lipid.* 100: 507.
5. Crabbe, E., H.C. Nolasco., G. Kobayashi and K. Sonomoto, 2001. *Process Biochem.* 37, p. 65-71.
6. Antolnin and F.V. Tinaut, 2002. *Bioresour Technol.*, 83: 111.
7. Demirbas, A., 2007. Importance of biodiesel as transportation fuel. *Energy Policy.* 35: 4661-4670.
8. Lin, C.Y., H.A. Jin and L.B. Hung, 2006. Fuel structure and properties of biodiesel produced by peroxidation process. *Fuel.*, 85: 1743-1749.
9. <http://www.oilgae.com/energy/sou/ae/re/be/bd/po/mus/mus.html>.
10. Yan, S., L.U. Houfang and L. Bin, 2008. Supported CaO Catalysts Used in the Transesterification of Rapeseed Oil for the purpose of Biodiesel Production. *J. Energy and Fuels* 22: 646-651.
11. Xuejun, L., P. Xianglan., W. Yujun and Z. Shenlin, 2008. Calcium Ethoxide as a Solid Base Catalyst for the Transesterification of Soybean Oil to Biodiesel. *J. Energy and Fuels* 22: 1313-1317.
12. Haitao, L. and X. Wenlei, 2006. Transesterification of soybean oil to biodiesel with Zn/12 catalyst. *J. Catalysis Lett.*, 107: 1-2.
13. Galen, J., Suppes, A. Mohanprasad, Dasari, J. Eric, Daskocil, J. Pratik, Mankidy and J. Michael, Goff, 2004. Transesterification of soybean oil with zeolite and metal catalysts. *J. Elsevier, Applied Catalysis A General*, 257: 213-223.
14. Di Serio, M., M. Ledda, M. Cozzolino, G. Minutillo, R. Tesser and E. Santacesaria, 2006. Transesterification of Soybean Oil to Biodiesel by Using Heterogeneous Basic Catalysts. *Ind. Eng. Chem. Res.*, 45: 3009-3014.
15. Kusdiana, D. and S. Saka, 2001. Kinetics of transesterification in rapeseed oil to biodiesel fuel as treated in supercritical methanol. *J. Elsevier, Fuel*, 80: 693-698.
16. Giridhar, M., K. Chandana and K. Rajnish, 2004. Synthesis of biodiesel in supercritical fluids. *J. Elsevier, Fuel* 83: 2029-2033.
17. Hak-Joo, K., K. Bo-Seung, K. Min-Ju, M.P. Yaung, K. Deog-Keum., L. Jin-Suk. and L. Kwan-Youn, 2004. Transesterification of vegetable oil to biodiesel using heterogeneous base catalyst. *J. Elsevier, Catalysis Today*, 93-95: 315-320.
18. Pasto, D., C. Johnson and M. Miller, 1992. *Experiments and Techniques in Organic Chemistry.* Prentice Hall, New Jersey.