ISSN 2347-4289

Transesterification Of Sunflower Oil Using Mg-Al-Co3 Hydrotalcite As A Catalyst

Priyanka Srivastava, Pratima Jain

Department of Chemistry, S.M.S Govt Science College, Gwalior, India.
Department of Chemistry, Govt. K.R.G College, Gwalior, India.
E.mail: shreemishthi101731@gmail.com

ABSTRACT: An efficient and facile synthesis of fatty acid methyl esters (FAMEs) using sunflower oil and methanol has been carried out in the presence of a solid base Mg-Al-CO3 hydrotalcite heterogeneous catalyst. This protocol promotes the environment friendly conditions as the hydrotalcites are non toxic, recyclable, takes less reaction time and is easy to work up. The hydrotalcite showed high activity for the transesterification reaction. The reaction parameters such as molar ratio of oil to methanol, reaction temperatures, time, catalyst loading ratios were also performed and the optimized conditions which gave maximum yields of 96.5% were at the molar ratio of 12:1 in 3 hours with 2wt % at 70 ^{0}C. The catalyst was recyclable and reused three times.

Keywords: Hydrotalcite, heterogeneous catalyst, fatty acid methyl esters (FAMEs)

1. Introduction

Since past two decades there has been a continuous demand for energy which have promoted researchers for production of altenative fuels which are environmental friendly orignated from renewable sources. Biodiesel is non toxic, biodegradable and one such altenative fuel as it reduces the environmental hazards like acid rain, green house effect, emmissions of CO2, SOx and unburned hydrocarbons[1]. Biodiesel is synthesized using various methods but the most common method among these is transesterification in which a vegetable oil or animal fat is reacted with methanol in the presence of a catalyst(homogeneous or heterogeneous) to produce fatty acid methyl esters and glycerol as a by-product. The use of homogeneous catalytic systems in the transesterification reaction were facing various technological problems like side chain reactions, emulsification, hydrolysis, saponification, and product separation which requires large quantities of water which is wasted and hence increases the cost of production [1],[2]. To reduce or eliminate these limitations and drawbacks of homogeneous catalysts heterogeneous catalytic system were developed and gained attention and importance as it reduced various technical problems especially the the product separation was easier and does not wasted large quantities of water and hence the cost of production was decreased. Many heterogeneous catalysts have been reported in literature which are environmentally friendly and reduces cost of production like Guomin et. al [3] used KF/Al_2O_3 catalyst for the transesterification of palm oil, the FAME yields were over 90% in 3 hrs at 65 ^{0}C. Ilgen et.al[4] used MgO supported KOH system for the transesterification of canola oil with a yield of 95.05% in 9 hrs with a stirring speed of 1000 rpm. Kim et al [5] synthesised a commercial super base catalyst $Na/NaOH/Al_2O_3$ and the FAME yield from soyabean oil was 94% in 2 hrs at 60 ^{0}C at a stirring speed of 300 rpm using n-hexane as a co-solvent. Gabriela M. Tonetto et. al [6] used four different catalyst powder of Me/Al_2O_3 (Me = Na, Ba, Ca, and K) to transesterify soybean oil with methanol with a FAME yield of 98.6% at 120 ^{0}C at 500 rpm in 6 hrs. Additionally layered double hydroxides (LDH) so called hydrotalcite have attracted the attention of researchers as a catalyst in transesterification reactions because of its surface area and basicity can be modified by chemical composition and preparation method. In the present study we have synthesized Mg-Al-CO3 hydrotalcite by hydrothermal method calcined and characterised by XRD and SEM and used in the transesterification of sunflower oil. We have synthesized the biodiesel product in 3 hours reducing the time of production by 1 hour as reported earlier in literature.

2 MATERIALS AND METHOD

2.1 Catalyst Preparation

The hydrotalcite was prepared by one pot hydrothermal reaction[7],[8] which was carried out at higher temperatures and autogenously pressure in aqueous media. Mixed salt solutions having Mg 2+ and Al 3+ in Mg/Al molar ratio of 3:1 were taken. The pH was maintained at 8.5 by adding to it the solutions of Na2CO3. The solution was then transferred to a 300ml pressure reactor vessel at 175^{0}C for 6 hours. The slurry was aged for 12 h, white precipitate was filtered, washed, dried and calcined at 723 K for 4 hours. The catalytic activity with various ratios of hydrotalcite is shown in table 1

Table 1- Catalytic activity of the catalyst

Entry	Ratio of hydrotalcite	Time(h)	Yield(%)
1	Mg–Al–CO3 (2:1)	3	87
2	Mg–Al–CO3 (3:1)	3	96.5
3	Mg–Al-CO3 (4:1)	3	93

Reaction conditions: molar ratio of methanol to oil 12:1, catalyst loading ratio 2 wt% at 70 ^{0}C.

2.2 Catalyst Characterization

The catalyst was characterized by XRD with Rigaku's D-300 X-Ray diffractometer using Cu-Kα radiation with a graphite diffracted beam monochromator (λ= 1.5418 A0). Measurement conditions was: 2θ range =2-700,

ISSN 2347-4289

scan speed: 20 per minute, step size=0.02, generator rating 40 kV,100 mA. The surface morphology of the catalyst was monitored using SEM Joel JSM 5600. The basicity of the catalyst was determined by hammett indicators[2]. The basicity of the catalyst was found to be H_>11.

2.3 Transesterification Reaction

The transesterification reaction was carried out in a 500 ml three neck round bottom flask. Initially it was charged with the calculated amount of methanol and catalyst which were stirred for about 10 minutes after that the sunflower oil was added to it and was equipped with a refluxing condenser and temperature controlled magnetic stirrer. The temperature was raised to 70 0C. The reaction was carried out for 3 hours under constant stirring. After the reaction was completed the product was kept to cool and was transferred to the separating funnel for 24 hours. After 24 hours two different layers were seen the lower one being glycerol and the above one being the biodiesel. Both the layers were separated and purified separately.

3 RESULTS AND DISCUSSIONS

3.1 XRD –

Metallic ratio of Mg/Al was measured and found to be 3.16 which is in good agreement with metallic ratio taken in solution i.e 3. The value of x [$x = M^{III}/M^{II} + M^{III}$] was found to be 0.24, suggesting purity of hydrotalcite [9]. The PXRD patterns for hydrotalcite Mg–Al–CO3 shows a c/3 value 7.76A˚ indicating gallery height of 2.96 ˚A suggesting the material to be reasonably crystalline and relatively in well order sheet arrangement[10]. The patterns of XRD showed peaks corresponding to hydrotalcite having layered structure as it depicted sharp and symmetric peaks at 11.3 and 23 corresponding to (003) and (006) reflections. On calcination of the hydrotalcite they are transformed to mixed oxides with MgO like structure showing the characteristic peaks at 43 and 63 as shown in fig 1(a) and (b). The calcined mixed oxides acts as a basic catalysts for the reaction which itself is made by thermal decomposition of Mg-Al layered double hydroxide. Many researchers agrees to this view [1],[2].

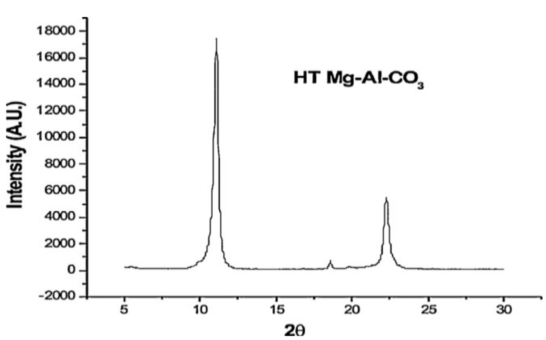
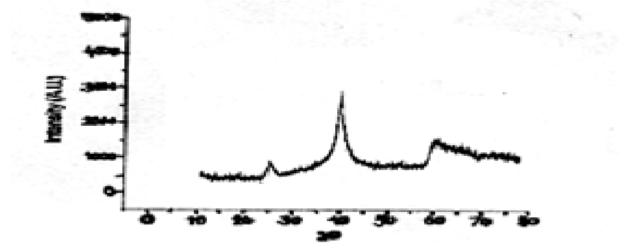


***Fig. 1 (a)** Uncalcined Mg-Al-CO3 HT*



(b) Calcined Mg-Al-CO3 HT

3.2 SEM –

Typical SEM images of Mg–Al–CO3 hydrotalcite indicates the existence of lamellar particles which are in rounded hexagonal shape and typical of hydrotalcites like material as shown in fig 2.

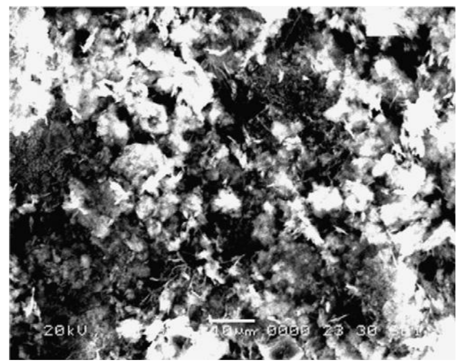


Fig. 2 Mg-Al-CO3 HT

3.3 Biodiesel Analysis –

The various physio-chemical properties of biodiesel made from sunflower oil were characterized according to the ASTM standards and is shown in table 2. The FAMEs obtained as a result and characterized by GC consists of methyl palmitate 8.43%, methyl stearate-0.75%, methyl oleate-30.19%, methyl linolenate-58.58%.

Table 2 - Physio-chemical properties of Biodiesel.

Sl.No	Properties	BP[a]	Standards*
1	Density at 20^{0}C(gm/cm3)	0.876	0.86-0.90
2	Viscosity aat 40 ^{0}C (cSt)	4.8	1.9-6
3	Flash point (^{0}C)	156	93mins minimum
4	Cloud point (^{0}C)	-6	Report
5	Pour point (^{0}C)	-12	Report
6	Copper strip corrosion	No.1a	No.3 max

[a]Biodiesel Product
**Standards as per ASTM Test Methods*

ISSN 2347-4289

4. OPTIMIZATION PARAMETERS OF THE-REACTION

4.1 Effect of Temperature –

The temperature effect on FAME conversion was studied with the catalyst at five different temperatures 50, 60, 70, 80, 90 ^{0}C. The best results were obtained at 70 ^{0}C as shown in fig 3.

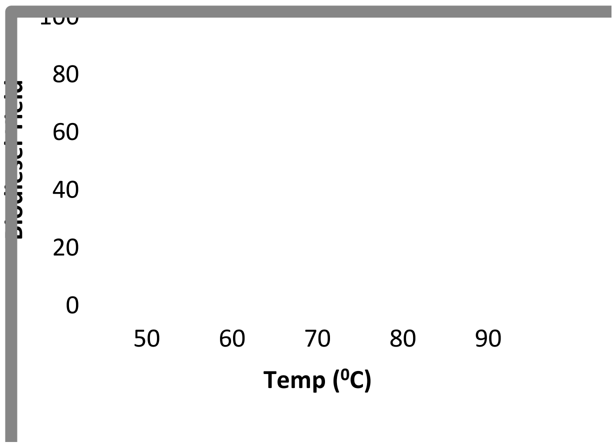


Fig. 3 *Effect of temperature on Biodiesel Yield*

Reaction conditions: molar ratio of methanol to oil 12:1, catalyst loading ratio 2 wt% in 3 hrs reaction time.

4.2 Effect of Time –

The effect of time was also studied. The studies were carried out using 1-6 hours. From the fig. 4 it is seen that the 4-5 hours is needed for the synthesis of biodiesel using hydrotalcite as a catalyst. The best yields were obtained at 3 hours.

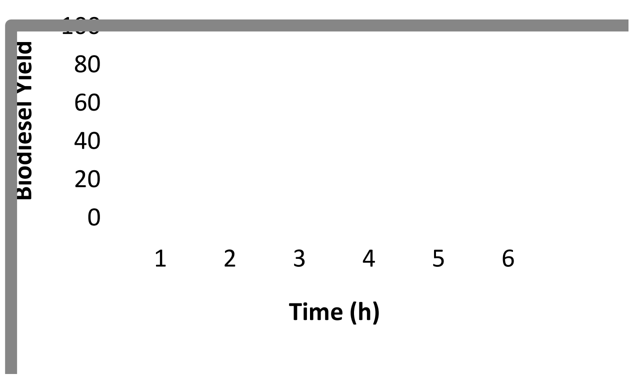


Fig. 4 *Effect of Time on Biodiesel Yield*

Reaction conditions: molar ratio of methanol to oil 12:1, catalyst loading ratio 2 wt% at 70 ^{0}C.

4.3Effect of Molar Ratio –

The effect of molar ratio of methanol to oil was studied. Various ratios like 3:1, 6:1, 9:1, 12:1, 15:1 were studied. The optimum molar ratio of methanol to sunflower oil was found to be 12:1. As the molar ratio increased the yield of biodiesel was also increased on further increasing the molar ratio from 12:1 no further significant increase in the yield was seenas shown in Fig. 5.

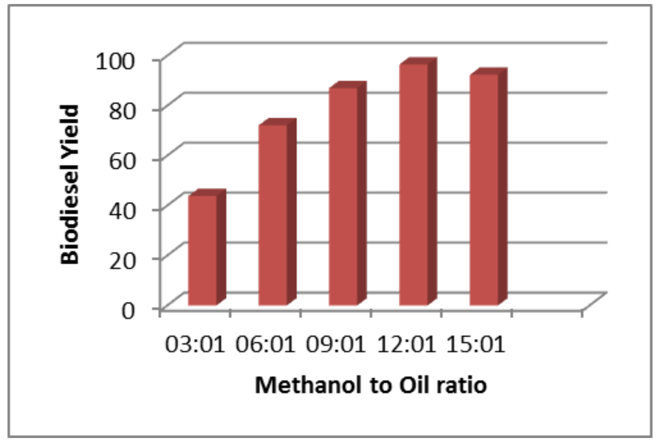


Fig. 5 *Effect of molar ratio on Biodiesel yield*

Reaction conditions: catalyst loading ratio 2 wt% at 70 ^{0}C in 3 hrs reaction time.

4.4Effect of catalyst loading % in the transesterification reaction –

The effect of catalyst loading wt% in the reaction was also studied and is shown in Fig. 6. The reactions were carried out using various loadings from 1-5 wt%. the optimum results were found to be 2 wt%. On further increasing the catalyst loading from 5 wt% the yield of biodiesel were decreased probably because of the mixing problems of the reactants catalyst and the products.

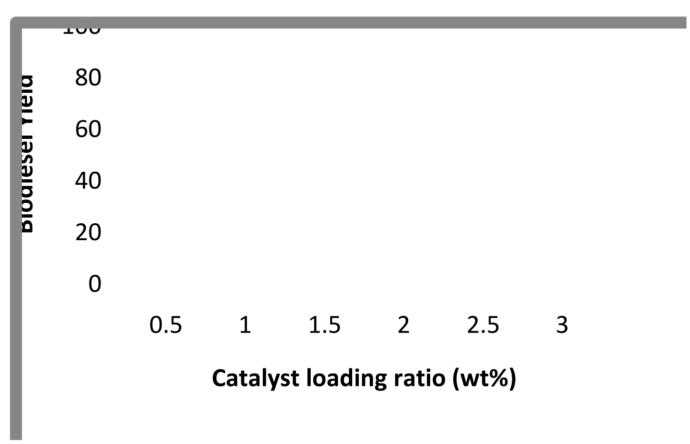


Fig. 6 *Effect of Catalyst loading ratio on Biodiesel yield*

Reaction conditions: molar ratio of methanol to oil 12:1, in 3 hrs at 70 ^{0}C.

4.5Recyclability of the catalyst –

The catalyst was recycled and reused three times as it was easily recovered as shown in Fig. 7.

ISSN 2347-4289

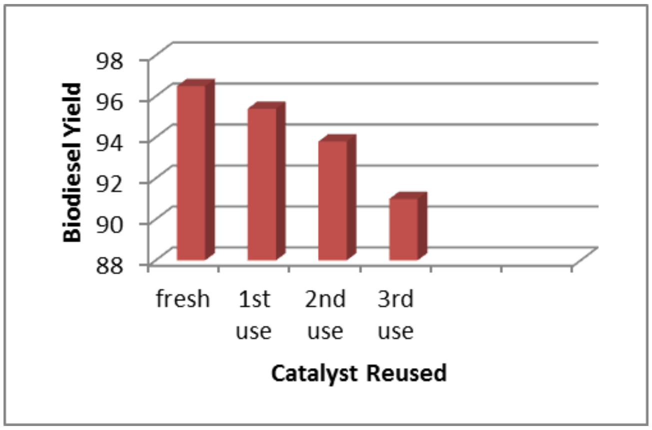


Fig. 7 *Recyclability of the catalyst*

5. CONCLUSION

The calcined Mg-Al-CO3 hydrotalcite was found to be an effective solid base heterogeneous catalyst in the transesterification of sunflower oil with methanol. The best catalytic activity of the catalyst was found to be with molar ratio of Mg/Al 3:1. The highest conversions of fatty acid methyl esters were obtained at molar ratio of methanol to oil 12:1, catalyst loading of 2 wt% in 3 hours reaction time at 70 ^{0}C. The catalyst is inexpensive, non-toxic, and recyclable, has high catalytic activity and is environmental and economically friendly and hence can be used as an effective catalyst for biodiesel synthesis commercially.

6. ACKNOWLEDGMENT

The Authors express thanks to Prof. D.D.Agarwal, S.O.S in Chemistry, Jiwaji university, Gwalior (M.P) and Dr. Savita Gupta Ind Swift.Ltd. and IUC-Indore for carrying out the spectral analysis.

6. REFERENCES

[1] H.Y.Zeng, Z.Feng, X.Deng, Y.Q.Li, “Activation of Mg-Al hydrotalcite catalysts for transesterification of rape oil,” Fuel vol. 87, pp 3071-3076, Apr 2008.

[2] Brito, E. Borges, M. Garin and A. Hernandez, “Biodiesel production from waste oil using mg-Al layered double hydroxide catalysts,” Energy and Fuels, Vol. 23, pp 2952-2958, Apr. 2009.

[3] X.Bo, X.Guomin, C.Lingfeng, W.Ruiping, and G.Lijing, “Transesterification of Palm Oil with Methanol to Biodiesel over a KF/Al2O3 Heterogeneous Base Catalyst,”Energy & Fuels, Vol. 21, pp 3109–3112, Nov 2007

[4] O.Ilgen and A.N.Akin, “Transesterification of Canola Oil to biodiesel using MgO loaded with KOH as a heterogeneous catalyst,”Energy & Fuels, No. 23, pp 1786–1789, April 2009.

[5] H.J Kim, B.S Kang, M.J Kim, Y.M Park, D.K Kim, J.S Lee, “Transesterification of vegetable oil to biodiesel using heterogeneous base catalyst,” Catal Today, Vol. 93-95, pp 315–320, July 2004.

[6] G.M.Tonetto,J.M.Marchetti,“Transesterification of Soybean Oil Over Me/Al2O3 (Me = Na, Ba, Ca, and K) Catalysts and Monolith K/Al2O3-Cordierite,”Top Catal, Vol. 53, pp. 755–762, March 2010.

[7] J.Lal, M.Sharma, S.Gupta, P.Parashar, P.Sahu, D.D.Agarwal, “Hydrotalcite: A novel and reusable solid catalyst for one-pot synthesis of 3,4-dihydropyrimidinones and mechanistic study under solvent free conditions,” Journal of Molecular Catalysis A: Chemical, vol. 352, pp 31–37, 2012.

[8] S.Gupta,P.hD thesis, S.O.S in Chemistry, Jiwaji University, 2007.

[9] F. Cavani, F. Trifiro, A. Vaccari, “Hydrotalcite-type anionic clays: Preparation, properties and applications,” Catal. Today, Vol. 11, pp 173–201, Dec 1991.

[10] F.M. Labojos, V. Rives, M.A. Ulibarri, “Effect of hydrothermal and thermal treatments on the physicochemical properties of Mg-Al hydrotalcite-like materials,” J. Mater. Sci, Vol. 27, pp 1546–1552, March 1992.