Ultrasonication Assisted Production of Biodiesel from Sunflower Oil by Using CuO: Mg Heterogeneous Nanocatalyst

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Abstract: Biodiesel is a clean, renewable, biodegradable, eco-friendly and alternative fuel used in the diesel engine. The present work was carried out at constant operational conditions such as methanol to oil molar ratio 6:1, catalyst concentration 0.25%, 30 minute reaction time and the reaction temperature at 60°C. Biodiesel was synthesized by transesterification of sunflower oil (SFO) with methanol, using CuO: Mg nanocatalyst. This nanocatalyst was prepared by quick precipitation method. The biodiesel yield of 71.78% was achieved under reaction condition. The presence of methyl ester groups at the produced biodiesel was confirmed using the Gas Chromatography-Mass Spectrometry (GC-MS). The FAME conversion yield up to 82.83 % could be obtained under the operating conditions.

Keywords: Transesterification, biodiesel, CuO: Mg nanocatalyst.

1. INTRODUCTION

The need for a renewable fuel source grows due to the ever-increasing demand for energy and depletion of fossil fuels. There are many options in this area, but unlike other energy sources, biofuels such as biodiesel have the capability of providing a fuel source perfectly suited to existing diesel engines[1]. Biodiesel is a clean, renewable, biodegradable, nontoxic produced from various oil feed stocks, including edible and non-edible vegetable oils, animal fats, microalgae and even from restaurant waste oils[2-4].

The most common way to produce biodiesel is the transesterification method, which refers to a catalyzed chemical reaction involving vegetable oil and alcohol to yield fatty acid alkyl esters (biodiesel) and glycerol. A catalyst is usually used to improve the reaction rate and the yield[5]. Recent research demonstrated that the use of different nanomaterials as a catalyst can be considered as an efficient way for the production of biodiesel[6, 7]. The catalysts after the reaction maintain their physical and chemical properties, and it can be reused without any loss in activity with the maximum yield[8].

Recent studies were focused more on ultrasonic-assisted method as it is one of the simplest methods and capable way to reduce reaction time compared to the conventional stirred procedure for the production of biodiesel[9]. Most researchers believe that the effect of ultrasonication on enhancing transesterification lies mainly in intensifying the mixing of the immiscible methanol and triglyceride phases[10-12]. It was demonstrated that ultrasonication also enhances heterogeneous catalyst activities in transesterification of plant oils[13].
In this study, the ultrasonic-assisted catalytic transesterification using CuO: Mg nano catalyst was studied for sunflower oil. GC/MS analysis was studied accurately to identify and confirm the presence of fatty acid methyl esters.

2. MATERIALS AND METHODS

2.1. Materials

Methanol, Copper Acetate \([\text{Cu (CH}_3\text{COO)}_2]\), Magnesium chloride \((\text{MgCl}_2)\), PVP and Sodium hydroxide \((\text{NaOH})\), were purchased from Merck Specialties Private Ltd, India. The Sunflower oil samples were purchased from local market of Trichy.

2.2. Preparation of CuO: Mg Nanocatalyst

In this quick precipitation method, two separate solutions, aqueous Copper acetate \((5\text{M})\) and aqueous NaOH were used separately. About 1 wt. % of PVP is added to copper acetate solution and the NaOH solution is added drop by drop and the stirring continued until the formation of a suspension. In order to dope, the dopant solution \((\text{MgCl}_2)\) was added to the same precursor solution at 5wt % concentration. After the completion of reaction, a large amount of black precipitate was formed which were collected by centrifugation dried in an oven for 3 hours.

The studies such as XRD, UV-Vis spectroscopy, FE-SEM and EDX analysis which were confirming the formation of CuO: Mg nano particles. (The characterization studies are not included in this paper since which has already published).

2.3. Biodiesel Production by Ultrasonication Method

For ultrasonic-assisted transesterification procedure, the 60 ml of sunflower oil was added to the premixed solution of methanol and catalysts (CuO: Mg). The mixture was then subjected to the ultra-sonication under a matrix of conditions: methanol to oil molar ratio of 6:1; catalyst concentrations in 0.25 wt. % of oil; at a time (30 min) with constant reaction temperature.

The product formed was then allowed to settle overnight to enhance separation in a separating funnel. The remaining water and unreacted methanol in the methyl esters were removed by heating at 110°C until the bubbles disappeared. The biodiesel was then collected and stored in an air-tight bottle at room temperature.
3. BIOFUEL CHARACTERIZATION

3.1. Visual Analysis

Fig.1 displays the color of synthesized SFO biodiesel by using CuO: Mg nano catalyst.

![Fig.1 Biodiesel from SFO](image)

3.2. GC-MS Analysis

The synthesized biofuel products were examined by gas chromatography to determine the composition of fatty acid methyl esters (Fig.2). Each peak corresponds to a fatty acid methyl ester component of SFO and was identified using the library match software. The identities of the FAME were verified by comparing the respective retention time data with mass spectroscopic analysis.

![Fig.2 Fatty acid composition of SFO](image)
The chemical composition of GC-MS result for SFO pure oil and biodiesel is briefly given in the table 1 & 2 respectively. The fatty acid profiles showed that the major compound present in the SFO is 9, 12-Octadecadienoic acid. The FAME is mainly of 9-Octadecenoic acid, methyl ester. The maximum FAME conversion calculated is 82.83 % in the ultrasonicator based method.

**Table 1**

**Fatty acid profile of SFO**

| Compound name                       | FFA (%) |
|-------------------------------------|---------|
| 7-Azanorbornene                     | 7.07    |
| 2-Pentenenitrile                    | 18.89   |
| 9,12-Octadecadienoic acid (Z,Z)-    | 74.04   |
| Total                               | 100.00  |
Table 2

FAME composition of SFO biodiesel

| Properties                        | % of total |
|-----------------------------------|------------|
| Most abundant FAME               | 54.29      |
| 9-Octadecenoic acid, methyl ester|            |
| Other FAME components (total)    | 28.54      |
| Total FAME conversion            | 82.83      |
| Others                           | 17.17      |

3.3. Biodiesel Yield (%)

The volume of biodiesel product was first measured and the volume yield percentage was calculated according to the following:

\[
Volume \ yield = \left( \frac{volume \ of \ the \ product}{volume \ of \ the \ oil} \right) \times 100
\]

The total yield from the biodiesel was finally calculated according to the formula:[14]

\[
Biodiesel \ yield \% = \text{FAMEs} \% \ from \ GC \ analysis \times Volume \ yield
\]

The yield of 71.78 % is obtained under the operating conditions.

4. CONCLUSION

The production of biofuel from sunflower oil with methanol was successfully synthesized using CuO: Mg nanoparticle as a heterogeneous catalyst by ultrasonication methods. This nanocatalyst was prepared by quick precipitation method. The biodiesel yield of 71.78% was achieved under reaction condition. The presence of FAME groups in the produced biofuel was confirmed using the GC-MS analysis. The FAME conversion yield up to 82.83 % could be obtained under reaction conditions. Hence the biodiesel, synthesized from the above given studies can be considered as a better source of energy and fuel over the conventional diesel.
REFERENCES

[1] El-Sheltawy S, El-Diwani G, Attia N, El-Shimi H. Reactive Extraction of Microalgae for Biodiesel Production; an Optimization Study. Journal of Solid Waste Technology & Management 2015;41.

[2] Alptekin E, Canakci M, Sanli H. Biodiesel production from vegetable oil and waste animal fats in a pilot plant. Waste Management 2014;34:2146-54.

[3] Banković-Ilić IB, Stojković JJ, Stamenković OS, Veljkovic VB, Hung Y-T. Waste animal fats as feedstocks for biodiesel production. Renewable and Sustainable Energy Reviews 2014;32:238-54.

[4] Abdullah NH, Hasan SH, Yusoff NRM. Biodiesel production based on waste cooking oil (WCO). International Journal of Materials Science and Engineering 2013;1:94-9.

[5] Bournay L, Casanave D, Delfort B, Hilion G, Chodorge J. New heterogeneous process for biodiesel production: A way to improve the quality and the value of the crude glycerin produced by biodiesel plants. Catalysis Today 2005;106:190-2.

[6] Hussain ST, Ali SA, Bano A, Mahmood T. Use of nanotechnology for the production of biofuels from butchery waste. International Journal of Physical Sciences 2011;6:7271-9.

[7] Qiu F, Li Y, Yang D, Li X, Sun P. Heterogeneous solid base nanocatalyst: Preparation, characterization and application in biodiesel production. Bioresource Technology 2011;102:4150-6.

[8] De S, Luque R. Nanomaterials for the Production of Biofuels. Nanomaterials for Sustainable Energy: Springer; 2016. p. 559-82.

[9] Chen G, Shan R, Shi J, Yan B. Ultrasonic-assisted production of biodiesel from transesterification of palm oil over ostrich eggshell-derived CaO catalysts. Bioresource Technology 2014;171:428-32.

[10] Attia N, Gadalla A, Ibiari N, El-Araby R, El-Diwani G. Studying the ultrasonic assisted transesterification of castor oil by using factorial design for optimization of biodiesel production. Afinidad 2014;71.

[11] Fayyazi E, Ghobadian B, Najafi G, Hosseinzadeh B, Mamat R, Hosseinzadeh J. An ultrasound-assisted system for the optimization of biodiesel production from chicken fat oil using a genetic algorithm and response surface methodology. Ultrasonics Sonochemistry 2015;26:312-20.

[12] He B, Van Gerpen JH. Application of ultrasonication in transesterification processes for biodiesel production. Biofuels 2012;3:479-88.

[13] Wen L, Wang Y, Lu D, Hu S, Han H. Preparation of KF/CaO nanocatalyst and its application in biodiesel production from Chinese tallow seed oil. Fuel 2010;89:2267-71.

[14] Elkady M, Zaataout A, Balbaa O. Production of Biodiesel from Waste Vegetable Oil via KM Micromixer. Journal of Chemistry 2015;2015.