PRODUCTION AND CHARACTERIZATIONS OF BIODIESEL USING CaO AS CATALYST FROM SHELL WASTE

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ABSTRACT

The increasing global demand for sustainable materials and the growing awareness of waste management challenges have fuelled the development of innovative strategies for recycling and valorising by-products from various industries. In an era where sustainability and waste reduction are paramount, the conversion of agricultural and marine waste into valuable products has become a focal point in both scientific research and industrial development. Among the many waste streams, crab shells and chicken egg shells are two commonly discarded materials that offer significant potential for upcycling into valuable products. The present study was carried out to prepare CaO nanoparticles from the shells through calcination and synthesize biodiesel from palmolein oil with CaO as a heterogenous catalyst. The synthesized biodiesel was characterized by GC-MS analysis which revealed the presence of eight fatty acid methyl ester (FAME) compounds.

KEY WORDS: crab shell, egg shell, nanoparticle, heterogenous catalyst

INTRODUCTION

Crab shells, primarily composed of chitin and its derivative, chitosan, are a rich source of bioactive compounds that hold tremendous potential in various fields, including medicine, agriculture, and environmental engineering. Chitin, a biopolymer found in the exoskeletons of arthropods, can be converted into chitosan, which has wide-ranging applications**.** Greater consumption and utilization of chicken eggs worldwide, prompts an expanded amount of disposed egg waste, mainly eggshell and eggshell membrane. The massive generation of waste products, poses a significant environmental challenge, impacting ecosystems and potentially human health through pollution and resource depletion [1]. The by-product eggshell weighs approximately 10% of the total mass (*ca.* 60 g) of hen egg.

In recent industrial development, there is gradual increase in the demands for energy and fossil /bio-fuels [2]. Biodiesel is a sustainable, non-toxic, and environmental friendly, a renewable alternative source to petroleum. Biodiesel is composed of monoalkyl esters of fatty acids and it has similar physical properties to petroleum diesel but unique advantages including being renewable, biodegradable, non-toxic and low emissions. Biodiesel is generally produced by transesterification of vegetable oils or animal fats with short-chain alcohols (generally methanol) in the presence of catalysts [3]. CaO was utilized as catalyzed for transesterification, as it is one of the catalysts that shows promise activity[4].

Calcium oxide (CaO) itself, as cheap, highly active and easily available, is one of the most used solid catalysts for transesterification reaction of different oils and fats to biodiesel. A way to improve its catalytic activity is to increase its specific surface by preparing it in the nano–form[5]. Calcium carbonate ($CaCO_3$) is one of the prime constituents of the crab shell, and its amount varies from 40 to 70% according to the species [6]. $CaCO_3$ in the crab shell can be calcinated at higher temperatures (above 800 °C) to prepare CaO, a heterogeneous base catalyst, which can be used for biodiesel production [7]. So the present study has been carried out to synthesize biodiesel from palmolein oil with CaO as a heterogenous catalyst and the synthesized biodiesel was characterized by GC-MS analysis

MATERIALS AND METHODS

Collection and preparation of crab and egg shells:

The collected crab and egg shells were rinsed with water to remove dust and impurities. The cleaned shells were dried and crushed using mortar and pestle. The powder was stored in an air tight container for further use.

Preparation of Calcium Oxide from molluscan shells:

The shell powder was placed in a muffle furnace (Labman Scientific instruments) and heated to 900 ^{o} C for two hours to convert the $CaCO_3$ in the shells to CaO. The calcined samples were stored in a closed vessel and kept in a desiccator to prevent reactions with carbon dioxide (CO_2) and humidity in the air.

Transesterification of palmolein oil:

Biodiesel synthesis from palmolein oil and methanol was conducted in the presence of CaO nanoparticles which acts the catalyst in the transesterification reaction. The methanol and oil ratio was 5:1. A known volume, 200ml of cooking oil was taken in a conical flask. It is warmed up to 60^{o} C in a water bath and maintained.

50ml of methanol is taken in another conical flask to which 4g of CaO nanoparticles are added to from methoxide solution. It is an exothermic reaction and generates heat. Magnetic stirrer is used to stir the mixture for 3 minutes.

Then the methoxide solution was added to the preheated oil which is at 60^{o} C. The mixture is stirred for 2 hours at 200rpm using magnetic stirrer. The temperature is maintained at 60^{o} C. Methanol and cooking oil undergo transesterification reaction to produce Fatty Acid Methyl Ester (FAME) and Glycerol. Glycerol is water soluble and it is not soluble in the oily biodiesel and it settles down. The crucial factors for the transesterification reaction are heat, magnetic plate and time. The temperature of the cooking oil should not exceed the boiling point of methanol (64.7^{o} C). The mixing should be stopped after some time. This mixture was transferred to separating funnel and allowed to settle for 24 hours. The yield of biodiesel was calculated by the following formula.

Yield % = (Volume of finished biodiesel / Volume of Palmolein oil used) x 100.

GC-MS analysis:

GC-MS were done for identification of FAME content. It was carried out on a Agilent 7820A GC and Agilent 5977E Series GC/MSD system equipped with a MS Detector and a DB-5 column was used operating in electron impact mode at -70eV; Helium was used as a carrier gas with a flow rate of about 1.2 ml/min. The oven temperature was programmed from 100^{o}V with an increase of 10^{o}C/min to 270^{o} C. Mass Hunter and MSD Chem station softwares were used for data acquisition.

Identification on mass spectrum was conducted using the data base of National Institute Standard and Technology (NIST ver.23), Spectra base and pubchem.

RESULT&DISCUSSION

Transesterification of palmolein oil

Transesterification of palmolein oil with methanol using crab shell's Cao and egg shell's Cao as a catalyst produced two products, Biodiesel and Glycerol. Biodiesel and glycerol separated due to their different densities because glycerol has a greater density than biodiesel. Plate 1a & b shows the two different phases separated in the separating funnel. Biodiesel was decanted and it was then subjected to GC-MS analysis to characterize and identify the compounds present in them.

Identification of compounds in the biodiesel

The synthesized biodiesel composition was determined by GC-MS analysis. (Figure 4 a,b).GC-MS analysis of sample 1 revealed 11compounds such as Undecanoic acid,10-methyl,methl ester, Tridecanoic acid, 12-methyl,methyl ester, Octadecanoic acid,3-hydroxy-2-tetradecyl,methyl ester,6-Octadecenoic acid, Glycidyl palmitate, Eicosanoid acid, methyl ester, 9-Octadecenoic acid(Z), oxiranylmethyl ester, Methyl 20-methyl-heneicosanoate,Hexadecenoic acid,2-hydroxy-1-(hydroxymethyl)ethyl ester,9-Octadecenoic acid(Z)-,2,3-dihydroxypropyl ester, C(14a)-Homo-27-nor-14.beta.-gammaceran-3.alpha.-ol. Among the 11 compounds 5 compounds were methyl ester.

The GC-Ms analysis of sample 2 (egg shell CaO - biodiesel) revealed the presence of 16 compounds namely Tridecanoic acid,12-methyl-, methyl ester, Octadecanoic acid,3-hydroxy-2-tetradecyl-,methyl ester, n-Hexadecenoic acid, Hexadecanoic acid,14-methyl-, methyl ester, Heptadecanoic acid,14-methyl -,methyl ester, Oleic Acid, Octadecanoic acid, Hexadecanoic acid, 2-hydroxy-1-(hydroxymethyl)ethyl ester, Glycidyl palmitate, Methyl 18-methylnonadecanoate,Oleyl chloride,9-Octadecenoic acid(Z), oxiranylmethyl ester, Glycidol stearate, Hexadecanoic acid, 2-hydroxy-1-(hydroxymethyl) ethyl ester,9-Octadecen-1-ol,acetate,(Z)-,9-Octadecenoic acid(Z),2,3-dihydroxypropyl ester. Among the 16 compound identified through GC-MS 5 compounds were methyl ester. Eight Fatty acid methyl esters were found in both samples.

Increase in demand for energy and consciousness about the environment have led to search for an alternative fuel which can supplement or replace fossil fuel. Biodiesel is considered as one of the most alternative fuel for diesel engines and it is nontoxic, renewable and biodegradable[8]. The utilisation of waste materials as a catalyst source not only lowers the overall cost of producing biodiesel, but it also added benefit of recycling natural mineral sources, making the process eco - friendly and green. When storing the catalyst and carrying out the transesterification reaction, an inert environment must be maintained. The industry that produces biodiesel might be enticed to this approach and it overcome the challenges such as intricate production procedures and the need for an expensive catalyst [9]. Thus, it is imperative to look for different sources of CaO catalysts that are both more stable and active and that can carry out the transesterication process under ambient circumstances [10].

Plate 1(a&b): Separation of biodiesel and glycerol

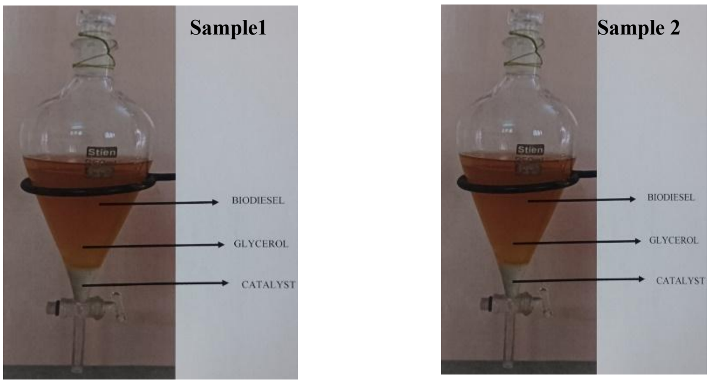

Figure 1: **GC-MS Analysis: Chromatogram of sample 1&2**

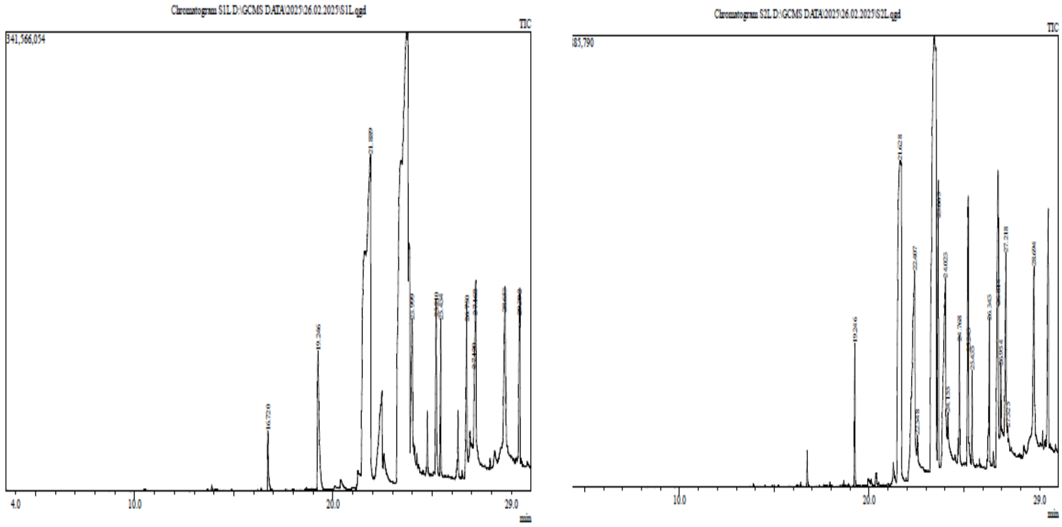

Table 1: Fatty Acid Methyl Esters (FAME) found in samples 1 & 2

S.No	RT	Name of the compound	Common name	Molecular formula	MW g/mol	Symbol	Area	Cas No
1	16.720	Undecanoic acid, 10-methyl-, methyl ester	Methyl isododecanoate	$C_{13}H_{26}O_2$	214.34	C12:0	81384226	111-82-0
2	19.2	Tridecanoic acid, 12-methyl-,	Methyl isomyrist	$C_{15}H_{30}$	242.	C15	15735	5129-58-8

	46	methyl ester	ate	O_2	39	:0	0356	
3	21.628	Octadecanoic acid, 3-hydroxy-2-tetradecyl-, methyl ester	Methyl 3-hydroxy-2-tetradecyloctadecanoate	$C_{33}H_{66}O_3$	510.858	C33:0	2170389997	17369-87-8
4.	25.434	Eicosanoid acid,methyl ester	Methyl arachidate	$C_{21}H_{42}O_2$	326.56	C20:0	280618285	1120-28-1
5	26.814	9-Octadecenoic acid (Z)-, oxiranylmethyl ester	Glycidyl oleate	$C_{21}H_{38}O_3$	338.514	C21:0	778065508	5431-33-4
6	22.548	Hexadecanoic acid, 14-methyl-, methyl ester	Methyl 14-methyl palmitate	$C_{18}H_{36}O_2$	284.468	C18:0	54068533	2490-49-5
7	26.750	9-Octadecenoic acid (Z)-, oxiranylmethyl ester	Glycidyl oleate	$C_{21}H_{38}O_3$	338.514	C21:0	390811411	5431-33-4
8.	23.663	Heptadecanoic acid, 14-methyl,-methyl ester	Methyl margarate	$C_{19}H_{38}O_2$	284.48	C17:0	511549892	2490-23-5

CONCLUSION

Biodiesel is an alternate and renewable energy fuel. CaO was used as a catalyst in the transesterification of the palmolein oil for the production of biodiesel and glycerol. The component present in the synthesized biodiesel was carried out using GC-MS analysis. Eleven compounds were identified in the crab shell sample and sixteen compounds were identified in the egg sample. Eight major FAME (Fatty Acid Methyl Esters) were present in both samples.

REFERENCES

1. Sanprit Aditya, Jaspin Stephen and Mahendran Radhakrishnan (2021). Utilization eggshell waste in calcium-fortified foods and other industrial applications: A review. *Trends in Food Science & Technology*. Volume 115, Pages 422-432.

2. Priti R. Pandit, and Fulekar, M.H (2019). Egg shell waste as heterogeneousnanocatalyst for biodiesel production: Optimized by response surface methodology.*Journal of Environmental Management*.Pages 319-329.https://doi.org/10.1016/j.jenvman.2017.04.100
3. Ziku Wei , Chunli Xu and Baoxin L., (2009).Application of waste eggshell as low-cost solid catalyst for biodiesel production. *Bioresource Technology*. Volume 100, Issue 11, Pages 2883-2885 https://doi.org/10.1016/j.biortech.2008.12.039
4. Mihajlo jovic, Milica mandic, Marija sljivic-ivanovic and Ivana Smiciklas (2019). Recent trends in application of shell waste from mariculture. *Studia Marina* 2019, 32 (1): 47-62. DOI: 10.5281/zenodo.3274471
5. IvanaB. BankovicIlic, MarijaR. Miladinovic, OliveraS. Stamenkovic and Vlada B. Veljkovic (2017). Application of nano CaO–based catalysts in biodiesel synthesis. *Renewable and Sustainable Energy Reviews*. Volume 72, Pages 746-760 https://doi.org/10.1016/j.rser.2017.01.076
6. Indah Raya, Erna Mayasari, Afdaliah Yahya,Muhammad Syahrul, and Andi Ilham Latunra (2015). Synthesis and Characterizations of Calcium Hydroxyapatite Derived from Crabs Shells (*Portunus pelagicus*) and Its Potency in Safeguard against to Dental Demineralizations. *International Journal of Biomaterials* Volume 2015, Article ID 469176, 8 pages http://dx.doi.org/10.1155/2015/469176
7. Devarapaga Madhu, Supriya B. Chavan, Veena Singh, Bhaskar Singh, and Yogesh C. Sharma (2016). An economically viable synthesis of biodiesel from a crude *Millettia pinnata* oil of Jharkhand, India as feedstock and crab shell derived catalyst. *Bioresource Technology*. Volume 214, Pages 210-217 https://doi.org/10.1016/j.biortech.2016.04.055
8. Viriya, E. N., Krasae, P., Puttasawat, B., Yoosuk, B., Chollacoop, N., and Faungnawakij, K. (2010). Waste shells of mollusk and egg as biodiesel production catalysts. *Bioresource Technology*, *101*(10), 3765–3767. https://doi.org/10.1016/j.biortech.2009.12.079
9. Chintareddy, V., Oshel, R., and Verkade, J. (2006). Room-Temperature Conversion of Soybean Oil and Poultry Fat to Biodiesel Catalyzed by Nanocrystalline Calcium Oxides. *Energy and Fuels - ENERG FUEL*, *20*. https://doi.org/10.1021/ef050435d

10. Laskar, I., Rajkumari, K., Gupta, R., Chatterjee, S., Paul, B., and Rokhum, S. L. (2018). Waste snail shell derived heterogeneous catalyst for biodiesel production by the transesterification of soybean oil. *RSC Advances*, *8*, 20131–20142. https://doi.org/10.1039/C8RA02397B

11. Istadi, I., Anggoro, D., Marwoto, P., Suherman, S., and Nugroho, B. (2009). Biodiesel Production from Vegetable Oil over Plasma Reactor: Optimization of Biodiesel Yield using Response Surface Methodology. *Bulletin of Chemical Reaction Engineering and Catalysis*, *4*. https://doi.org/10.9767/bcrec.4.1.7115.23-31