″GLYCEROL A BI-PRODUCT OF BIO-DIESEL AND GREEN SOLVENT FOR ORGANIC TRANSFORMATIONS: PHYSICO ORGANIC CHEMISTRY OF ORGANIC TRANSFORMATION″

MINOR RESEARCH PROJECT
COMPLETION REPORT

Submitted To

UNIVERSITY GRANTS COMMISSION
WESTERN REGIONAL OFFICE
PUNE-411007

Submitted by

Dr. PRAMOD D SONAWANE
MAHARASHTRA EDUCATION SOCIETY′S
ABASAHEB GARWARE COLLEGE, PUNE-411004

JULY-2022

Part-A: Synthesis of Bio-Diesel from pure vegetable and used cooking Oil

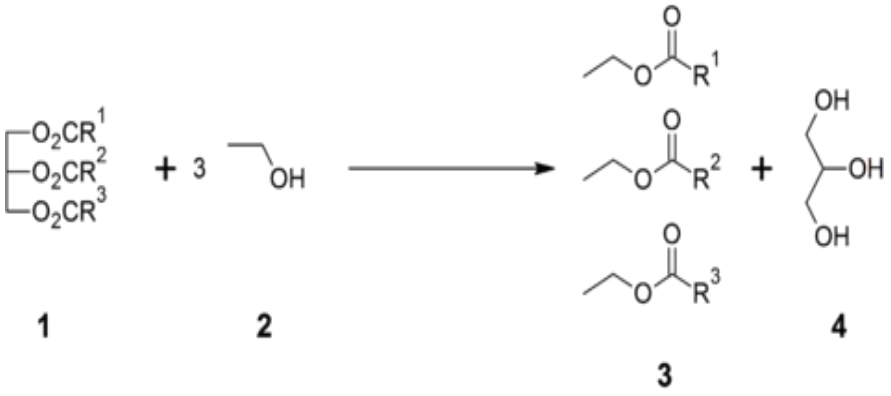
---

Executive Summary:

1.1. Introduction: This part is related to the synthesis of Bio-Diesel using pure vegetable oil & used cooking oil and separation of the bi-product, glycerol formed therein. There are various methods employed for the synthesis of biodiesel among these, the trans-esterification of glycerides of refined/ edible types of oils using alcohol, in presence of an acid or a base catalyst is most common so we have optimised the method so as to use the base catalysed method and used that same method for the synthesis of Bio-Diesel using commercial soybean oil, sunflower oil, rice bran oil, castor oil and waste oil as raw materials.

ABOUT BIO-DIESEL

Bio-diesel is a monoalkyl ester and can primarily be obtained from trans-esterification of virgin and cooked vegetable oils like sunflower oil, palm oil, soybean oil etc. Trans-esterification is a chemical reaction wherein, alcohol reacts with the triglycerides of vegetable oils in presence of a catalyst giving rise to ester (bio-diesel) and glycerol is obtained as a bi-product as per the following reaction shown in scheme 1.



Scheme 1. Transesterification reaction

The oils used requires some pre-treatment so as to use them for synthesis of Bio-Diesel, so pre-treatment procedures like, determination of acid value, peroxide value and saponification value was done using standard prescribed procedures from the literature and then the oils were employed for actual synthesis. After the synthesis, appropriate techniques of separation were deployed and the waste glycerol was separated from the Bio-Diesel.

To confirm the formation of Bio-Diesel and glycerol some physical properties of both were determined the values of which are given in the report in Table 1-4, along with the yields of Bio-Diesel and glycerol. For further confirmation spectroscopic analysis were carried out.

ABOUT GLYCEROL: Glycerol is known traditionally over centuries to have several applications in soap, detergent and pharmaceuticals industry. It is also used as a sweetening agent, but only recently it has been explored as a possible green solvent for various transformations.

Efforts are being already made to convert glycerol into a value-added chemical or utilizing it as a precursor for the synthesis of bio-mass based solvents.

The non-volatile nature of glycerol and its immiscibility with hydrophobic solvents enables the reaction products to be removed by simple separation techniques like liquid phase extraction. High boiling point of glycerol was beneficial in carrying out the organic transformations which were taking place at high temperature.

So, taking into consideration the following amazing physico-chemical properties of glycerol as a (i) Non-toxic, bio-degradable and recyclable liquid manufactured from renewable sources (ii) striking similarity with water and ionic liquid (iii) easily separable by extraction or distillation (iv) cheaper and easy availability,

The present work was aimed to synthesize biodiesel from virgin and waste cooking oil and use the by-product glycerol as a possible green solvent for organic synthesis and as a reducing agent for synthesis of metal nano-particles. The potential of glycerol as a green solvent for the organic and inorganic synthesis has not been recognized yet.

1.2 Result and Discussion

The synthesis of Bio-Diesel from pure vegetable oil was carried out using base catalysed esterification reaction. We have used several oils like, sunflower, castor, soyabean, rice bran etc. The procedure which was followed from the literature has to be optimised to suit our needs and availability in the laboratory. Several fabrications and modifications were carried out for the monitoring of temperature and addition of catalyst. Out of the oils used, synthesis using soyabean and sunflower oil gave good results comparable with the literature. While rice bran oil and castor oil always showed haziness and the separation of glycerol from Bio-Diesel was not fruitful. Multiple attempts and optimisation procedures did not yield any result.

Outcome:

The synthesis of Bio-diesel was successfully carried out using sunflower and soyabean oil.

The use of rice bran and castor oil for the synthesis, shows no phase separation and turbidity occurred.

Synthesis using waste cooking oil required various other pre-treatments as compared to virgin oil.

The pre-treatment procedures of determination of saponification value, Iodine and Peroxide value shows comparable results with the literature value.

The physico-chemical properties like, specific refractivity, viscosity, density of the biodiesel and glycerol were determined and were comparable with literature value.

The confirmation of biodiesel and glycerol was done using IR spectroscopy.

1.3 Conclusion

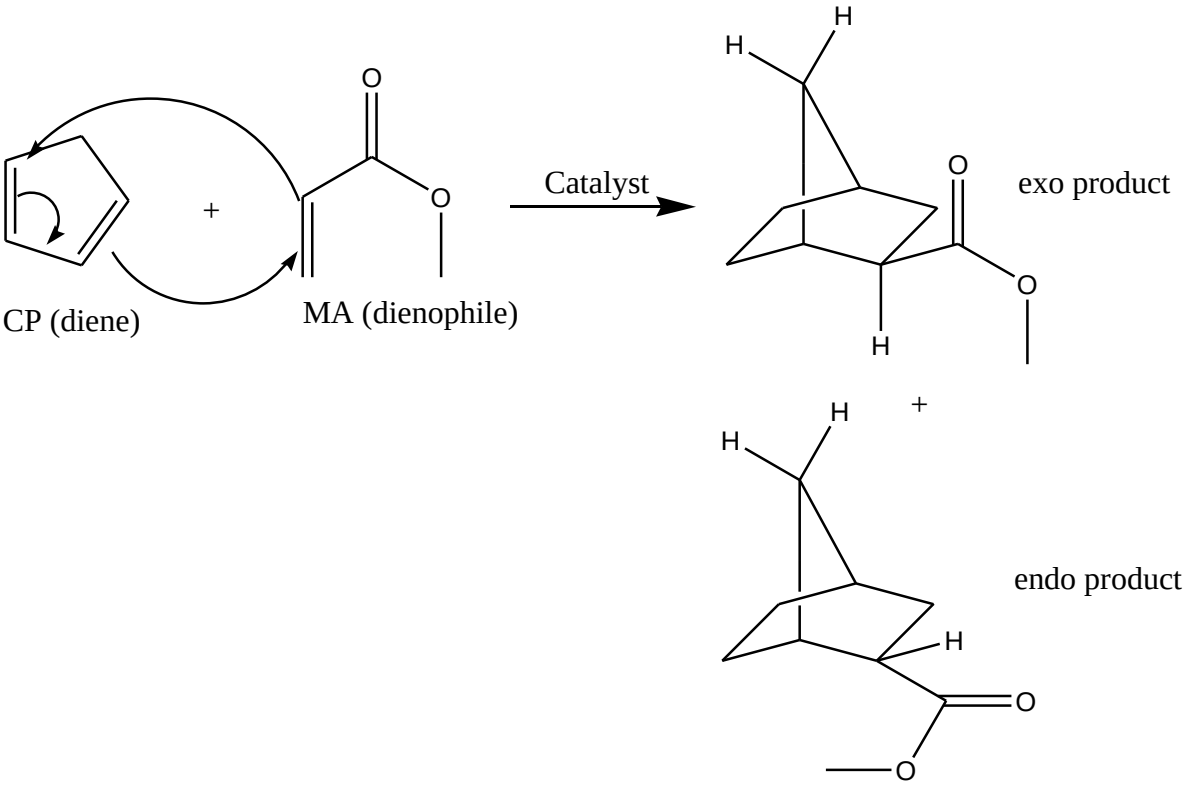
The synthesis of Bio-Diesel using sunflower oil and soyabean yielded good result and the separation of glycerol was carried out successfully. Multiple attempts with castor and rice bran oil produced turbidity and separation of glycerol from it was not possible. Synthesis using waste oil was successfully done after pre-treatment with acid was done.

Part B: Use of glycerol as a green solvent for organic and inorganic transformations

---

2.1. Introduction: In this part we describe the use of waste product i.e., glycerol as a possible green solvent for various organic transformation. We have initially focussed on the Diels -Alder reactions as they are very useful for the formation of ring structured organic moieties and the literature shows that solvent play a major role in the synthesis of cycloadduct with specific stereochemistry.

Diels -Alder reactions is one of the most useful and important reaction in synthetic organic chemistry for the synthesis of six membered rings using various dienes and dienophiles giving rise to a cycloadduct. The cycloadduct thus formed may be stereo chemically oriented in space to give an endo or exo as a major or minor product. It shows excellent stereo selectivity and is also useful in synthesizing biologically active molecules which are of paramount importance in organic chemistry.



Various solvent medias like water, aqueous and non – aqueous salts solutions are employed in the past to carry out Diels- Alder reaction. It is known that, water can alter the rates of this reaction greatly.

As far as reactions of Diels- Alder in non – aqueous solvent media are concerned extensive work is this area has been carried out. The reaction using LDPE which obviates the requirement of very high external pressure. Later, this solvent has been used by several researchers and has found that LDPE alters the rate of reaction of their interest.

In this context, due to all the properties of glycerol as mentioned earlier, its utilization as a solvent for organic synthesis emerges as a challenging, feasible and promising approach. In fact, Glycerol had been employed as a solvent in the middle of last century. but because of its high viscosity and high cost was neglected then by researchers.

In the present work, we have used cyclopentadiene and methyl acrylate as our diene and dienophile for the reaction and various proportions of solvent starting from 100 percent glycerol to 100 percent water were employed for the reaction. The reaction was carried out at a constant temperature of 27^{o}C using the constant temperature water bath purchased for the same purpose from the funding received from the project, appropriate glass jackets were fabricated for the same.

2.2. Result and Discussion: The results shows that glycerol can be successfully employed as a green solvent for organic transformations like Diels-Alder reactions.

However, high viscosity of glycerol requires lot of optimizations of the reactions as compared to water.

Diels -Alder transformations using several other dienes and dienophiles were attempted, but no product was obtained. It may be probably due to high viscosity of glycerol, which prohibits the diffusion of diene and dienophile. Another reason may be the stereochemical orientation in space of the diene and dienophile.

The same reactions when carried out at higher temperature gave promising results conforming our theory of viscosity.

The glycerol can be used successfully at high temperatures were the diffusion of diene and dienophile becomes easier.

Owing to the upsurge in the synthesis of newer inorganic nano materials and the success of organic reactions, in the meanwhile we attempted to use glycerol as a reducing agent and fuel for the synthesis of multiferroics material.

Several common and novel multiferroics nano materials using d block and lanthanide metals were synthesized. The results of both these syntheses are very promising and encouraging, prompting us to attempt more organic transformations. However, the crunch of money prevented us from such attempts.

ii) Research Findings: The basic aim of this research work was twofold, one to synthesize Bio-Diesel using pure vegetable and used or waste cooked oil and to separate the waste created and attempt to reuse this waste as a green solvent for organic transformations. Thus, to practice the 3 principles of green chemistry of reduce, recycle and reuse. We were successful in synthesizing Bio-Diesel using pure and used oil with some modifications and optimization of methods available in literature. The otherwise waste by-product named glycerol was successfully separated from the Bio-Diesel. The separated glycerol was purified and employed as a green solvent for organic as well as material synthesis.

2.3. Conclusion: The well-known organic transformation like Diels-Alder reaction was successfully carried out using the waste glycerol as a solvent.

The effect of variation of solvent and cosolvent was also studied at constant temperature for a given set of diene and dienophile.

The high viscosity of glycerol suppresses the diffusion of diene and dienophile to form a cyclic adduct as compared to pure water. Therefore, it is recommended to conduct the study at higher temperatures so that a corelation between viscosity and diffusion can be established.

An attempt was also made to use the glycerol for inorganic transformations. The upsurge in the synthesis of multiferroics nano materials using several reducing agents prompted us to synthesize such nano multiferroics materials using the waste glycerol as reducing agent as well as a fuel.

These attempts were found to be successful to synthesize calcium based multiferroic materials so, attempts of the same with few metals from the f block and the findings were successful and encouraging.

Following materials were synthesized.

$CaFe_2O_4$

$CuFe_2O_4$

Further the studies of doping the above nano ferrites with small amount of lanthanides were carried out as shown below:

$SmCuFe_2O_4$

$GdCuFe_2O_4$

Further, these ferrites were tested successfully as ethanol sensor and antimicrobial agent against Serratia and Bacillus spp. The study of thermal stability and magnetic properties using VSM was carried out. The materials were found to be stable and ferromagnetic.

Outcome of the Project:

- Oral and Poster presentation in conferences and seminars, out of which one received best poster award.
- One publication: Synthesis of Aloe vera shaped Silver Nano powder by using Bio-Diesel By-product Glycerol, *Chemical Sci. Trans.*, **2021**, 10(01), 9-14.