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Biodiesel Production as an application on Heterogeneous Catalysis

A graduation research project
Submitted to the Department of chemistry in partial
fulfillment of the requirement for the completion of a degree
of Bachelor of science in chemistry.

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Abbreviations

HPAs	Heteropoly acids
TGA	Thermal gravimetric analysis
DTA	Differential thermal analysis
DSC	Differential scanning calorimetry
FFA	Free fatty acid
CO	Carbon monoxide
HC	Hydrocarbon
PM	Particulate matter
ZnO	Zinc oxide
CuO	Copper oxide
POMs	Polyoxometalates

Acknowledgment

First, we thank Allah for the completion of this research, which is a good conclusion to the bachelor’s degree. By God’s grace and mercy, he provided us with the means to attain this knowledge, and provided us with teachers and an university. We thank our families who continued to support us throughout this journey. We thank our project supervisor, Dr. Aliyah Alsharif, for her efforts and advice.

Abstract

This project consists of a general introduction about catalysis field, and presents the physical and chemical properties of tungstophosphoric acid HPW and its application on biodiesel production. Also, it describes the proposed mechanism for biodiesel synthesis using HPW catalyst through esterification and transesterification reactions. Literature reviews about biodiesel synthesis by HPW are also provided.

Biodiesel is produced on a large scale as an eco-friendly substitute to fossil fuels. Catalytic homogeneous processes using strong acids, alkalis, and natural oils which have been realized in industry. However, these traditional methods have several disadvantages.

So, this review describes the esterification and transesterification reactions as an alternative route of biodiesel production, which has advantages over traditional way.

الخلاصة

هذا المشروع يحتوي على مقدمة عامة عن مجال الحفز الكيميائي, ويعرض بعض الخصائص الكيميائية والفيزيائية للحفاز الحمضي التنغستوفوسفوريك وكذلك عن كيفية استخدامه في انتاج الديزل الحيوي. كما يعطي توضيح لميكانيكية تفاعل تحضير الديزل الحيوي باستخدام الحفاز الحمضي من خلال تفاعل الاسترة والاسترة التبادلية. اخيراً تم إضافة بعض الدراسات السابقة عن انتاج الديزل الحيوي باستخدام هذا الحفاز.

يتم إنتاج وقود الديزل الحيوي على نطاق واسع كوقود بديل صديق للبيئة. حيث يتم تحضير هذا الوقود صناعيا عن طريق العمليات الحفزية المتجانسة باستخدام الأحماض القوية. ومع ذلك، فإن هذه الأساليب التقليدية لها عيوب عديدة. لذلك، تشرح هذه الورقة تفاعلات الأسترة والأسترة التبادلية باعتبارها طريق بديل لإنتاج وقود الديزل الحيوي، والذي يتمتع بمزايا مقارنة بالطريقة التقليدية.

1. Introduction

90% of chemical reactions include catalysts in one or more of their steps, making catalysis a significant area of study in chemistry [1]. Due to environmental concerns, catalysis seems to be much more significant today than it was in the past and is one of the main drivers of advancement in our society. According to a survey of American companies, the production of chemicals and fuels generates more money annually than all other industrial sectors combined. Catalysis was involved in more than 60% of the 63 main products and 90% of the 34 process improvements [1]. This highlights the importance of catalysis in the fuel and chemical sectors. This project aims to give a short introduction about the catalysis, as well as a brief overview of the one common acid catalyst, which is HPW, and an example on heterogeneous catalysis, biodiesel production. Only heterogeneous catalysis is included in this review.

1.1 Catalysis

In 1835, the Swedish chemist Berzelius is the first used the term "catalysis" in 1835, The word catalysis is derived from the Greek word "kata," which means down, and "lysin," which means loosen. In 1894, provided a meaningful description: “Catalysis is the acceleration of a slow chemical process by the presence of a foreign material [2].

More than a century later, every student is taught that a catalyst lowers the activation energy of a reaction, accelerating, he also learns that the catalyst interacts with the reactant molecule by attaching itself to it. The catalyst is not exhausted and can change a large number of molecules even if it takes part in the process, Figure 1.1. Therefore, it can still change huge quantities but just needs to be present in catalytic proportions. Even though catalysis is one of the fundamental concepts of chemistry and the great majority of chemical compounds have undergone one or more catalytic stages during their synthesis [2].

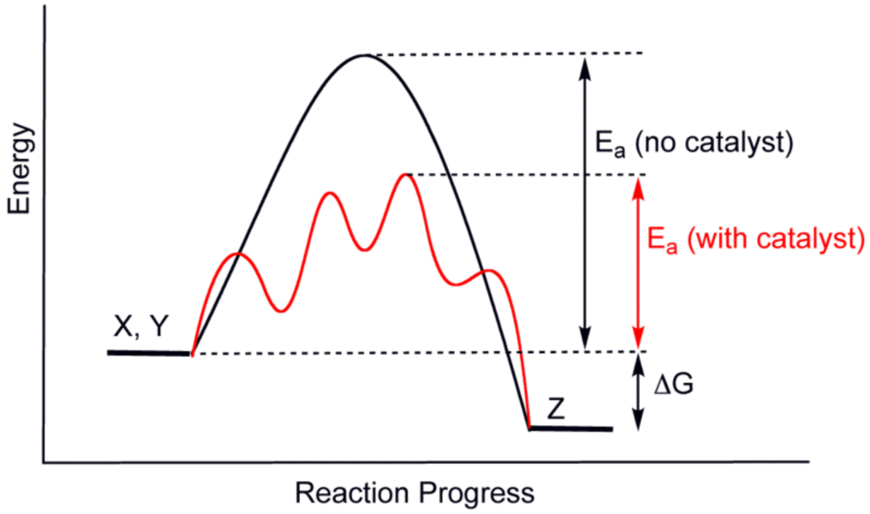


Figure 1.1: Schematic drawing for reaction progress with catalyst and no catalyst [3].

1.2 Types of catalysis

Catalysis is classified into homogeneous and heterogeneous catalysis. Any catalyst that is in the same phase as the reaction mixture is called homogenous catalyst [4]. On the other hand, there is one that is in a different phase than the reactants; typically, the reactants are liquids or gases, while the catalyst is a solid is called heterogeneous catalyst [5].

1.2.1 Heterogeneous Catalysts

Heterogeneous catalysts have the benefit of easy separation from the product formed without the requirement of washing. Reusability of the catalyst is another advantage of the heterogeneous catalysts [6].

1.2.2 How heterogeneous catalyst work?

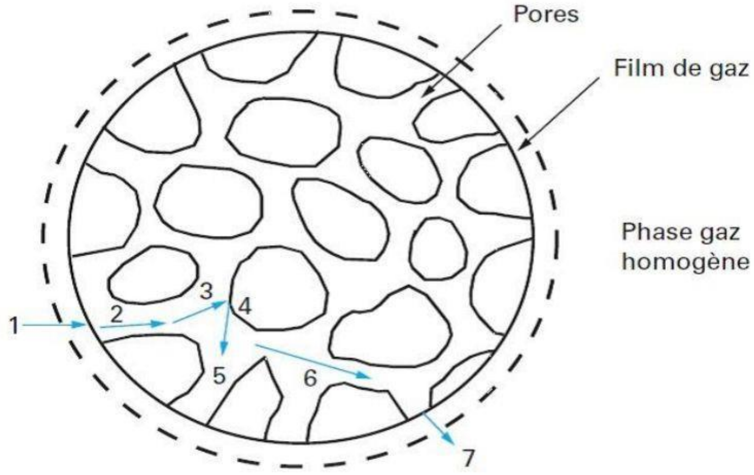


Figure 1.2: The heterogeneous catalytic cycle [7].

Here we identify seven main steps [8-9]:

1) External transport of substrate molecules by gas phase diffusion to the outer surface of the catalyst (film diffusion).

2) Inward transport of substrate molecules through pores to active sites on the inner surface of the catalyst (pore diffusion).

3) Adsorption of substrate molecules on the surface (chemisorption).

4) Interaction between molecules adsorbed on the surface to form a product (chemical reaction).

5) Product adsorption.

6) Internal transport of product through pores to the outer surface of the catalyst.

7) External transport of product through the boundary layer to the bulk fluid phase.

2. Catalysis by $H_3PW_{12}O_{40}$

Catalysis with heteropoly acids (HPAs) and related polyoxometalate systems is a field of growing importance. Several industrial processes based on polyoxometalates catalysis have been developed and commercialized. Due to their unique physicochemical properties, polyoxometalates can be profitably used in homogeneous, biphasic, or heterogeneous systems, providing a broad operational choice. In many cases polyoxometalates provide higher activities and selectivities and allow for cleaner processing compared to conventional catalysts. The high effectiveness of polyoxometalates as acid catalysts is primarily due to their strong Brönsted acidity, greatly exceeding that of ordinary mineral acids and solid acid catalysts and also propertiy important polyoxometalates ability of polyanions to stabilize organic intermediates, and lack of side reactions like sulfonation, etc., [10].

The structure was so new and appeared so complicated that the name "Keggin" for this polytungstate and for the series $[X^{n+}M_{12}O_{40}]^{(8-n)-}$ was born, where X is the heteroatom, x is its oxidation state, and M is the peripheral atom (usually Mo^{6+} or W^{6+}), Table 2.1.

Table 2.1 A different heteroatom (X) used in Keggin compounds $[X^{n+}M_{12}O_{40}]^{(8-n)-}$ [11].

Chemical formula	**M= Mo**	**M= W**
$[X^{n+}M_{12}O_{40}]^{(8-n)-}$	Si^{IV}, Ge^{I}, P^{V}, As^{V}, Ti^{IV}, Zr^{IV}, S^{IV}	As^{V}, Al^{III}, Fe^{III}, Co^{II}, Co^{III}, Cu^{I}, Zn^{II}, Cr^{III}, Mn^{IV}, Te^{IV}, Ga^{III}

Figure 2.1 shows a fragment of the structure of the Keggin heteropoly acid $H_3[PW_{12}O_{40}].6H_2O$ determined by single-crystal X-ray analysis. The crystal lattice is formed by packing heteropoly anions into a body-centred cubic structure. The Keggin structure is composed of a central tetrahedron XO_4 surrounded by 12 edge- and corner-sharing metal-oxygen octahedra MO_6.

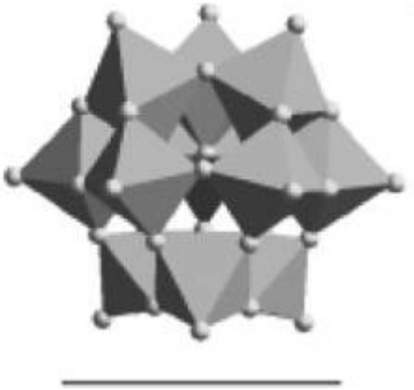


Figure 2.1: The Keggin structure of the $[XM_{12}O_{40}]^{x-8}$ anion [12].

Doubly hydrated protons $H^+ (H_2O)_2$ link four neighbouring anions by forming hydrogen bonds with the terminal W=O oxygens [13], Figure 2.2

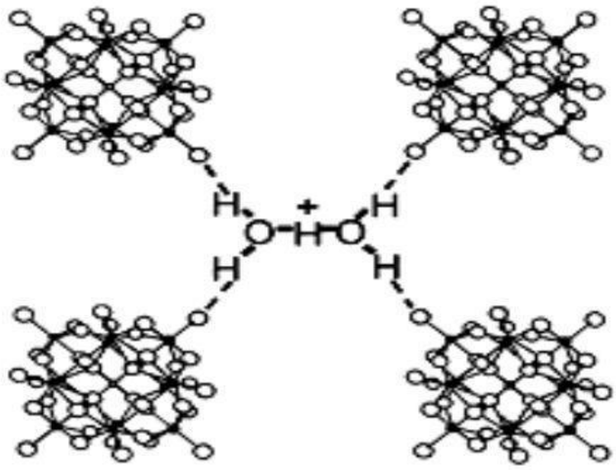


Figure 2.2: structure of $H_3PW_{12}O_{40}.6H_2O$.

2.1 Thermal stability

The thermal stability of heteropoly compound is of great importance for their use in heterogeneous catalysis. Some compounds are stable and can be applied as catalysts in moderately high temperatures, up to 300-350 ℃ [14].

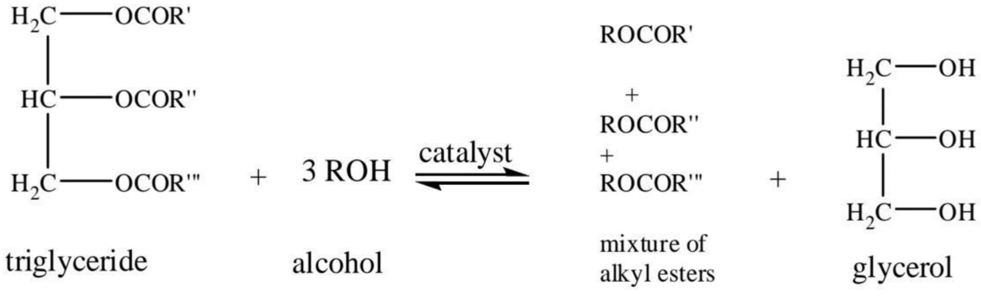
Thermal decomposition of polyoxometalates (to eventually form a mixture of oxide) is a complex multistage process. The catalyst activity may be irreversibly lost at an early stage of decomposition. For example, solid acid catalysts based on tungsten heteropoly acid ($H_3PW_{12}O_{40}$) probably lose activity at the onset of thermal decomposition of the Keggin structure, when the acid protons are lost [15]. Usually, thermal stability is determined by thermal analytical methods (TGA) thermal gravimetric analysis, (DTA) differential thermal analysis, (DSC) differential scanning calorimetry) frequently in combination with other techniques, such as X-ray diffraction, infrared spectroscopy (IR), solid state (NMR), etc. Generally, Keggin-type heteropoly compounds are the most stable among various polyoxometalates. The decomposition temperature ℃ for the most typical Keggin heteropoly acids, as estimated from TGA, decreases in the following series [16]:

$H_3PW_{12}O_{40}$	>	$H_4SiW_{12}O_{40}$	>	$H_3PMo_{12}O_4$	>	$H_4SiMo_{12}O_{40}$
465		445		375		350

3. Application on heterogeneous catalysis

3.1 Biodiesel production

Biodiesel is a renewable fuel comprised of mono alkyl esters of fatty acids. Biodiesel is recognized as a “green fuel” that has several advantages over conventional diesel. Biodiesel is simple to use, biodegradable, nontoxic, and essentially free of sulfur and aromatics. Biodiesel is usually produced from vegetable oils and animal fats via their trans- esterification reaction or from free fatty acids via their esterification, Scheme 3.1 [6].



Scheme 3.1: Reaction for oil transesterification.

3.1.1 Triglycerides

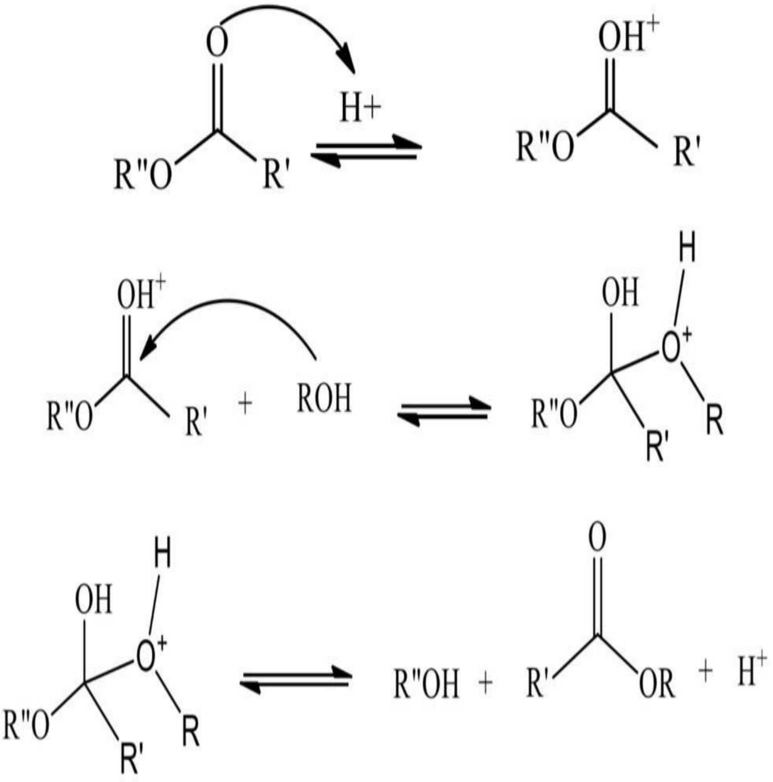
In biodiesel production process, raw materials account for almost 75 % of total biodiesel cost. Basically, all vegetable oils and animal fat can be used as feedstock for biodiesel production. Most of these oils and fats have a similar chemical composition; they consist of triglycerides with different amounts of individual fatty acids. The major fatty acids are those with a chain length of 16 and 18 carbons, whereas the chain could be saturated or unsaturated [6].

3.1.2 Free Fatty Acid Oils (FFA Oil)

Biodiesel is receiving increased attention as an alternative, non–toxic, biodegradable, and renewable diesel fuel. Its properties vary somewhat depending on the oil feedstock and alcohol used but it can always be used as a direct substitute for diesel fuel. Biodiesel has a higher cetane number than diesel fuel, no aromatics, almost no sulfur, and contains 10% to 11% oxygen by weight. These characteristics of biodiesel reduce the emissions of carbon monoxide (CO), hydrocarbon (HC), and particulate matter (PM) in the exhaust gas compared to petroleum–based diesel fuel. In spite of its desirable properties as a diesel fuel substitute, biodiesel from food–grade oils is not economically competitive with petroleum–based diesel fuel. Lower–cost feedstocks are needed. The objective of this study was to develop a process for producing fuel quality biodiesel from low–cost feedstocks with high FFAs [17].

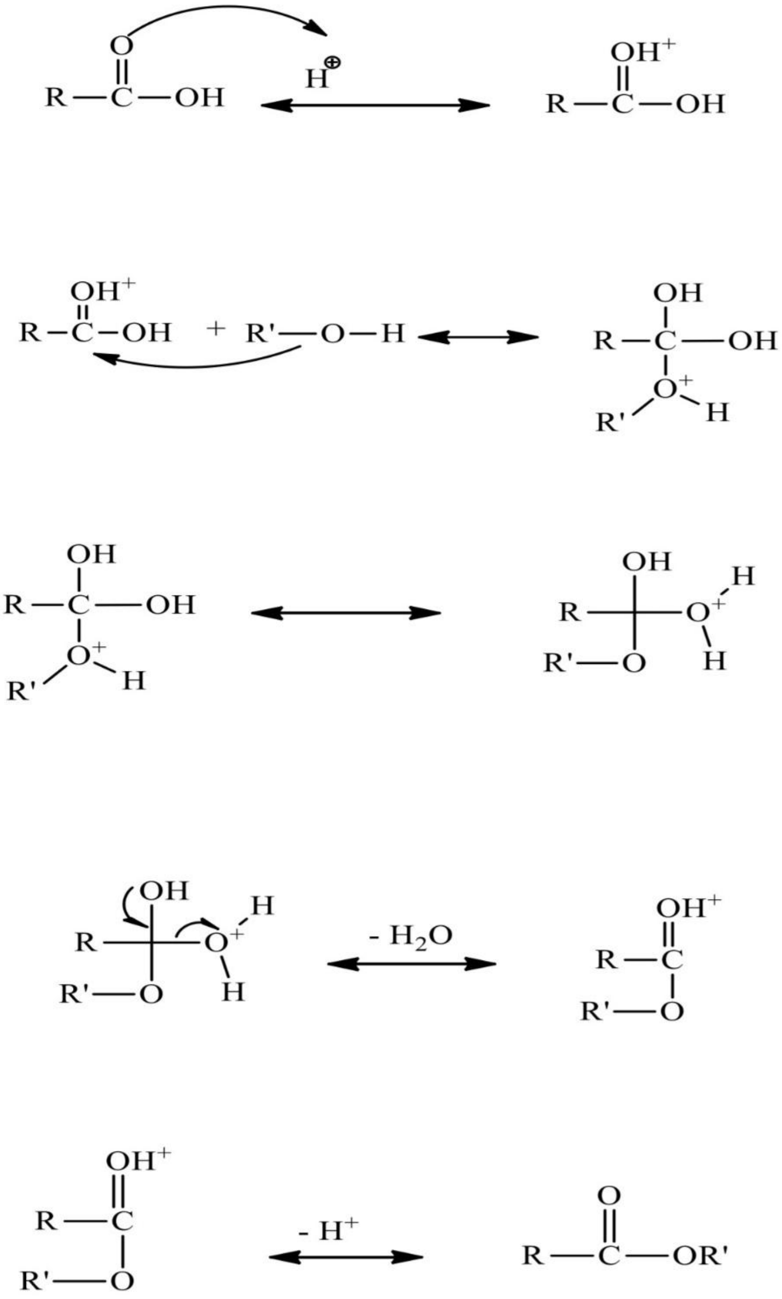
3.2 Reaction Mechanism

Biodiesel production involves chemical reactions occurring under heterogeneous catalytic conditions. Conversion of Triglycerides or free fatty acid oils into biodiesel involves processes that utilize catalysts effectively. These fundamental elements constitute an important stage in the biodiesel production process, requiring a precise understanding of the chemical processes and appropriate operating conditions to ensure product quality and process efficiency. The mechanism of acid catalyzed transesterification involves three steps as shown in Scheme 3.2. The first step is the protonation of the carbonyl group by the acid catalyst. The second step is nucleophilic attack from the alcohol forming a tetrahedral intermediate. In the last step, there is proton migration and breakdown of the intermediate [18].



Scheme 3.2: Mechanism of acid catalyzed transesterification.

The mechanism of acid catalyzed esterification is shown in Scheme 3.3. The first step is protonation of the carbonyl group of the acid. The second step is nucleophilic attack by alcohol. The following steps involve proton transfer from one oxygen atom to another one subsequent, elimination of water leads to the protonated ester. Then the catalyst regenerated and soon [19].



Scheme 3.3: Mechanism of acid catalyzed esterification [19].

3.3 Advantage of biodiesel

It is renewable, it can be used in most diesel equipment with no or only minor modifications, it can reduce global warming gas emissions, it can reduce tailpipe emissions, including air toxins [20].

Biodiesel engines 100% domestic fuel. Neat biodiesel fuel is non-toxic and biodegradable. If the washing is carried using H_3PO_4 and the catalyst used in manufacturing process is KOH then the wash liquid can prove to be an excellent fertilizer this will help to reduce price of biodiesel. As biodiesel is prepared from vegetable oils, so for more production of biodiesel more production of oil seeds is required which will lead to more green coverage and hence result in improved ecology [21].

4. Previous studies about biodiesel production

Recently, HPAs have been reported on, as the attention on environmentally friendly catalysis for esterification and transesterification reactions grows. It was reported that HPAs exhibited high activity for biodiesel production in homogeneous systems or heterogeneous forms supported on SiO_2, Ta_2O_5, ZrO_2, or other carriers [22].

Sudhakar and Pandurangan [23], reported that for producing biodiesel via transesterification of neem oil with methanol using a various weight percentage of $H_3PW_{12}O_{40}$ (10, 20, 30%) was impregnated on KIT-6 and it was characterized by diferent physicochemical techniques. Moreover, its catalytic activity was examined by liquid-phase transesterification of neem oil under different experimental conditions. Among the different wt% catalyst, 20% catalyst showed highest neem oil conversion and selectivity at an optimized reaction temperature of 60 °C. Further, the spent catalyst was recovered and recycled three times, and it showed activity losses of less than 4%.

Zhang et al. [24], studied the catalytic performance of phosphotungstic acid ($H_3PW_{12}O_{40}$) and basic amino acid to self-assemble series of acid-base bifunctional composite catalysts. The strength of acids and bases could be adjusted by changing the concentrations and types of amino acids and then used the prepared catalyst for reaction time, reaction temperature, catalyst loading, and methanol/oleic acid (MeOH/OA) molar ratio producing biodiesel from oleic acid (OA). The effects of process parameters such as on the catalytic reaction were investigated. They found that the maximum biodiesel yield of 97.0% was achieved at the MeOH/OA molar ratio of 5.9, the catalyst loading of 8%, reaction time of 6 h, and reaction temperature of 65°C. Furthermore, the stability and reusability of the prepared catalyst were also demonstrated.

Fioravante et al. [25], used cesium-modified phosphotungstic acid ($Cs_{2.5}H_{0.5}PW_{12}O_{40}$) as a heterogeneous catalyst for transesterification of canola oil with methanol. The canola oil conversion reached 55% at room temperature after 24 h. The reusability tests showed that the conversion of canola oil to biodiesel was maintained.

Esmi et al. [26], prepared three solid acid catalysts, namely mesoporous aluminophosphate-supported 12-tungstophosphoric heteropoly acid (HPW/MAP), mesoporous aluminosilicate-supported 12-tungstophosphoric heteropoly acid (HPW/MAS), and gamma alumina-supported 12-tungstophosphoric heteropoly acid ($HPW/\gamma\text{-}Al_2O_3$) and characterized. The catalytic performance of the catalysts was studied through alcoholysis reaction using unrefined green seed canola oil as the feedstock. The maximum biodiesel yield of 82.3% was obtained using 3 wt.% of HPW/MAS, with a methanol to oil molar ratio of 20:1, at 200 ◦C over 7 h. The reusability study of HPW/MAS showed that it can maintain 80% of its initial activity after five runs.

5. Conclusion

Synthesis of biodiesel through esterification and transesterification reactions providing environmentally friendly option for hazardous synthetic pathways to achieve clean sustainable environment, maintaining the health and safety of people.

Low surface area of HPW limits their application in biodiesel production. However, HPW supported on mesoporous supports improve their catalytic activity by increasing the available surface area.

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