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Kinetic Study of Transesterification Reaction of Edible Oil Using Heterogenous Catalyst

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Abstract

$AlPO_4$ solid acid catalyst was prepared in order to use it in transesterification reaction of edible oil after supporting it with tungsten oxide. The maximum conversion of edible oil was obtained 78.78% at catalyst concentration (5gm.), temperature 70°C, 30/1 methanol/edible oil molar ratio, and time 5hr. The study of kinetics of the transesterification reaction of edible oil indicates that the reaction has an order of 3/2, while the value of activation energy for transesterification reaction is 51.367 kJ/mole and frequency factor equal 26219.13(L/ mol.minute).

Keywords: $AlPO_4$, transesterification, edible oil, Heterogeneous Catalyzed Reaction

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1- Introduction

Because of the rising price and depletion of plant energy sources, the energy organization made several studies to find alternative energy production sources [1]. Biodiesel is an excellent product of clean, renewable energy produced from renewable biological sources like vegetable oil and fat of animals. Biodiesel is defined as fatty acid ester-based on the American Standard Test of Materials (ASTM) **[2].**

Biodiesel is less dangerous than diesel and friendly to the environment because the less emission of carbon dioxide, sulfur dioxide and outlet combustion does not contain the aromatic compound. It could be used in compression-ignition (diesel) engines **[3,4].**

Biodiesel contains alkyl esters generated from the esterification of free fatty acid (FFAs) or the transesterification of triglycerides (TGs), with the low molecular weight of alcohols [5]. Biodiesel has the same influx and burning characteristics as petroleum-based diesel. Therefore it may be used as a substitute for diesel or, more typically, in fuel blends **[6]**.

Pure biodiesel produces around 90% of the energy released by natural fuel. Thus the reassembles of engine torsion, and horsepower are the approximate projected engine completion [7].

Low-cost feedstocks, predictably, should undergo considerable pre-treatment prior they could be used to make biodiesel [8].

Feedstocks made from edible oil and grease waste have been suggested to reduce biodiesel synthesis expenses **[9].**

Amorphous Aluminum phosphate can be used as support and catalysts because it is a bifunctional acid-base.

It can be used in several processes as catalysis like condensation, cracking, rearrangement, alkylation, isomerization, dehydration and esterification [10, 11, and 12].

Studying the kinetics of transesterification reaction were very important in the selection of the most favorable transeterification conditions for maximizing the production of biodiesel , Kinetic models may offer different levels of detail and predictive capabilities, as they can take into account mass and heat transfer phenomena, as well as thermodynamic equilibrium. In this research WO3/AlPO4 was used for transesterification of edible oil to produced biodiesel and studied the kinetic for transesterification reaction.

2- Material

Most materials were obtained from local markets. $AlPO_4$: The Aluminum phosphate is manufactured locally from [Al $(NO_3)_3.9H_2O$ and $(NH_4)_2HPO_4$). Table **1** details the chemicals used, along with their characteristics.

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Table 1. Chemical compounds and their properties

Chemicals	Phase	Formula	Density (g/ml)	Molecularweight (g/gmol)	Purity (wt%)	Supplier
ammonium meta tungsten	Solid	$(NH_4)6H_2W_{12}O_{40}–x\ H_2O$	4.6	2956.2	99.5%	China
Nitric acid	Liquid	HNO_3	1.51	63.01	72%	CDH, India
Ammonia	Liquid	$NH_4.xH_2O$	0.91	17.03	25 %	Belgium
Methanol	Liquid	CH_3OH	0.792	32.04	99.5%	India
Ethanol	Liquid	C_2H_5OH	0.789	46.07	99.9	India
Sodium Hydroxide	Solid	NaOH	2.13	40	98%	India
Phenolphthalein	solid		1.28	318.33	99%	France
Edible oil (sunflower Oil)	liquid		0.92	876.16		From restaurant

3- Experimental Work

AlPO4 was synthesized according to Xie and Yang [13] , The amorphous catalyst was prepared by mixing 30.01 gm of Al $(NO_3)_3$ $.9H_2O$ and 9.24 gm of $(NH_4)_2HPO_4$ with 300 ml deionized water utilizing a stirrer magnetic for thirty minutes to have homogenous mixture, then nitric acid was added drop wise until the mixture reached PH 1.7. Ammonia 25wt% solution added dropwise until reach PH 8 to have super saturation mixture and continue stirring for 60 min.

These materials stayed on a magnetic stirrer for one hour. Then the solution was washed with a double volume of deionized water and filtered under vacuum using filter paper. The catalyst was further dried at 100°C for 24 hours before being calcined at 500°C for three hours. The synthesis of an aluminum phosphate sulfated catalyst involves the inclusion of promoters like tungsten, which would significantly improve edible oil's esterification process, resulting in increased biodiesel stability and selectivity.

The wet-impregnation method added tungsten promoters, First, AlPO4 was impregnated with an aqueous sol of ammonium metatungstate $((NH_4)_6(H_2W_{12}O_{40}.nH_2O)$. A dropwise impregnation process was utilized to vary preload percentages of WO_3 on it. The generated catalyst was later dried over the night at 100°C and calcinated in air for three hours at 500°C. After preparation of the catalyst different analysis made on the samples

4- Result and Discussion

4.1. Characterization of the Catalyst

Fig. **1** shows x-Ray diffraction (XRD) of the prepared catalyst , it can be found that the synthesized catalyst has an amorphous phase and this is corresponding to Xie and Yang [13] , while the prepared catalyst have a surface area of 185.83 m^2/g and pore volume of 0.645 cm^3/g

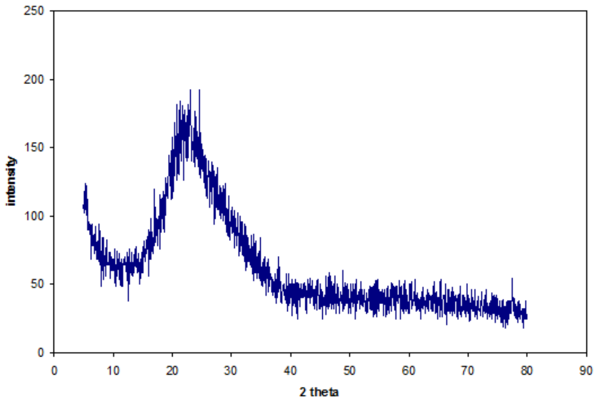

Fig. 1. X-ray diffraction of $AlPO_4$

On the other hand the atomic force microscopy (AFM) method was used to find the average particle size. The result showed that the catalyst had an average particle size of 5.865 nm. Fig. **2** show the histogram of particle distribution.

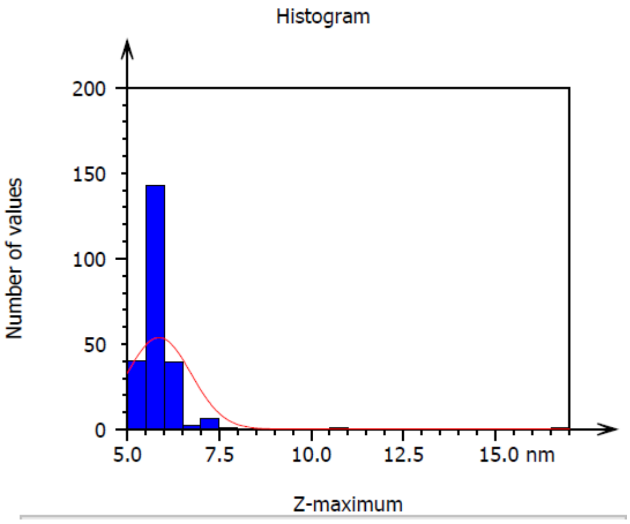

Fig. 2. Histogrsm of Particle distribution

4.2. Effect of Reaction Time on Conversion

The effects of reaction time on the conversion of edible oil were studied at different reaction time (0-6 hr) with 35% tungsten promoter at different temperature, 350 rpm, methanol/edible oil ratio (30/1) and 5 wt% of catalyst.

It can be shown from Fig. **3** that low activity of catalyst at time 1 hr and temperature of 50°C (6.7 %), while increasing time leads to increase the conversion of edible oil until it reaches equilibrium at time 5 hr (47.32%) , on the other hand the conversion at time 1 hr and temperature 70°C was 37.5% and it reaches equilibrium also at time 5 hr and the conversion in this time was 78.79%.

However, increasing the reaction time to 6 hr gives the same conversion at all temperature and this is agreement with the studies of Abbas and Abbas [14] who pointed to esterification reaction of oleic acid with H2SO4 as catalysts, the results of this research found that the best time of esterification reaction was 3 hr.

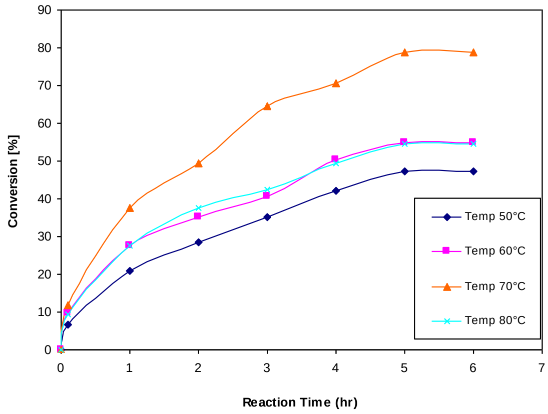

Fig. 3. Effect of reaction time on edible oil conversion

4.3. Effect of methanol/edible oil ratio on Conversion

One of the most important factors that effect on transesteridication reactions to produced biodiesel was Methanol/edible oil ratio. In biodiesel reaction one mole triglyceride (TG) react with three mole of methanol to produce biodiesel as shown in equation 1 **[15]** .

$$Triglyceride(TG) + 3Methanol \overset{catalyst}{\leftrightarrow} esters + glycerol \tag{1}$$

So to increase the conversion of biodiesel produced excess amount of methanol was needed.

Fig. **4** shows the effect of methanol/edible oil ratio where four amount of ratio were used (15/1,20/1,30/1 and 35/1) while other conditions were fixed (temperature 70°C , catalyst amount 5 gram, percentage of WO3 promoters 35% and time of 5 hours).

It can be shown from the figure that increasing methanol /oil ratio leads to increase the conversion of edible oil and this is due to increasing the amount of edible oil reacts to produced biodiesel [16].

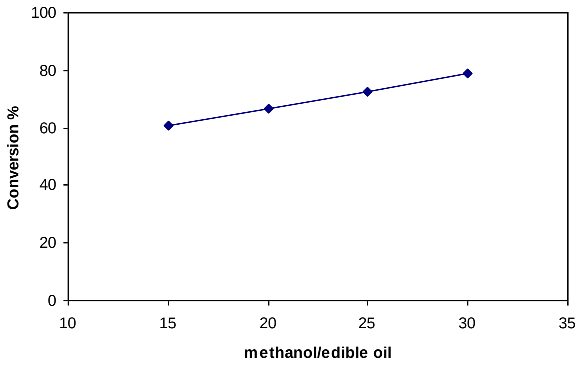

Fig. 4. Effect of methanol/oil molar ratio

4.4. Kinetic Study of Transesterification

The transesteriication reaction of edible oil consist of three reaction in each reaction one mole of methanol react as shown in equation 2,3 and 4

$$Triglyceride(TG) + methanol \leftrightarrow diglyceride(DG) + R'CO_2R \tag{2}$$

$$Diglyceride(DG) + methanol \leftrightarrow monoglyceride(MG) + R'CO_2R \tag{3}$$

$$Monoglyceride(MG) + methanol \leftrightarrow glycerol + R'CO_2R \tag{4}$$

By ignoring the intermediate reaction of monoglyceride and diglyceride the overall reaction can be shown in equation 5

$$Triglyceride(TG) + 3methanol \leftrightarrow 3R'CO_2R + glycerol\,(GL) \tag{5}$$

The reaction of transesterification carried in a batch reactor and to study the kinetics of the reaction it's important to make an assumption to simplify the mathematical modeling of transesterification

1- The reaction of transesterification is not effected from free acid and so no soap present.
2- The reaction do not affect form water (AlPO do not affect in the presence of water) so saponification can be negligible.
3- The tranesterification reaction is a reversible reaction so using excess amount of methanol make the reaction to go forward (no reverse reaction happen).

To find the order of the reaction nth order equation was used as shown in equation 5 [17]

$$CA^{1-n} - CA_0{}^{1-n} = k(n-1)t \tag{5}$$

By trial and error the most significant order was 1.5 which gave value of R^2 between 0.9728 at temperature 80°C and 0.9927 at temperature 70°C as shown in Fig. **5**

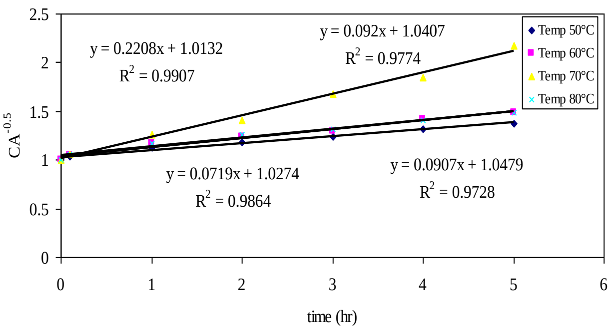

Fig. 5. $CA^{-0.5}$ VS Time at different temperature (50,60,70 and 80°C) with methanol/edible oil (30/1), 35% WO_3 and 5gram of $AlPO_4$

Equilibrium constant can be found from figure 5 by drawing $CA^{-0.5}$ versus time, and then a straight line will be produce with slope of 0.5. Table **2** shows the value of equilibrium constant for forward reaction at different temperature.

Table 2. Equilibrium constant of transesterification reaction

Temperature (°C)	K
50	0.1438
60	0.184
70	0.4416
80	0.1814

To find the activation energy of the reaction Arrhenius law will be applied. From Arrhenius law ($k=k_0e^{-E/RT}$) by plotting ln k versus 1/T a straight line will be formed with a slope of (-E/R) and intercept k_0 , where E is the activation energy , k_0 frequency factor and R gas constant as shown in Figure 6.

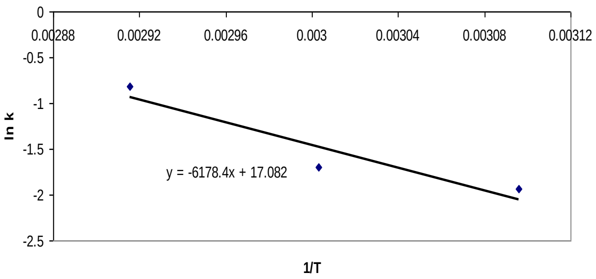

Fig. 6. ln (k) versus (1/T)

It can be concluded figure 6 that the value of activation energy (E) = 51.367 kJ/mole while the frequency factor equal 26219.13. The activation energy found in the present work is compared with those reported in the literature by Brahmkhatri *et al*.[18] (44.6 kJ/ mol), Aranda *et al*.[19] (42 kJ/ mol), Sarkara *et al*.[20] (39.5 kJ mol-1) and Patel and Brahmkhatri .[21] (52.4 kJ /mol)

5- Conclusion

AlPO4 catalyst was synthesized successfully with amorphous phase and high surface of 185.83 m^2/g and pore volume of 0.645 cm^3/gm. The conversion of edible oil obtained was 78.78 % after 5 hr of reaction with 5 gram of catalyst and 30/1 methanol/edible oil molar ratio. The results show that transesterification reaction follow the order of 3/2 and this indicate that the reaction was external diffusion control with activation energy of 5.136 KJ/mol.

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دراسة حركية تفاعل الاسترة للزيوت المستخدمة باستعمال عامل مساعد غير متجانس

ايهاب برهان ياسين [1] و حيدر عبد الكريم رشيد [1] و محمد جابر العاني [2]

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الخلاصة

تم تحضير العامل المساعد الحامضي الصلب $AlPO_4$ من اجل تفاعلات الاسترة للزيوت المستخدمة بعدة عملية تحميل العامل المساعد باوكسيد التنكستن . ان اعلى تحول تم الحصول عليه هو 78,78 % عند تركيز عامل مساعد 5 غم , درجة حرارة 70°م , نسبة الميثانول/ الزيت المستعمل 1/30 وزمن 5 سا. ان دراسة حركية تفاعل الاسترة للزيوت المستخدمة تبين ان درجة التفاعل هي 2/3 و طاقة التنشيط هي 51,367 كيلو جول/مول ومعامل تردد يساوي 26219,13 لتر/مول. دقيقة.

الكلمات الدالة : استرة , زيت مستخدم, تفاعلات العوامل المساعدة الغير متجانسة