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KOH-Impregnated Walnut Shell as a Novel Heterogeneous Catalyst for Biodiesel Production; Optimization of Impregnation Conditions

M. Farahani[1], R. Ghanei*[2]

1 Department of chemical engineering, Islamic Azad University, Shahrood branch, Shahrood, Iran
2 Department of chemical engineering, Islamic Azad University, Farahan branch, Farahan, Iran

Corresponding author: rghaneie@iau-farahan.ac.ir

Abstract:

An increasing demand of energy and reduction of world petroleum-based energy recourses encourage human to use a renewable energy. Biodiesel which is produced from vegetable oils and animal fats can be used as an alternative for diesel fuel with excellent environmental characteristics. Strong alkali materials including NaOH and KOH, as catalyst, are soluble in reaction mixture. It makes the recovery of catalyst difficult and expensive. In order to solve such difficulties, utilization of supports for stabilizing the alkali component is suggested. Walnut shell which is a porous material is a good choice for alkali impregnation. In the present study, effect of impregnation condition of KOH including temperature, solution concentration, and number of impregnation repetition on transesterification of frying oil were investigated. The optimum conditions for impregnation were determined by means of response surface methodology and are as follows; temperature 68.96°C, solution concentration 3.5 M, and number of repetition 2. At such condition, reaction conversion was 99.78% and the mentioned catalyst was deactivated after four usage of reaction.

Keywords: Experimental design, Frying oil, Response surface, Transesterification, Wet impregnation

1. Introduction:

Due to the increase of world population and also rise of fuel price and environmental problems, introducing an ecofriendly and renewable energy source is vital. Bio fuels such as biogas, bioethanol, and biodiesel are important variations of renewable energy (Chakraborty *et al.*, 2010). Bio diesel is a kind of renewable and biodegradable fuel which is similar to the diesel that can be produced from vegetable oils or animal fats. This fuel can be used in diesel engines in blend with petrodiesel or neat. High performance of biodiesel has been confirmed by valid global organizations. Depending on the ASTM, biodiesel is a mixture of mono alkyl esters of long chain fatty acid which can be produced from renewable fatty raw materials including vegetable oils or animal fats (Janaun and Ellis, 2010). Fig.1, illustrates a schematic of transesterification reaction in which one molecule of triglyceride reacts with three molecules of methanol in the presence of a catalyst to form three molecules of methyl ester (biodiesel) and one molecule of glycerol (Yaakob *et al.*, 2012). Biodiesels are highly similar to the petro-diesel, and thus using such fuel in diesel engines does not require fundamental changes. However few adjustments in the timing are necessary due to the differences in some physical properties such as heating value and cetane number (Sania *et al.*, 2014). Table 1 summarizes some important physical properties of biodiesel and petrodiesel depending on the ASTM method (Wan Omar and Saidina Amin, 2011).

Due to the high activity of strong alkali like NaOH and KOH in the transesterification of triglycerides, there is a high demand for using these chemicals as catalysts in the commercial plants (Leung *et al.*, 2010). This type of catalyst is soluble in the reaction mixture which makes the recovery of catalyst difficult and expensive after the completion of the reaction. As a result, in order to simplify the recovery process and also reuse these catalysts, it is proposed to stabilize the active component on porous and insoluble materials as supports (Lam *et al.*, 2010; Noiroj *et al.*, 2009). As can be seen from Table 2, most conducted studies regarding the use of supports were employed synthetic and expensive materials.

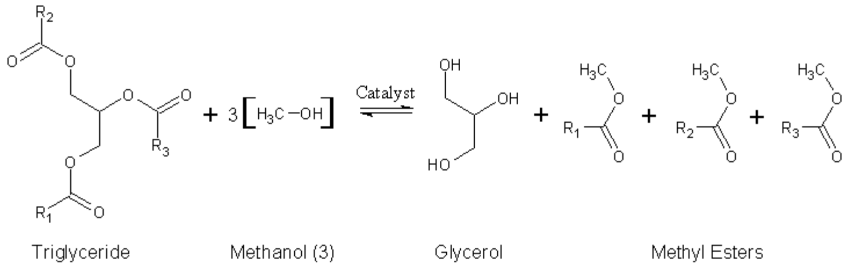

Fig. 1: Schematic of transesterificatin reaction (Yaakob *et al.*, 2012)

Table 1: Comparison of some physical properties of biodiesel and petro diesel (Wan Omar and Saidina Amin, 2011)

Property	***Biodiesel***	***Petrodiesel***
ASTM No.	ASTM D 6751	ASTM D 975
Composition	Methyl esters of fatty acid C_{12}-C_{22}	Hydrocarbons C_{10}-C_{21}
Specific Gravity (g/l)	0.85	0.88
Flash Point (K)	333-353	373-443
Cloud Point (K)	258-278	270-285
Pour Point (K)	243-258	258-289
Water content (% vol.)	0.05	0.05
Carbon content (% wt.)	87	77
Hydrogen content (%wt.)	13	12
Oxygen content (%wt.)	0	11
Sulfur content (%wt.)	0.05	0.05
Cetane number	40-55	48-60

Table 2: Examples of stabilization of alkali materials in solid supports

Catalyst	***Feed***	***Operating Conditions***	***Ref.***
KOH/Al_2O_3	Palm oil	Methanol/oil = 15:1 Catalyst amount = 25 wt.% T = 70 °C t = 2-3 h	Noiroj *et al.*, 2009
KOH/NaY	Palm oil	Methanol/oil = 15:1 Catalyst amount = 10 wt.% T = 70 °C t = 2-3 h	Noiroj *et al.*, 2009
KOH/MgO	Mutton fat	Methanol/oil = 12:1 Catalyst amount = 9 wt.% T = 65 °C t = 20 min	Lam *et al.*, 2010

Walnut fruit contains hard woody shell which can transform to different types of activated carbon. Activated carbon can be used in food industry including sugar and oil production, metal extraction, and water purification and waste water treatment (Dai and Antal, 1999). Walnut shell is the useless byproduct of food industry which has relatively porous tissue and consequently it can be a good candidate for catalyst support. Similar researches including the utilization of charcoal and coconut shell as supports for catalyst impregnation has been reported (Bagramov, 2010). As a result, it is expectable that walnut shell can be successfully employed for alkali (KOH) impregnation. In the present study, the catalyst of transesterification was prepared through the impregnation of KOH on pretreated walnut shell in different conditions including impregnation temperature, solution concentration, and number of repetition. The effect of these factors was then investigated on biodiesel production (reaction conversion) in a uniform condition. All experiments were designed using response surface methodology.

2. Materials and Methods

2.1. Materials

Fully washed walnut shell was supplied from daily home waste and was crushed to particle size of 1.2-2 mm. Potassium hydroxide (85%), Hydrochloric acid (37%), and Methanol (99.8%) were supplied from Merck. Frying oil with the brand of “Varamin” was purchased from local markets.

2.2. Methods

2.2.1. Catalyst preparation:

Sufficient amount of walnut shell was washed with boiling water several times. The washed shells were then remained under solar radiation for 24h. Next, dried shells were crushed and sieved to prepare adequate amount of support with size of 1.2-2 mm. Prior to the impregnation, 10g of the prepared support was placed in a furnace for 1h, at the temperature range of 100-120°C to remove the possible moisture. Then, 100ml of KOH solution was added to 10g of dried support into a 250ml flat bottom flask and impregnation was carried out for 24h at 600 rpm. Varying factors were as follows: Temperature 40, 60, and 80°C; KOH solution concentration 0.5, 2, 3.5M. The impregnated supports was filtered and washed with distilled water. The prepared catalyst was then dried under solar radiation and ambient temperature (average temperature of 30°C) for 24h. Impregnation process was repeated two and three time for some samples according to the experimental design. The design of experiment was performed using response surface methodology. An unblocked Box-Behnken design with three factors including temperature, solution concentration, and number of repetition was employed.

2.2.2. Catalyst Characterization:

Surface area and the pore size of catalyst samples were measured using Belsorp Max apparatus in “Research Institute of Petroleum Industry”, Tehran. This measurement was performed using adsorption and desorption of N_2 at 77K according to ISO 500901 and ISO 9277. Prior to the beginning of the main process, the samples were degassed for 7h at the temperature of 60°C under vacuum condition.

The X-ray diffraction (XRD) patterns of the optimized catalyst was also recorded on a Bruker D8 Advance X-Ray Diffractometer equipped with a graphite monochromator, copper radiation, and scintillation counter (detector) in the range of $2\theta = 5–80°$.

2.2.3. Catalyst Evaluation in Biodiesel Production:

100g frying oil was used for each reaction. The oil was preheated to 60°C in a 250ml three neck flat bottom flask which was placed on a magnetic heater-stirrer and equipped with a condenser and temperature controlling system. In order to remove the moister, proper amount of catalyst was put in a furnace for 1h at 100-120 °C before the beginning of the reaction. 5wt% of catalyst (basedon oil weight) and methanol with a molar ratio (MeOH/Oil) of 12:1 were added to the reactor. Reaction was carried out for 5h at 60 °C under mixing rate of 1000 rpm. At the end of the reaction, catalyst was separated using paper filter and reaction mixture was transferred to a decanter. After enough settling, alcoholic phase including glycerol and unused methanol was separated from produced biodiesel. Then produced biodiesel was washed with hot distilled water to remove any remained KOH in ester phase. After the washing processes (usually 3 times), purified biodiesel was heated up to 110 °C for 20min for eliminating any water trace.

2.2.4. Catalyst Reusability Test

In the aim of evaluating the catalyst reusability, the optimum impregnation conditions were first determined and the prepared catalyst was then used in the transesterification at similar operating conditions for several times. It should be noted that the utilized catalyst was separated for another reaction without any treatments. This procedure was continued until the deactivation of the catalyst.

3. Results and Discussion:

3.1. Catalyst Characterization:

Surface area and pore size of two samples including walnut shell before and the impregnated walnut shell (in optimum condition) was measured and reported in Table 3 and the obtained data are compared with other reported data. The obtained surface area of the current study was comparable with other supports including snail shell and egg shell, however the pore volume and diameter of the mentioned samples were much less than the other reported data. This can be a negative point in the case of oil transesterification and it can be concluded in this case only the outer surface of catalyst is active. Also, a slight increase in the surface area was observed after the impregnation which may be due to the swelling of walnut shell.

Table 3: BET results for prepared catalyst in comparison to similar studies

Catalyst	***Surface area (m^2/g)***	***Pore Volume (m^3/g)***	***Pore Diameter (nm)***	***Ref.***
Walnut shell (before imperegnation)	0.423	1.39e-3	3.29	Present work
Walnut shell (after impregnation)*	0.529	1.417e-3	3.29	Present work
Snail shell	0.5	0.9	98.6	Viriya-empikul *et al.* 2012
Egg shell	0.5	0.9	99	Viriya-empikul *et al.* 2012
Meretrix shell	0.2	1.1	99	Viriya-empikul *et al.* 2012
Lime	6.064	3.792e-2	25.3	Ghanei *et al.* 2013
* Optimum impregnation conditions were applied				

XRD pattern for optimized catalyst was illustrated in Fig. 2. According to this figure amorphous structure of walnut shell is obvious. Three distinct peaks are addressing to the impregnated KOH.

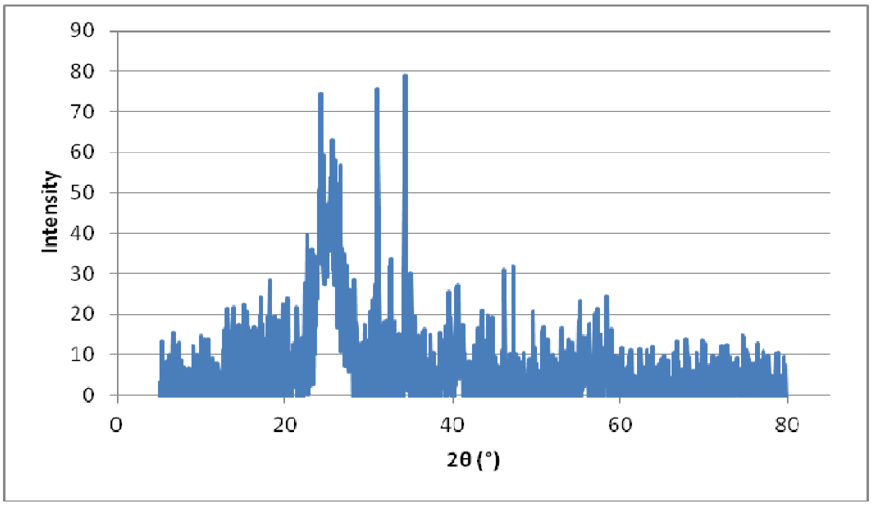

Fig. 2: XRD pattern for the optimized catalyst

3.2. Optimization of Impregnation Conditions:

A three-factor three-level one block Box-Behnken design using response surface methodology was performed to optimize the impregnation conditions including temperature, solution concentration, and loading repetition (Table 4). All samples of catalysts were prepared based on conditions which are illustrated in Table 4. The mentioned catalysts were then evaluated in the production of biodiesel. Conversion of each reaction was also reported in Table 4, as response of design.

Table 4: Experimental design for optimizing impregnation conditions and transesterification conversion as response

Run No.	*Impregnation Solution Concentration (M)*	*Impregnation Temperature (°C)*	*Impregnation Repetitions No.*	*Loading percent* (%)*	*Reaction Conversion (%)*
1	0.5	60	1	7.9	1.72
2	2	40	3	147.2	83.54
3	2	80	1	79.3	46.83
4	2	60	2	112.8	79.08
5	2	60	2	114.5	79.26
6	0.5	60	3	21.8	60.67
7	2	60	2	99	78.65
8	2	80	3	225.8	85.09
9	0.5	80	2	17.52	48.51
10	3.5	40	2	194.4	90.61
11	0.5	40	2	15.7	46.43
12	3.5	60	1	155.6	77.61
13	2	40	1	68	43.43
14	3.5	80	2	206.8	94.39
15	3.5	60	3	286.2	98.63
* Percentage of impregnated KOH to walnut shell					

Following correlations were obtained after analyzing the experimental results (response) versus designed factors by means of Minitab® software:

$$Y = -104.5 + 41.3A + 83B + 0.7C - 3.1A^2 - 12.3B^2 - 6.3AB \tag{1}$$

Where "Y" is reaction conversion (%), "A" is impregnation molar concentration of solution (M), "B" is number of impregnation repetition, and, "C" is impregnation temperature (°C). R-squared value for this correlation was obtained 99.2 % which is because of excellent agreement between experimental data and selected model. The analysis of variance (ANOVA) can be seen in Table 5. The "Prob < F" value for the quadratic model was significant (<0.05) which indicates the fact that the model terms are significant. The F-value for response was quite high; giving more emphasis to the variance that was explained by the model. Moreover, p-values of the studied variables were found to be less than 0.05, implying their significant effects on the responses. Fig. 3, shows the predicted data using adjusted model versus actual data. Closeness of points to line y=x refers to the accuracy of model.

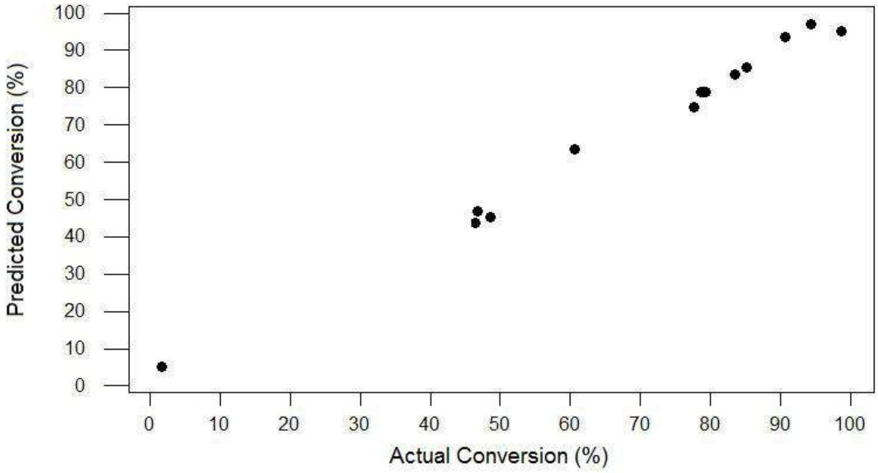

Fig. 3: Predicted versus actual chart for selected model

Table 5: ANOVA values for conversion

Source	***DF***	***Seq SS***	***Adj SS***	***Adj MS***	***F***	***P***
Regression	9	9405.06	9405.06	1045.01	73.22	0.000
Linear	3	8345.96	8345.96	2781.99	194.91	0.000
Square	3	697.84	697.84	232.61	16.30	0.005
Interaction	3	361.25	361.25	120.42	8.44	0.021
Residual error	5	71.37	71.37	14.27		
Lack of fit	3	71.17	71.17	23.71	241.5	0.004
Pure Error	2	0.20	0.20	0.10		
Total	14	9476.42				

The effects of mentioned factors on reaction conversion were depicted in Figures 4-6 in 3D charts (response surface). According to Fig. 4, the increase of impregnation solution concentration has a positive effect on the conversion rate, especially when the impregnation was not repeated. This effect was not observed to this extent with the increase of repetition number. However, it should be noted that the number of repetition in the load of KOH appears to have a positive effect on the conversion rate. Such an effect was confirmed on low concentrations. In the high concentrations, on the other hand, this effect was decreased when the number of repetition was exceeded 2. Similar results were observed by Noiroj *et al.* (2009) and Borges *et al.* (2012). Such interactions between these factors are considerable.

Fig.5 demonstrates the positive effect of repetition. Although this factor has a positive effect, it appears that more than two repetitions are not useful and also no more increase in conversion was observed. Impregnation temperature has not considerable effect on the conversion. No remarkable interaction was observed between these two factors.

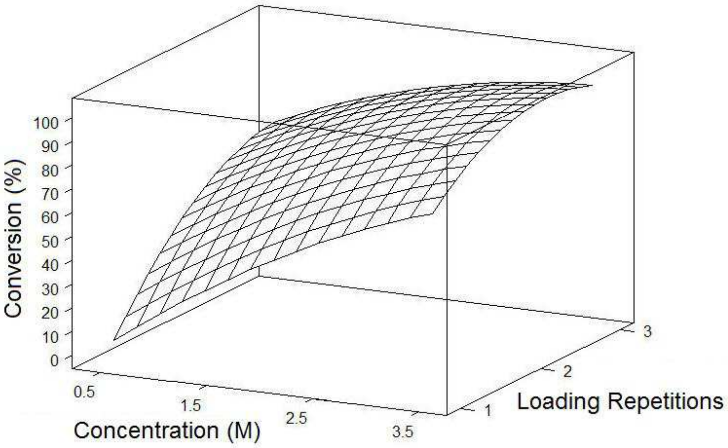

Fig. 4: Conversion versus impregnation solution concentration and loading repetition (impregnation temperature = 60°C)

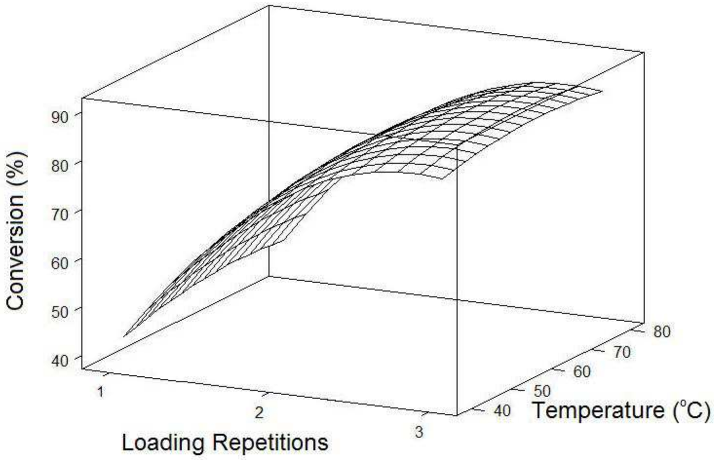

Fig. 5: Conversion versus loading repetition and impregnation temperature (impregnation solution concentration = 2 M)

Two main points including positive effect of impregnation solution concentration and weak effect of temperature were confirmed in Fig. 6 and a slight interaction between these two factors is seen. The effect of temperature was also increased with the increase of solution concentration.

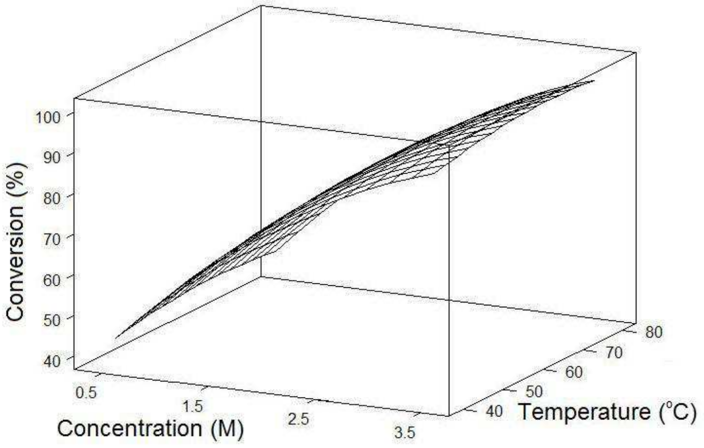

Fig. 6: Conversion versus impregnation solution concentration and impregnation temperature (loading repetition = 2)

In order to maximize the reaction conversion, the mentioned factors were optimized using response optimizer section of software and the obtained optimum conditions were as follows: impregnation solution concentration 3.5 M, temperature 67.7°C, and loading repetition 2.4. At the mentioned conditions, predicted conversion rate was 99.9%. Since the repetition is not a continuous value, the amount of 2.4 is not achievable, thus further optimization was performed in levels of 2 and 3 for this factor. Therefore, maximum of conversion was expected to be 97.85% when the impregnation solution concentration is 3.5M, temperature 68.96°C, and loading repetition equal to 2. Optimum catalyst was prepared in the obtained optimum conditions and was evaluated in biodiesel production. At the mentioned conditions reaction conversion was observed equal to 99.78% which is 1.9% higher than the predicted value.

3.3 Catalyst Reusability Test:

Optimum catalyst was reused in transesterification several times. The results were demonstrated in Fig. 7. Depending on the obtained data, deactivation process of catalyst started in the second use and after four use the catalyst was completely inactive. This result is in accordance to Noiroj *et al.* (2009) and Borges *et al.* (2012). In the impregnation of KOH on Al_2O_3, 91.07% and 3.18% of conversions were achieved on the first and third use, respectively. Although the important role of support is obvious, leaching of KOH by reaction mixture and catalyst deactivation rate is remarkable.

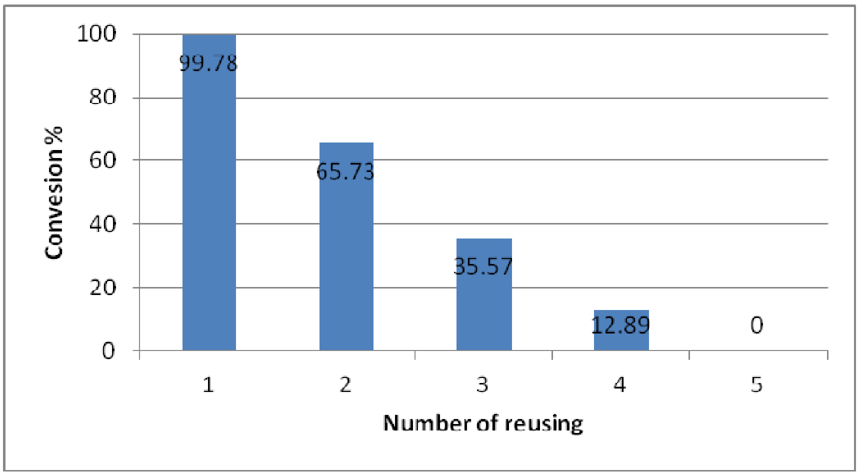

Fig. 7: Catalyst activity after some reusing

4.0 Conclusion:

In the current study, walnut shell as a useless byproduct of food industry and daily domestic use was successfully applied for preparing heterogonous catalyst by impregnation of KOH. Impregnation condition including solution concentration, temperature, and repeat of impregnation were investigated and optimized using response surface methodology. Optimum conditions were determined and equal to 3.5 M, 68.96°C, and 2, respectively. At these conditions, predicted and observed conversion for transesterification of frying oil to biodiesel was 97.85% and 99.78%, respectively. Deactivation rate of catalyst was considerable and in fifth use it was completely inactive.

5.0 Acknowledgment:

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