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Homogeneous and new heterogeneous developed catalysts for the production of biodiesel from the waste canola cooking oil

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ABSTRACT

Identification of renewable energy feedstocks as the substitutes for fossil fuels is a challenging task for researchers. This study aims to show the potential of using biomass-based catalysts in the biodiesel production process. And, the effects of ten different ordinary and green catalysts of KOH, NaOH, $Zn(NO_3)_2$, natural zeolite of clinoptilolite, clinoptilolite-NaOH, clinoptilolite-KOH, clinoptilolite- $Zn(NO_3)_2$, waste cinnamon bark (WCB)-NaOH, WCB-KOH, and WCB- $Zn(NO_3)_2$ on the yield of transesterification reaction were studied. The synthesized catalysts were characterized by FTIR, XRD, and FESEM-EDX analyses. Based on the reported results, Clinoptilolite-KOH and WCB-NaOH composite catalysts afforded the highest yields of produced biodiesels. Chemical compositions of the produced biodiesels were identified by GC and GC-MS analyses. Lauric acid methyl ester (57.5%) and Palmitic acid methyl ester (30%) are the most dominant FAME in the biodiesels produced by clinoptilolite-KOH and WCB-NaOH catalysts. However, for other catalysts, Linoleic acid and oleic acid methyl esters are the most dominant FAME in the produced biodiesels. The produced biodiesels are in density and viscosity ranges of 0.86 to 0.91 (g/cm^3) and 2.4 to 20 (mm^2/s) with acid values less than 0.5 (mg KOH/g).

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1. Introduction

The rising world population and economic development led to an increase in the consumption of oil-based fuels [1]. However, various researchers studied on the production of sustainable and renewable energy sources because of the gradual reduction in crude oil resources and the environmental problems associated with fossil fuels [2, 3].

Biodiesel is a non-toxic and renewable source of energy that can be used individually or it can be mixed with petroleum diesel in existing compression engines [4, 5].

Different methods can be used for biodiesel manufacturing such as micro-emulsion, pyrolysis, and transesterification [6, 7]. Among them, transesterification is a famous method in which, biodiesel was generated from the transesterification of triglyceride in vegetable oils with monoalkyl alcohols in the presence of a feasible catalyst [8- 10]. Biodiesel has several advantages in the environmental aspect including biodegradability, lower toxicity level, environmentally friendly, and higher values of combustion efficiency and cetane number [11,12]. By use of cottonseed, soybean, and other food-grade vegetable oils as the raw materials, the production cost of biodiesel is relatively high and it consists of about 70 to 95% of the raw material costs [13]. Hence, by using non-food feedstocks such as micro-algae, animal fats, and waste cooking oil the production cost is reduced efficiently to about 90-70% [14].

Nowadays, the main countries which were produced biodiesel on the industrial scale, select production methods in alignment with their natural resources. For example, the United States, Argentina, and Brazil utilize soybean oil as the raw material for biodiesel production, while Europe relies on rapeseed oil and China predominantly centers on waste oil [15].

Non-food feedstocks mainly contain high free fatty acids and when they were used as the biodiesel feedstock with an alkaline catalyst like NaOH or KOH, a viscous foaming soap by-product was produced causing the catalyst deactivation and unpurified biodiesel product. Therefore, the yield of produced biodiesel decreased sharply [16-18]. In the transesterification process, the choice of appropriate catalyst is important. By using a homogeneous acidic catalyst, removing free fatty acids is not required. However, serious drawbacks of low reaction rate and highly corrosive environment are concluded [19]. Alkaline catalysts have been mostly employed in industrial processes and they show high production rates and proper yield of products. However, they lead to saponification in the reaction medium, waste generation and they cannot be reused [20]. The use of heterogeneous catalysts for the biodiesel production process has many advantages such as good reusability, easy separation, and wide availability that lead to reduced final cost of product [21, 22]. Therefore, researchers used different new heterogeneous catalysts for transesterification reactions. For example, $\text{SO}_4/\text{Fe-Al-TiO}_2$ catalyst was prepared and used by Gardy et al. [23] for converting the waste cooking oil into biodiesel by using simultaneous esterification-transesterification reactions. A high yield of produced biodiesel with good recyclability and stability performance was indicated with feedstocks containing 20 w% free fatty acids. Xie and his co-workers [24] synthesized HPW/UiO-66-2COOH catalyst for biodiesel production from low-cost acidic oils. The selected catalyst shows a relatively good yield of reaction with proper reusability. Helmi and Tahvildari [25] used KOH/clinoptilolite catalyst for the production of biodiesel via the electrolysis technique. Moreover, Helmi et al. [26] developed a phosphomolybdic acid/clinoptilolite green catalyst for converting waste cooking oil into biodiesel.

They use the response surface methodology for optimization of the used operation parameters.

The biomass-based catalysts have been proven effective for the synthesis of biodiesel because they are very suitable for waste management and their biodegradability [27,10, 28]. Furthermore, catalysts based on agricultural wastes are inexpensive, non-toxic, widely available, and non-corrosive.

Many solid catalysts were mentioned in the literature for biodiesel production [29,30]. However, based on our knowledge, WCB has not used previously as a catalyst for biodiesel production. Waste agricultural products may be used as the templates for the synthesis of different catalysts for the biodiesel production process. For example, Mulkan and his co-workers [27] developed a new solid catalyst based on jackfruit peel waste for the transesterification reaction of waste frying oil. They optimized the reaction parameters by using the central composite design method and they reported a maximum reaction yield of 92.83% by the calcinated ash at 500°C. The sulfonated magnetic porous biochar-based catalyst, produced from rice husk, is used by Saidi et al. [31] for biodiesel production with a maximum conversion yield of about 98% under optimal conditions. Moreover, a novel solid catalyst based on the dragon fruit peel ash was produced by Khiangte and his co-workers [32] for the production of biodiesel from soybean oil and they report a process yield of 99% at room temperature in a time of 5 h with 8 wt% amount of the used catalyst.

In the present work, Clinoptilolite and waste cinnamon bark were selected as the cheap and eco-friendly components of inorganic and organic solid templates, and different types of homogeneous and heterogeneous catalysts were synthesized by using pure and the binary composites of clinoptilolite, waste cinnamon bark, zinc nitrate, sodium and potassium hydroxides. The synthesized catalysts

were characterized and they were used for the production of biodiesel. Finally, the yields of produced biodiesels and their compositions were compared.

2. Experimental

2.1. Materials

The used chemicals in this study are methanol (CH_3OH) (99.9 % purity), anhydrous sulphuric acid (H_2SO_4) (purity>98.6 %), sodium hydroxide (NaOH) (purity 99 %), and potassium hydroxide (KOH) pellets (purity 99 %) which were purchased from Ghatran-shimi (Tehran, Iran). Zinc nitrate hexahydrate ($\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$) was purchased from Sigma Aldrich. Natural zeolite of clinoptilolite was prepared from Semnan mines (Iran). The cinnamon bark was purchased from the supermarket. The clinoptilolite and cinnamon bark particles were ground to sizes less than 0.1 mm and washed three times with double distilled water and ethanol and finally, they dried in 120°C oven for 2 hours. The essential oil of powder cinnamon bark was extracted by using the soxhlet extraction method with the solvent of ethanol (3 hours).

Whatman filter paper (541 grade) was used for the separation of biodiesel from the solid catalyst. The waste canola cooking oil was prepared from the restaurant.

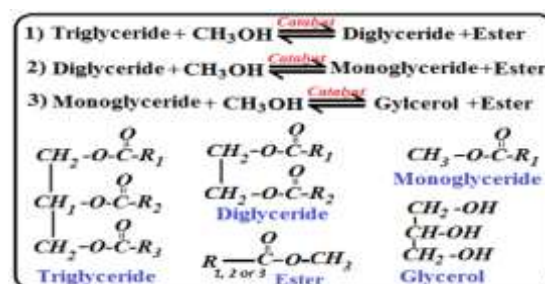


Fig. 1. Reaction mechanism for the biodiesel production process.

2.2 Biodiesel production method

The values of process parameters were selected based on the reported values in the literature [10, 22, 28, 33] and some primary experiments. For pre-treatment of the waste canola cooking oil, the waste oil was firstly vacuum filtered using Whatman filter

paper (Grade 42). For the esterification process, 300 ml of the waste oil was preheated for 15 min at 45°C in an Erlenmeyer in continuous stirring mode, then sulphuric acid (2M, 1.5 Volume%) was added to the oil and mixed for a further 15 min. Then, methanol (1:15 molar ratio) was added to the mixture and the system was heated to 75°C and mixed for 1 hour (rpm=500) by using a heater stirrer. The mixture was phase separated by decantation for 24 hours and the esterified oil phase was separated and washed three times with hot water. Finally, it was stored for transesterification reaction. The free fatty acid contents of the used oil samples before and after the esterification processes were determined by titration method, and it was found that the acid quantity of the used canola oil decreased from 13.98 to about 0.5 (mg KOH/g oil) during the esterification process. The excess methanol was recovered using a rotary evaporator.

The biodiesel production mechanism is sketched in figure 1. As can be seen, in the transesterification reaction, triglycerides reacted with alcohol molecules, and a mixture of mono-alkyl esters was produced. In this reaction, the glycerine was produced as a by-product.

For the transesterification process, a 250 ml conical flask, which is connected to a reflux condenser, is used and the system is immersed in a glycerine bath to maintain the desired temperature. The constant conditions of 65°C, atmospheric pressure, 1 hour reaction time, and mixing rate of 500 rpm were used for the transesterification reaction.

For a typical transesterification process, the methanol-catalyst solution was prepared by mixing 0.2 g of the solid catalyst with 60 ml methanol for 15 min. 10 ml of esterified oil was heated to 65°C and the methanol-catalyst solution was added to it and they mixed for 60 min. Then, the mixture was phase-separated by decantation for 24 h and the upper phase was collected. The produced biodiesel

was washed three times with distilled water and it remained for 60 min in a rotary evaporator at 80°C for separation of any remaining water or alcohol. All experiments were done in duplicate, and the average data were reported.

Finally, the excess methanol was recovered by distillation.

The yields of produced biodiesel were calculated using the following formula:

Yield of biodiesel (%) =

$$\frac{\text{weight of produced biodiesel}}{\text{weight of waste oil}} \times 100$$

2.3. Catalyst production methods

In this work, different catalysts were synthesized and they were used for the transesterification process. NaOH, KOH, Zn (NO₃)₂, and the natural zeolite of clinoptilolite were used as the pure catalysts. Moreover, they were used for synthesizing composite catalysts based on two cheap and eco-friendly supports of clinoptilolite and waste cinnamon bark.

As mentioned in the literature [30, 34] natural zeolites, like clinoptilolite, are highly porous materials with high specific surface area and they can increase the physical contact between the oil molecules and catalyst surface. Therefore, the production of composite catalysts from the usual catalysts like NaOH, KOH, Fe₃O₄, and ZnNO₃ can increase the activity of catalysts simultaneously with decreasing the cost of materials. In this work, the production of composite catalysts based on clinoptilolite is relatively similar to the reported results of literature [30, 34], but WCB is selected as another eco-friendly porous material and it was used as a new template for the produced composite catalysts.

For synthesizing of composite catalyst of NaOH-clinoptilolite, 0.1 g of NaOH was mixed with 20 ml of distilled water, and 2 g of solid filler of clinoptilolite was added slowly to them in the

stirring mode. The system was mixed for 1 hour. Then, it dried for 4 hours in an oven (100°C) and calcined for 2 hours in a 400°C muffle furnace in an inert atmosphere. Finally, the produced composite was powdered and stored in the closed flask.

Other solid catalysts of KOH-clinoptilolite, Zn(NO₃)₂-clinoptilolite, NaOH-WCB, KOH-WCB, and Zn(NO₃)₂-WCB were synthesized in the same way.

2.4. Characterization methods

Fourier Transform Infrared Spectroscopy (FTIR) was used to study the changes in the surface chemistry and functional groups of the produced catalysts. A Unicam 4600 FTIR spectrometer (Mattson, USA) was used over scanning wave numbers between 400 to 4000 cm⁻¹. The KBr disc without a sample was used for the collection of the background.

Field-emission Scanning Electron Microscope (FE-SEM) (TESCAN BRNO-MIRA3 LUM) operating at 10 kV accelerating voltage, was used to determine the morphology and particle size of the produced catalyst in the magnification of 100 kx. A D8-advanced X-ray diffractometer analysis (XRD) (BRUKER AXS, Karlsruhe, Germany), was used for the determination of the crystalline phases of the synthesized catalyst by using Cu-K α X-ray as a radiation source, (wavelength $\lambda = 1.541874 \text{ \AA}$) in a 2θ range of 4°–60°.

GC and GC-MS analyses were used for the identification of chemical compositions of the produced bio-oils. For GC-MS analysis, an Agilent 7890 system with a capillary column (100 m length, 0.25 mm initial diameter, and thickness of 0.2 μm) was used. The temperature of oven was increased as follows: (i) 140 °C for 5 min, (ii) from 140 °C to 240°C at a heating rate of 4°C/min. The constant helium flow rate of 10 mL/min with a split ratio of 1:100 was used for carrier gas. The detector and injector temperatures were held constant at 260°C.

A Varian Cp 3800 gas chromatography system with a capillary column (30 m length and 0.25 mm ID) and equipped with a flame ionization detector was used for GC analyses. The injector and detector temperatures were set to 180 and 200°C. The oven temperature was maintained at 60 °C for 3 min, then it increased to 180°C at the rate of 5°C/min and remained constant at 180°C for 20 min, then the temperature of the oven further increased to 200°C at 10°C/min. Then, it was kept constant at 200°C for 5 min. Argon carrier gas with 1 ml/min flow rate was used. Moreover, the injection volume was 1 μl and the split ratio was 1:5.

The density of the produced biodiesel was measured by using a hydrometer following the ASTM D1298 test method. By using the ASTM D445 test technique, the Kinematic viscosity of the produced biodiesel was assessed with an Ostwald's viscometer at 40°C. All experiments were done in duplicate, and the average data were reported.

3. Results and Discussion

3.1. Catalyst characterization

The active surface functional groups presented in different catalysts based on clinoptilolite and waste cinnamon bark were identified by FTIR analysis and the results are depicted in figure 2. Figure 2 (a) shows the FTIR spectra of particles based on the waste cinnamon bark. For the pure cinnamon bark, the broad peak of about 3400 cm⁻¹ shows the presence of O-H bonds in the water, alcohols, or phenol molecules [33] which were decreased sharply in modification processes. This phenomenon can show a decrease in the concentration of these molecules during calcination or drying processes. The peak located at about 2924 cm⁻¹ refers to C-H functional groups in cyclic or aliphatic alkyls [35]. The broad bonds observed in about 1500 to 1600 cm⁻¹ can be attributed to C=C bonds in the polycyclic aromatic rings [22] that were observed in all the samples. The peaks located at

1052 to 1246 cm^{-1} may be associated with the vibrations of C-O bounds of carboxylic acids or alcohols [36, 22, 33]. As can be seen, these components have not appeared in $\text{Zn}(\text{NO}_3)_2$ -WCB and KOH-WCB particles.

Figure 2 (b) shows the FTIR patterns of the zeolite-based catalysts; the peaks in about 1000 to 1100 cm^{-1} arose from the stretching vibrations of Si-O-Si bonds [22].

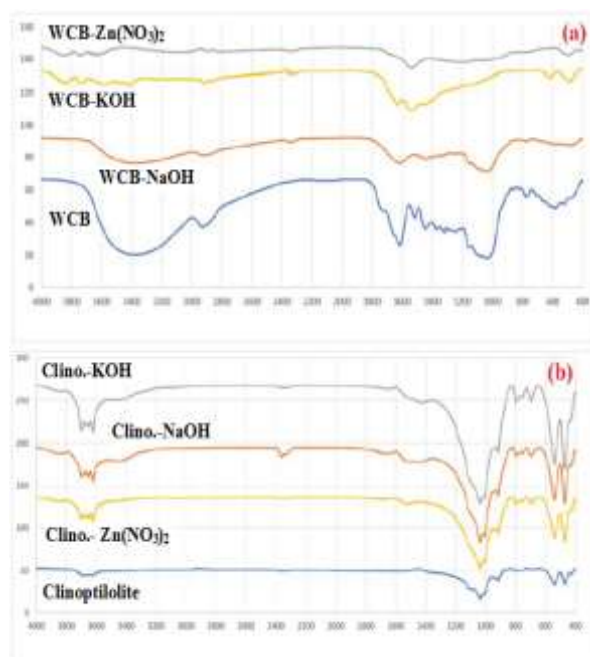


Fig. 2. The results of FTIR analyses for the synthesized catalysts. (a): catalysts based on WCB. (b): catalysts based on clinoptilolite.

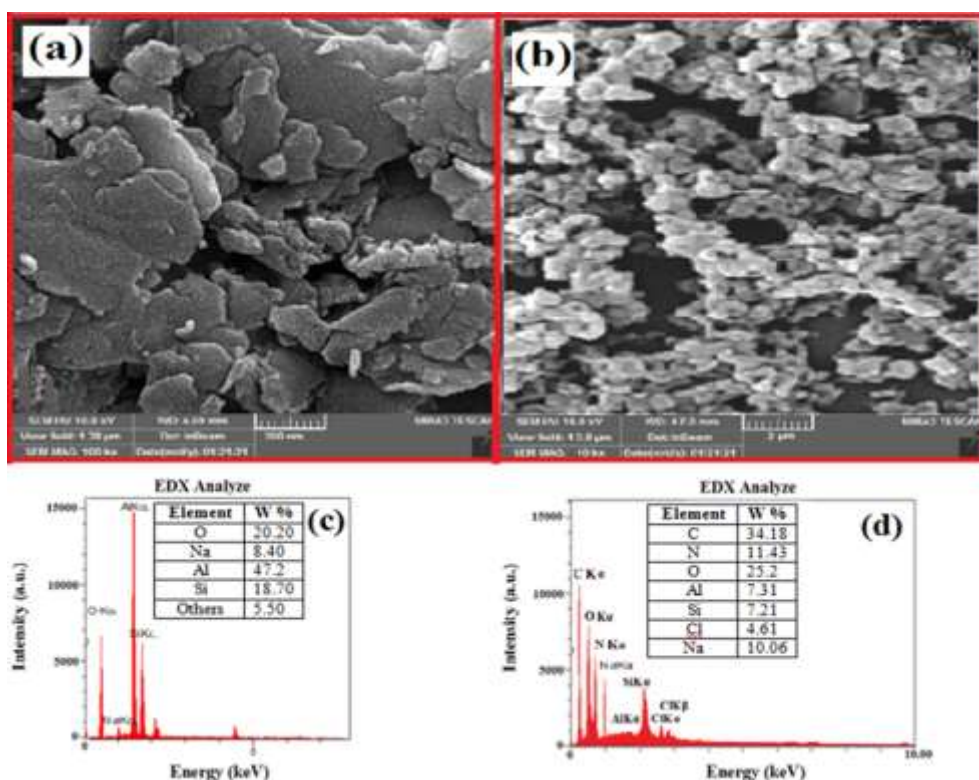


Fig. 3. The results of SEM analyses of (a): NaOH-clinoptilolite and (b): NaOH-WCB. And the EDX analyses. (C): NaOH-clinoptilolite, and (d): NaOH-WCB.

The peak appeared at about 460 cm^{-1} in FTIR results of $\text{Zn}(\text{NO}_3)_2$ -WCB particles, depicts the presence of Zn-O bonds in the produced particles.

The vibration bands at about 950 to 1250 cm^{-1} in figure 2 (b) result from the alumina-silicate structural units in the zeolite-based particles [37].

Moreover, the sharp peaks in about 450 cm^{-1} to 550 cm^{-1} are related to metal oxides [38] and they were increased during the treatment of clinoptilolite by NaOH, KOH, and $\text{Zn}(\text{NO}_3)_2$ metal oxides.

The SEM images and the EDX analysis results for two samples of NaOH-clinoptilolite and NaOH-WCB are depicted in Fig. 3. The clinoptilolite-based particles have plate shapes with different sizes between 40 to 500 nm. However, the NaOH-WCB particles are agglomerates that have relatively spherical shapes and with mean particle sizes of about 1000 nm. The EDX analyses show that Al, Si, and O are the main elements in the clinoptilolite-based catalyst and C, O, N, and Na are the main elements in the WCB-based catalyst.

The XRD analysis results for two samples of NaOH-clinoptilolite and NaOH-WCB powders were reported in Fig. 4. The main peaks in the 2θ angles of 18° , 26° , 31° , 39° , 42° , and 43° in clinoptilolite-based particles, are related to clinoptilolite natural

zeolite [39]. However, a very amorphous phase with no sharp peak was detected in WCB-based particles. Small peaks that appeared at about 32° in the XRD histogram of two samples may be attributed to sodium oxide [40, 41], and the validation was performed using JCPDS cards (No. 03-1074).

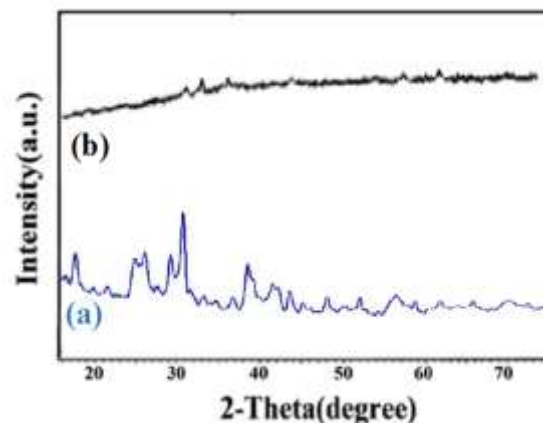


Fig. 4. The XRD analyses results of (a): NaOH-clinoptilolite and (b): NaOH-WCB.

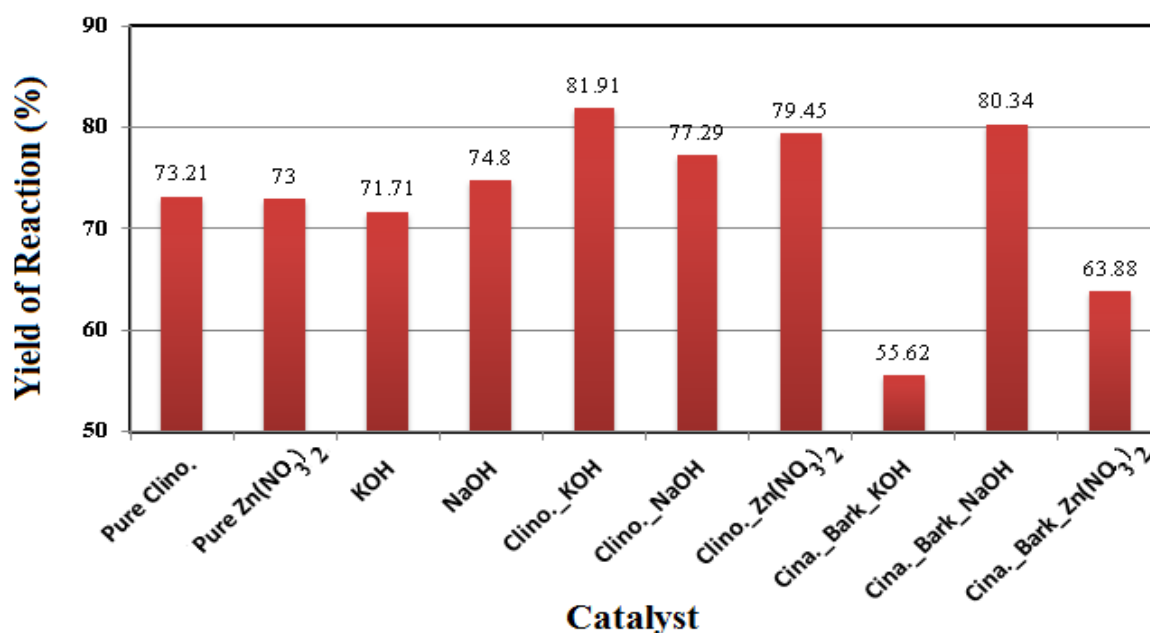


Fig. 5. The yield of produced biodiesel by using ten different catalysts.

3.2. Yields of the produced biodiesels by different catalysts

The use of solid supports in the structure of the used catalyst has many advantages such as: easy separation of catalyst, reducing the bad

environmental effects, and reducing the cost of processes [42, 43]. Among them, heterogeneous catalysts produced from waste or eco-friendly materials have drawn significant attention in recent years [42]. In this work, two low-cost and eco-

friendly solid supports were used and the obtained results were compared.

The efficiencies of the produced biodiesels by using different catalysts are shown in Fig. 5. As can be seen, the efficiencies of reaction by using different catalysts are relatively high. Clinoptilolite-KOH and WCB-NaOH show the best reaction yield. However, WCB-KOH shows the least value of the reaction yield.

By using the pure catalysts of clinoptilolite, $Zn(NO_3)_2$, NaOH, and KOH the reaction efficiencies are between 71% and 74%. But by addition of NaOH, KOH, and $Zn(NO_3)_2$ to clinoptilolite, the reaction efficiency increased to about 80%. Joorasty and his co-workers [34] reported the relatively same results for biodiesel produced from *Amygdalus scoparia* oil. They synthesize NaOH/c clinoptilolite- Fe_3O_4 particles as a novel catalyst for producing biodiesel. Bambase et al. and Liao and Chung [44, 45] reported the

relatively same results for NaOH and KOH-doped CaO catalysts. Based on their results, higher NaOH/KOH concentrations result in more OH ions loaded into the porous structure of CaO and increase the rate of methyl ester synthesis.

For the catalysts based on the WCB support, the NaOH-WCB shows the best results with reaction efficiency higher than 80%. However, For WCB-KOH and WCB- $Zn(NO_3)_2$ catalysts, the decrease in reaction yield may be attributed to the decrease in the catalyst's active surface because of heterogeneities. Methanol and the used canola oil are relatively immiscible; therefore, the contact between the catalyst and the reagent is limited. Bambase and his co-workers [44] showed the same results.

Easy recovery and reusability are some of the advantages of heterogeneous catalysts in comparison with homogeneous catalysts.

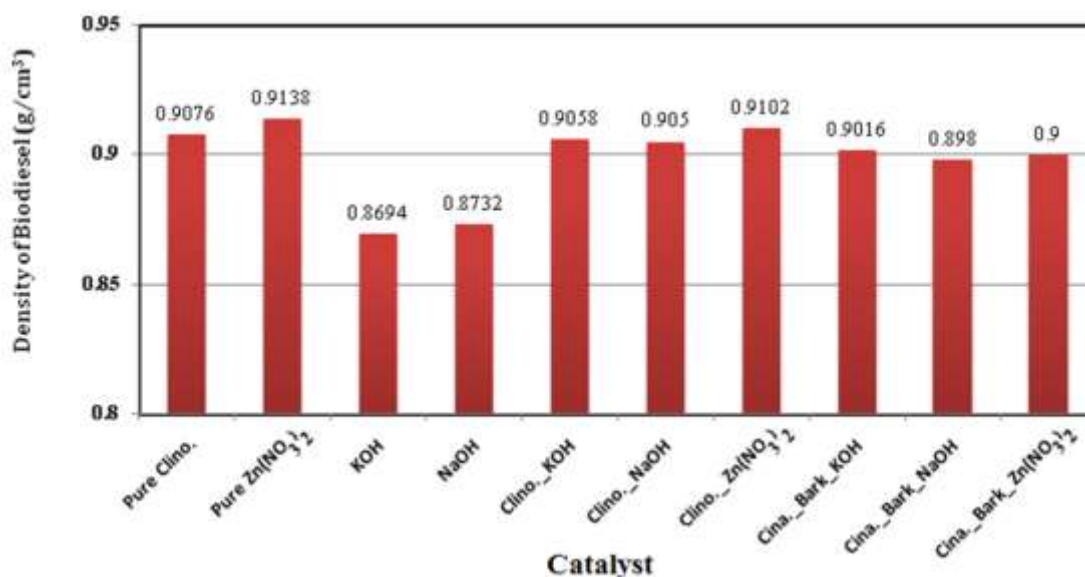


Fig. 6. Densities of the produced biodiesels by using ten different catalysts.

For exploring the reusability of the produced catalysts, the WCB-NaOH catalyst was selected and after each run, it separated from the reaction medium by centrifugation. The separated catalysts were washed with ethyl acetate and hexane to eliminate

any pollutants. Then, they were dried in an oven at 95°C for 5 h. The activity of the recycled catalyst was investigated at the same reaction conditions and for four consecutive rounds. The yield of reaction for the conversion of waste canola cooking oil into

the biodiesel product decreases after each experimental run, from 81 % in the first run to the yield of about 73 % in the fourth run. The observed decrease in the yield of reaction may be related to the leakage of active sites of catalyst, which minimizes the capacity of regenerated catalyst for the generation of the same catalytic power after each run.

3.3. Comparison between the characteristics of the produced biodiesels

In this study, the waste canola oil (0.921 g/cm^3) is used for the production of biodiesel. The densities of different biodiesels are usually between 0.86 g/cm^3 and 0.90 g/cm^3 [46]. A comparison between the densities of the produced biodiesels by ten different catalysts was developed in Fig. 6. Minimum densities of the produced biodiesels are related to biodiesels produced from pure KOH and NaOH catalysts and the maximum densities are obtained by

using $\text{Zn}(\text{NO}_3)_2$ and clinoptilolite- $\text{Zn}(\text{NO}_3)_2$ catalysts.

The differences between the densities of the produced biodiesels obtained from different catalysts are related to their different chemical compositions, which are studied in the next section. For example, the density of Linoleic acid methyl ester is about 0.895 g/cm^3 , which is higher than other detected fatty acid methyl esters.

Viscosity is an important parameter for the produced biodiesels which has a major role in the atomization of fuel [47]. For the vegetable oils used for the production of biodiesel, usually, it is needed to lower viscosity by transesterification reaction [48]. In this reaction, the triglycerides, which are highly unsaturated fatty acids, transform into mixtures of more saturated long-chain fatty acid esters. During the transesterification reaction,

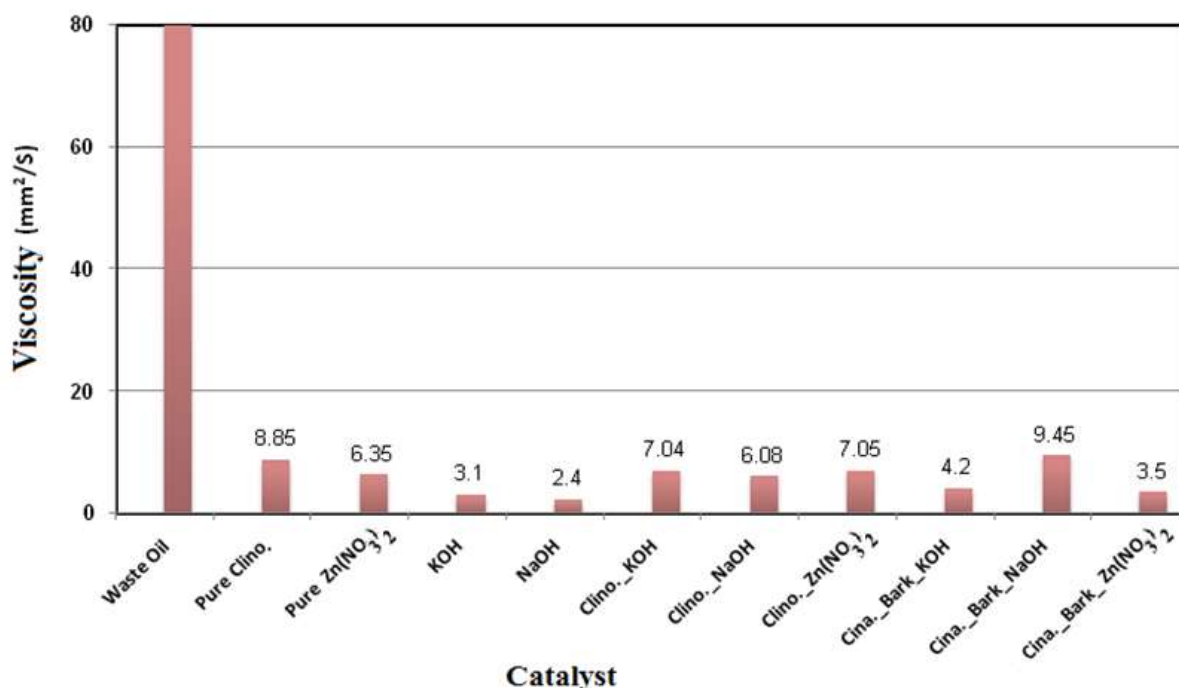


Fig. 7. Viscosity of the produced biodiesels by using ten different catalysts.

the viscosity of vegetable oils was decreased by an order of magnitude [49]. Fig. 7 shows the viscosity of produced biodiesels. As can be seen, the viscosities of the produced biodiesels were 3.1, 2.4,

7.04, and 9.45 mm^2/s for the used catalysts of KOH, NaOH, zeolite-KOH, and WCB-NaOH, which were formed from canola waste cooking oil with a viscosity of $80.1 \text{ mm}^2/\text{s}$.

3.4. Composition of the produced biodiesel

The chemical compositions of the produced biodiesels by using ten different catalysts were detected by the GC-MS method and the results are reported in table 1. The fatty acid compositions of waste canola cooking oil are as follows: Lauric acid (3%), myristic acid (7%), palmitic acid (6%), stearic acid (1.5%), oleic acid (61%), linoleic acid (21%), eicosenoic acid (1%).

As can be seen, seven fatty acid methyl esters of lauric acid methyl ester, myristic acid methyl ester, palmitic acid methyl ester, linoleic acid methyl ester, oleic acid methyl ester, stearic acid methyl ester, and eicosenoic acid methyl ester are the main components of the produced biodiesels. These results are in relative agreement with the reported results of Kassem and his co-workers [50].

As mentioned by Mulkan et al. and Buasri and his co-workers [27, 33] in a transesterification reaction the triglyceride molecules of waste oil (with different molecular weights and different chains) are reacted with the short-chain alcohols and converted to fatty acid methyl ester and glycerol molecules in the presence of a suitable catalyst. Various catalysts with different active sites may lead to different FAME because they produce different intermediates and may have different reaction mechanisms.

In this work, by using the composite catalyst of clinoptilolite-KOH, the least molecular weight fatty acid methyl esters were produced. However, the use of pure NaOH as the catalyst leads to the production of fatty acid methyl esters with higher molecular

weights in comparison with others. Moreover, the use of WCB as the catalyst support leads to the production of fatty acid methyl esters with lower molecular weights in comparison with clinoptilolite.

4. Conclusions

The esterification /transesterification processes of waste canola cooking oil were examined by using ten different pure and composite catalysts. For increasing the physical contact between the oil molecules and catalyst surface, two high porosity and eco-friendly solids of clinoptilolite and WCB were used as the solid base for the composite catalysts. By using these composite catalysts, biodiesel with a yield of higher than 80% was achieved. Moreover, the viscosities of the produced biodiesels were significantly lower than the viscosity of starting waste oil. Fatty acid methyl esters of lauric acid methyl ester, myristic acid methyl ester, palmitic acid methyl ester, linoleic acid methyl ester, oleic acid methyl ester, stearic acid methyl ester, and eicosenoic acid methyl ester are the main components of the produced biodiesels, and the composition of the produced biodiesels can be controlled by using different catalysts. This work, shows the potential of using WCB as an agricultural waste as well as the low-price mineral of clinoptilolite for the production of useful catalysts in biodiesel production processes. Finally, some of the produced biodiesels were analyzed and found to fulfill ASTM D6751 [50] requirements.

Table 1. Chemical composition of the produced biodiesels by using ten different catalysts of (C1=KOH, C2=Zn(NO₃)₂, C3=Clinoptilolite, C4=NaOH, C5=Clinoptilolite-NaOH, C6=Clinoptilolite-KOH, C7= Clinoptilolite-Zn(NO₃)₂, C8=WCB-KOH, C9=WCB-NaOH, C10=WCB-Zn(NO₃)₂).

Chemical	Mw (g/ml)	Density (g/cm ³)	Type of Catalyst									
			C1	C2	C3	C4	C5	C6	C7	C8	C9	C10
1 Lauric acid m.e. ¹	C ₁₃ 214.3	0.87	8.78	-----	6.01	-----	-----	57.5	-----	-----	-----	10.85
2 Myristic acid m.e.	C ₁₅ 242.4	0.855	15.33	----	----	5.00	5.05	14.38	----	28.35	----	42.35
3 Palmitic acid m.e.	C ₁₇ 270.5	0.852	12.0	32.34	---	10.11	----	----	----	----	30.25	31.23

4	linoleic acid <i>m.e.</i>	C ₁₉ 292.5	0.895	----	37.35	32.83	4.91	44.29	---	45.77	27.46	22.22	4.38
5	Oleic acid <i>m.e.</i>	C ₁₉ 296.5	0.874	33.44	27.18	45.83	34.89	28.29	2.65	41.02	32.66	20.35	3.08
6	Stearic acid <i>m.e.</i>	C ₁₉ 298.5	---	10.58	1.48	3.58	34.11	14.82	18.0	2.69	----	17.74	----
7	Eicosenic acid <i>m.e.</i>	C ₂₁ 324.5	0.883	11.59	----	7.2	2.01	----	7.47	4.39	4.11	2.42	5.60
others				8.30	1.70	4.65	9.00	7.55	2.32	6.14	7.42	7.02	2.51
¹⁻ Methyl Ester.													

Conflicts of Interest

The author declares that there is no conflict of interest regarding the publication of this manuscript.

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