Heterogeneous Catalytic Modified Process in the Production of Biodiesel from Sunflower Oil, Waste Cooking Oil and Olive Oil by Transesterification Method

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ABSTRACT

Using transesterifiction of sunflower oil, olive oil and waste cooking oil with methanol and heterogeneous catalyst made by clinoptilolite, biodiesel was obtained. With molar ratio of alcohol to oil 1:7 and mentioned catalyst (3 wt%), yield of biodiesel from sunflower oil, cooking waste oil and olive oil were: 97%, 95% & 92% respectively. SEM images showed the average particle sizeof 342.44 nm. FTIR spectrum showedno impurity in produced biodiesel. The products were compared to the consuming Petro-dieselin Tehran according ASTM standard cloud point, pour point, freezing point, cetane number, iodine value, saponification number, heating value, acid value, viscosity, density andflash point.

Keywords: Biodiesel, transesterifiction, clinoptilolite, waste cooking oil, sunflower oil, olive oil

INTRODUCTION

Biodiesel has attracted much attention because it is biodegradable, renewable, and is non-toxic (importantly when fuels leak into the environment). The fuel is free of sulfur and aromatics, while petro-diesel fuel may contain 500 ppm sulfur dioxide and 20-40wt% aromatics [1-5]. Recent studies showed that applying biodiesel may reduce various cancers and toxic aerosols by 95% and 90% respectively, which resulted in improved environmental condition [6 ,7].

More than 350 different oilseeds already have been found throughout the world that have the potential to produce biodiesel[8]. In general, the main sources are classified into four categories as below [9,10]:

1- Animal fats: chicken fat and lard

2- Edible vegetable oil: sunflower, soybean, olive and coconut

3- Inedible vegetable oil: Jatrophacurcas, Calophylluminophyllum, Moringaoleifera and Croton megalocarpus

4- Waste cooking oil and recycled oil

Biodiesel can be used in any mixture with petro-diesel fuel, as it has very similar characteristics (cetane number, viscosity, heating value, etc)[11,12]and also in any diesel engine without modification [13,14]. Biodiesel density affects engine fuel injection system. Lower fuel density and viscosity will lead to more improved atomization and mixing characteristics. Higher density cause increased particulateemission and NOx. Low density indicates decreased saturated hydrocarbon chain. The viscosity of the fuel depends on its structure and decreases by increasing double bonds. Biodiesel freezing point will increase by

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increasing the carbon number in hydrocarbon chain. Cloud point is temperature in which microcrystals are formed in biodiesel. Highercetane number leads to shorter ignition delay and faster ignition in combustion chamber. Increasing length of fatty acid will raise the cetane number [15,16]. Acid numbers greater than one represent fuel stability and should be lower than one for oil. If the acid number is greater than one, some alkali catalysts will react with the FFA(free fatty acid) to neutralize them. Iodine value shows the oil saturation, hence the higher valuessuggest the higher tendencyto oxidation, gum and resin formation and so polymerization.

Biodiesel is mainly produced by triglyceride transesterification with short chain alcohol such as methanol or ethanol in the presence of acidic or alkali catalysts. Methanol is the commonly used alcohol in this process, due in part to its low cost [17], however alkali catalysts are more interesting via short reaction time, noncorrosive, lower cost and higher biodiesel yield [18]. Homogeneous alkaline catalysts for transesterification are include: Sodium hydroxide, sodium methoxide, potassium hydroxide, potassium hydride, sodium hydride, sodium amide and potassium amide [19-21]. In recent years much attention has been paid to heterogeneous catalysts(CaO, MgO, etc) to produce biodiesel [22]. Some preferences for heterogeneous catalysts including easy separation form reaction mixture and being non-corrosive [23,24].

Zeolites of the chemical industry is of particular importance and applications [25,26].clinoptilolite is one of the most common naturally occurring species of zeolites of Heulandite family which has higher ratio of Na^+& K^+cations on their changeable sites. clinoptilolitestructure,Si/Al ratio, physical and chemical properties may improve by heating or applying inorganic acids[27]. There are huge resources of naturally occurring zeolites particularly clinoptilolite and mordenite in Semnan and Miyaneh province, Iran. Miyane zeolite because of higher purity is more important. The zeolite contains more than 75% pure clinoptilolite and some impurities include mordenite and quartz. The Si/Al ratio in this zeolite is greater than 4.5 which is persisted in presence of acid and heat .

Common processes of biodiesel production is mixing triglyceride and alcoholic phases in the presence of catalyst in a closed reactor[28-34].Application of mechanical stirrers is the most common way for reactants mixing ,The temperature should keep constant during the reaction between two phases [35-37].

In the present work, we studied transesterification using heterogeneous catalysts made by clinoptilolite and also biodiesel yield from sunflower oil, olive oil and waste cooking oil.

EXPRIMENTAL

Materials

Sodium sulfate (99%), potassium hydroxide (99%) from MerkCompany.Clinoptilolite was provide by a mine at Semnan, east of Iran.

We use BATEC PC21 furnace, RLABINCOM-81 stirrer and a Lab TECH vacuum oven.

Catalyst Preparation

In this work we used heterogeneous catalysts made by a natural occurring zeolite, Clinoptilolite. The catalyst was mixed with saturated potassium hydroxide solution and keep under stirring condition for 5 days to raise the activity and enhance the alkali catalyst, Clinoptilolite. Final sediment was under vacuum oven at 90 C for 3-4 days. In order to final processing the catalyst was placed in a furnace at 300 C for 2 hours.

Catalyst Characterization and Analysis

The synthesized product was characterized by SEM and XRD. Particle size and catalyst morphology determined by A EM-3200 SEM made by KYKY. A PSTADI XRD was used with the following characteristics:

Radiation:1.5460, Generator:40 Kv,30 M, detector: Image Plate/Stationary/fixed Omega

Scan Type: 2Theta

Biodiesel Production from Oil

Reaction Conditions

In the present study, we considered the same reaction conditions in order to camper three different oil.

Two grams sodium sulfate were added to a 50 g oil (sunflower oil, olive oil and waste cooking oil)to dehydrating the oil. The solution was heated at 60 C for 20 min. The heterogeneous catalysts (30wt %) and methanol were added to heated solution in flask with molar ratio of 1:7 (oil to alcohol) to reflux it. Heater stirrer was set on 65C with 300 rpm stirring rate for 3 hrs. After transesterification, resultant product transferred to a 250 cc decanter to extract the biodiesel. Two different phases were seen because of different density of compounds. The upper and lower phase were biodiesel and glycerol, respectively. In order to remove impurities such as alcohol, catalysts and saponified residues in final biodiesel, the product was water washed twice (20% Vol) to reach neutral pH. This heterogeneous catalyst is reusable and also recyclable.

Biodiesel yield from sunflower oil, waste cooking oil and olive oil were 97%, 95% and 92 % respectively.

RESULTS AND DISCUSSION

Analysis

Different analytical methods like SEM and XRD applied to evaluate the biodiesel quality and synthesized catalyst. Particle size of synthesized catalyst are shown on SEM pattern in Figure 1.

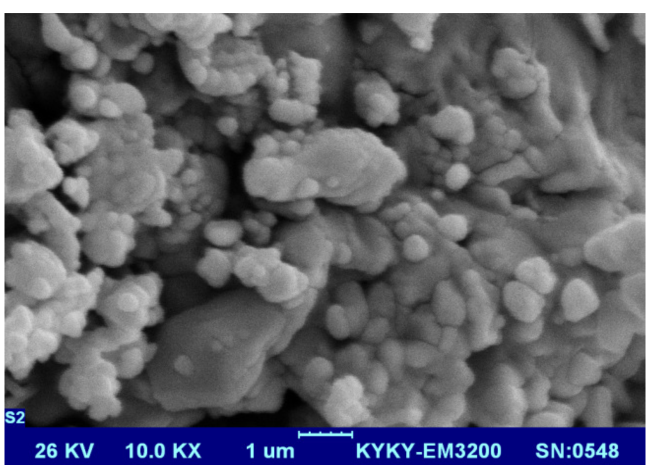

Figure 1. SEM image of the heterogeneous catalyst which made by Clinoptilolite.

SEM images (×10000) indicted particle size of 342.44 nm. The particles show remarkable activity that leads to the increased yield of biodiesel production in transesterification reaction.

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XRD Diffractogram Analysis

According to the heterogeneous catalyst and Clinoptilolite diffractograms, one can only conclude that, $K_2AL_{3.34}SL_{3.34}O_{13.35}$ due to vigorous reaction with potassium hydroxide converted to $K_2AL_2SL_{2.8}O_{8.16}.3H_2O$, as modified nature of crystalline material is apparent with comparison of compound associated diffractograms.

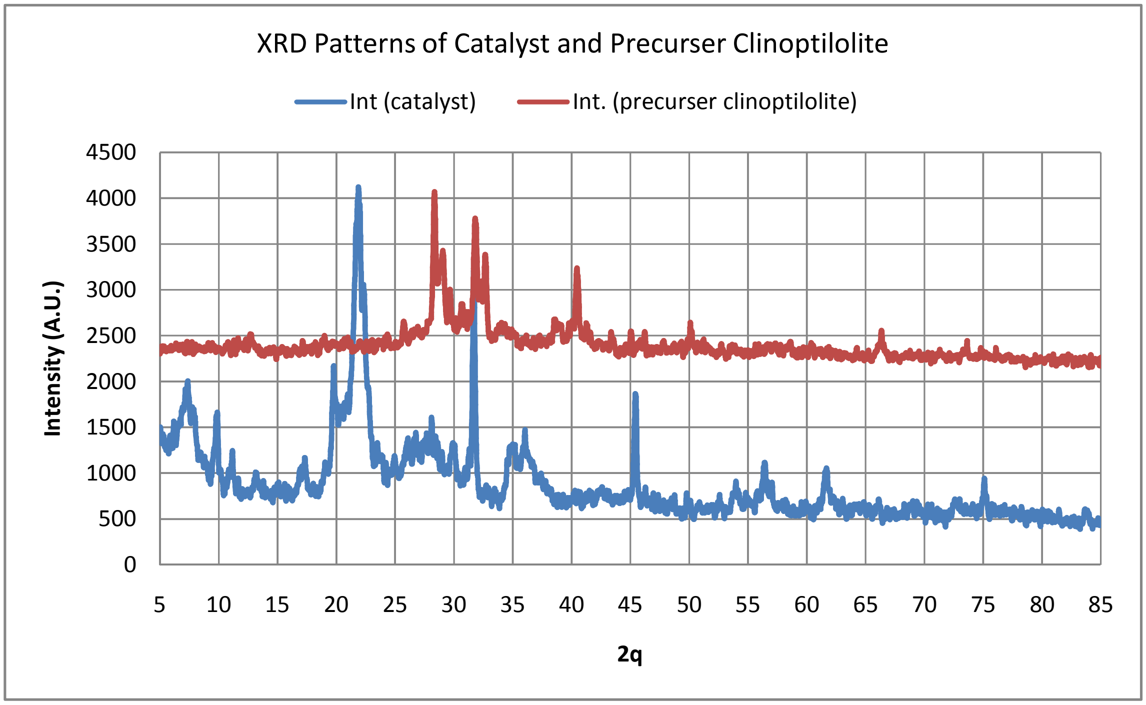

Figure 2. Heterogeneous catalyst and Clinoptilolite XRD diffractograms

GC Chromatogram Analyses

GC-MS analysis was performed on 2200/3800 varian,Australia,column:VF-5Ms, flow rate: 1ml/min, injection temp:28^{O}CTo characterization methyl esters in biodiesel, we made a GC-MS chromatogram from each oil.

The spectra results were listed in table 1.

Table 1. Percentage of fatty acids in oils by GC-MS spectra

Fatty acid	Structure	Sunflower oil (%)	Olive oil (%)	Burned oil (%)
Myristic acid	C14:0	0.07	0.35	-
Palmitic acid	C16:0	6.95	10.7	11.32
Palmitoleic acid	C16:1	0.08	0.51	-
Stearic acid	C18:0	3.7	3.75	3.61
Oleic acid	C18:1	28.42	62.2	24.5
Linoleic acid	C18:2	58.74	20.1	52.92
Linolenic acid	C18:3	1.04	1.05	6.87
Arachidic acid	C20:0	0.24	0.95	0.18
Eicosenoic acid	C20:1	0.14	0.11	0.09
Behenic acid	C22:0	0.62	0.15	0.51

Fatty acid contents of each oil represent the composition of methyl esters in biodiesel.

Biodiesel Characteristics of Each Oil

According ASTM standards, allowable range of each fuel was determined. Resultant numbers in table 2 indicate all 3 produced biodiesel is in standard ranges. In addition, consuming petro-fuel diesel in Tehran is also shown in table to compare with.

Table 2.Properties of biodiesel produced by sunflower oil, cooking waste oil and olive oil in presence of heterogeneous catalyst made by Clinoptilolite.

Property	ASTM method	Petrodiesel (Tehran)	Biodiesel Burn oil	Biodiesel sunflower	Biodiesel olive oil
Cloud point ^{o}C	D-2500	1	0	-2	0
Freeze point ^{o}C	-	-5	-7	-8	-4
Pour point ^{o}C	D-97	-4	-6	-6	-2
Density (g/cm^3)	D-4052	0.831	0.88	0.87	0.88
Kinematic at $30^{o}C(mm^2/s)$	D-445	3.1	3.9	4.1	4.15
Flash point ^{o}C	D-93	86	173	181	178
Higher Heating Value (HHV)		45	39.41	39.51	39.6
Saponification Value (SV)		-	201.22	195.14	197.25
Iodine Value (IV)	EN1412	-	136.75	135	95.81
Acid no. (mg NaOH/mg)	D-974	-	0.03	0.018	0.012
Cetan Number (CN)	D-976	44	42.65	45.2	51.97

In the light of obtained results, we found that lowest density is related to the sunflower oil. However, this value is higher than petro-diesel which is the problematic issue to consuming pure biodiesel in diesel engines. Biodiesel derived by olive oil had the highest density. According the results, sunflower derived biodiesel had the lowest freezing point, pour point, cloud point which indicate increased double bond between carbons. Lower cloud point represents the higher purity of the compound. Thus, sunflower derived biodiesel was the purest among other one. According table 2 data, sunflower derived biodiesel is the most appropriate choice for cold climate other than two other types. Olive derived biodiesel had the highest cetane number which made it to the most qualified fuel. Flash point is an important issue in transport and storage safety aspects. Sunflower derive biodiesel had the highest flash point. Olive oil derived biodiesel had the lowest acid value (number) and higher stability. Furthermore, lower iodine number in olive oil derived biodiesel made it more resistant to oxidation.

Biodiesel FTIR Spectra

We used FTIR spectra to ensure the reaction progress and triglyceride conversion to biodiesel (methyl ester),by using a NICOLET 8700 Thermo scientific, USA spectrophotometer. The biodiesel impurities include FFA, alcohol, water, mono glyceride, diglyceride. All of them have OH functional group which displayed a peak at 3200- 3500 cm^{-1} .Peak at 1743 cm^{-1} is related to C=O functional group in methyl esters. Peaks at 1150- 1350 cm^{-1} are related to the

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torsional vibrations of CH2 groups. which shows the reaction progress in kinetics point of view.

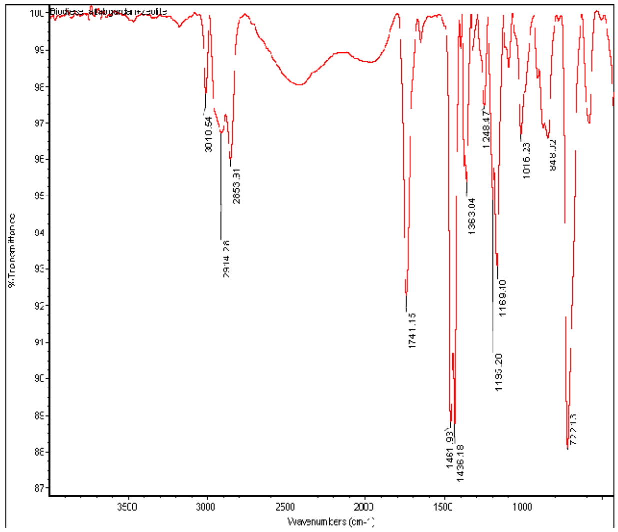

Figure 2.Sunflower derive biodiesel FTIR spectrum

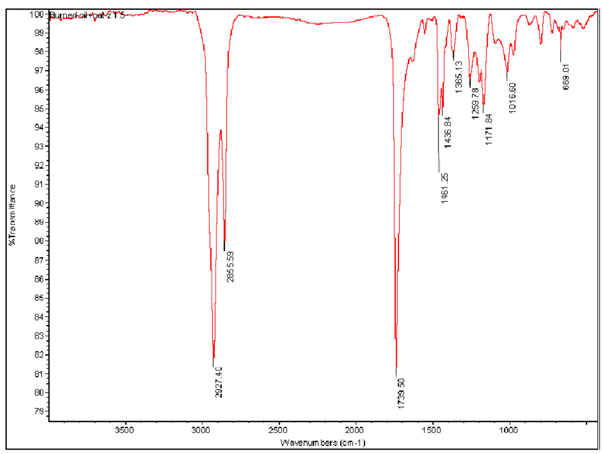

Figure 3.Waste cooking oil derived biodiesel FTIR spectrum

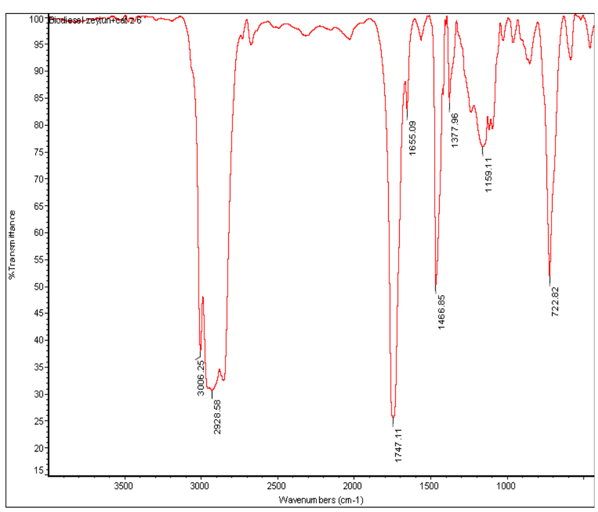

Figure 4. Olive oil derived biodiesel FTIR spectrum

CONCLUSION

In present work, we compered three biodiesel derive from sunflower oil, waste cooking oil and olive oil using heterogeneous catalyst made by Clinoptilolite. Applying the heterogeneous catalyst lead to increased biodiesel yield, the reaction rate and needs little water washing.

Clinoptilolite may absorb the water spontaneously and because of its natural occurring and more availability than synthetic catalyst, heterogeneous catalyst are preferred in comparison with the homogenous ones. SEM images of heterogeneous catalyst made by Clinoptilolite showed the average particle size of 342.44 nm. Catalyst properties were determined by XRD and showed the $K_2AL_2SL_{2.8}O_{8.16}.3H_2O$ structure for the catalyst. To identify the biodiesel, we used GC-MS for all three oil. FTIR spectrum shows the biodiesel impurity. The biodiesel yield were 97%, 95% and 92% for Sunflower, waste cooking oil and olive oil respectively. ASTM standard based fuel tests for each obtained biodiesel represented in table 2 and the results were compared with the consuming petro-diesel in Tehran. According table 2, sunflower derived biodiesel is the most desirable choice in cold climate because of its lower cloud point and pour point than other biodiesel and also petro-diesel. In addition, due to the higher flash point than others, the former biodiesel is safer during transportation and storage. Olive oil derived biodiesel with high cetane number is the best choice for engines that need high quality fuel. Furthermore, olive oil derived biodiesel is the most stable among others.

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