

تنقية وقود الديزل الحيوي باستخدام الكربون المنشط المحضر من بقايا الشاي المستنفذ

عبدالرحمن باسل فاضل، محمد مجبل نياي، عبدالقادر يوسف عبدالقادر

قسم الكيمياء، كلية العلوم، جامعة الموصل، الموصل، العراق

المخلص:

تضمنت الدراسة الحالية تحضير وقود الديزل الحيوي (استرات المثل) من زيت القلي المستنفذ من خلال تفاعل انتقال الاسترة المحفز بالقاعدة. بعد فصل الناتج العرضي (الكليسيرول) تم تنقية الديزل الحيوي (استرات المثل) الناتجة وذلك باستخدام الكربون المنشط المحضر من بقايا الشاي المستنفذ. ولقد قورنت النتائج المستحصلة مع نموذج الديزل الحيوي المنقى باستخدام طريقة الغسل بالماء، وطريقة التنقية باستخدام هلام السليكا. أظهرت النتائج أن تنقية الديزل الحيوي باستخدام الكربون المنشط أعطى حصيلة من استرات المثل وخواص احتراقية أفضل مقارنة بطرق التنقية الأخرى المستخدمة. كما تم إعادة تنشيط الكربون المنشط المستنفذ واستخدامه لنفس الغرض مرة أخرى. وأظهرت النتائج أيضاً أن الكربون المنشط المستنفذ المعاد تنشيطه هو الآخر قد أعطى حصيلة أعلى وخواص احتراقية أفضل مقارنة بطرق التنقية الأخرى المستخدمة.



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ORIGINAL ARTICLE

Purification of biodiesel using activated carbons produced from spent tea waste

Abdelrahman B. Fadhil *, Mohammed M. Dheyab, Abdul-Qader Y. Abdul-Qader

Department of Chemistry, College of Science, Mosul University, Mosul, Iraq

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KEYWORDS

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Abstract Waste cooking oil was converted into biodiesel through base catalyzed transesterification. After separating the glycerol, the crude methyl esters were purified using activated carbons produced from spent tea waste. Yield and fuel properties of the produced biodiesels were compared with those purified by using silica gel and conventional method namely water washing method. The study revealed that using activated carbons for the purification of biodiesel resulted in higher yield and better fuel properties compared to those purified using silica gel and water washing method. Furthermore, the spent activated carbon was regenerated and reused for the same purpose. However, the results showed that the yield and fuel properties of those purified using the regenerated activated carbon were also better than those purified using silica gel and water washing method.

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1. Introduction

The production of biodiesel from edible oils competes with the use of land for food production. Moreover, the price of edible plant and vegetable oils is usually higher than petro diesel. Thus, finding a cheaper feedstock such as waste cooking oil for biodiesel production reduces the cost of biodiesel produc-

tion since the feedstock costs constitutes approximately 70–95% of the overall cost of biodiesel production. Hence, the use of waste cooking oils and non-edible oils should be given higher priority over the edible oils as biodiesel feedstock (Chhetri et al., 2008; Canakci, 2007). The purity level of the biodiesel has strong influence on its fuel properties. Especially, the amount of glycerides and triglycerides present in the fuel can cause serious problems in application. Another factor that must be taken into account is that the fuel must be almost free of water, alcohol, glycerin and catalyst; thus, the ester layer has to be treated. Therefore, the refining step of the products obtained by transesterification is very important (Karaosmanoglu et al., 1996; Predojevic, 2008).

In this study, the production of biodiesel from waste cooking oil through base catalyzed transesterification was investigated. After separating the glycerol, the crude methyl esters were purified using activated carbons produced from spent tea waste. The results were compared with those purified by using silica gel and water washing methods. Properties of the produced fuels were measured and compared with those purified using other methods. Furthermore, the spent activated

* Corresponding author.

E-mail address: abdelrahmanbasil@yahoo.com (A.B. Fadhil).



carbon was regenerated and reused again for the same purpose.

2. Materials and methods

2.1. Preparation of carbon adsorbents

Tea is the second drink after water in Iraq. Therefore, large amounts of tea are consumed, accumulated and discarded. Such biowaste could be an attractive precursor for activated carbon (AC) preparation. Spent tea waste (STW) was collected from local coffee shops within the city of Mosul, north of Iraq. STW was washed thoroughly with tap water and by distilled water several times, then it was dried in an oven at 50 °C for 5 h. The dried STW was sieved using a 20–40 mesh sieve, and the particles of 30–40 mesh were used as a precursor for activated carbon (AC) production. Two types of activated carbons were prepared from STW as follows:

For batches, 20 g of the dried STW was placed into a quartz tube, and the tube was in turn placed into an electrical tubular furnace. The furnace was heated gradually until a temperature of 600 °C was reached. The activation was conducted at this temperature for 120 min, to produce thermally activated carbon (AC_{TH}). The second type was prepared through placing 20 g of the dried STW into a stainless steel tube which was placed into an electrical tubular furnace. The sample was heated gradually in a flow of steam until a temperature of 600 °C was attained. The activation was performed at this temperature for 120 min to produce (AC_{ST}). The yield of the produced carbons was calculated as following:

$$\text{Yield}\% = \frac{W_{\text{ACproduced}}}{W_{\text{STWused}}} \times 100$$

Silica gel was thermally activated at 105 °C for 5 h and was kept in a sealed container to be used later.

2.2. Assessment of the produced carbon adsorbents

Surface area of the prepared activated carbons (ACs) was determined by their adsorptive capacity of iodine, referred to as iodine adsorption number (IAN). The quantity of iodine adsorbed per gram of the activated carbon was determined by titration against the standard solution of sodium thiosulphate according to ASTM (1999). Adsorption capacity for the prepared carbons was determined through their adsorption of methylene blue (MB) from its aqueous solution. Surface properties of the produced carbons such as PH, total acidity and oxygen surface groups were determined. The surface functional groups of the activated carbons were analyzed by a Fourier transform infrared (FTIR) spectroscope.

2.3. Preparation of the raw oil

Waste cooking oil (WCO) was collected from local restaurants within the city of Mosul, north of Iraq and used as a feedstock for biodiesel production. At first, 500 g of the oil was mixed with freshly activated MgSO₄, and left overnight to eliminate any water content. Then the oil was filtered by using cloth filter to remove any solid impurities and MgSO₄ particles, and was kept in a sealed container to be used later. Mean molecular

weight of the oil was determined according to the formula presented by (Zhu et al., 2006):

$$MW = 56.1 \times 1000 \times 3 / (SV - AV) \quad (2)$$

where, SV is the saponification value and AV is the acid value.

2.4. Transesterification of waste cooking oil

Five hundred grams of the oil was poured into a 250 mL three necked round bottomed flask equipped with a mechanical stirrer, and a condenser, and placed in water bath. Freshly prepared catalyst solution (KOH = 0.75% w/w of oil dissolved in methanol in a ratio of 6:1 MeOH–oil) was introduced into the reactor. The mixture was refluxed for 1 h at (60 °C) with continuous stirring. After the reaction was over, the mixture was transferred into a separating funnel and left to settle for 24 h. Two layers were obtained, the upper was the methyl esters (ME) and the lower was the glycerol. Glycerol layer was discarded, and the methyl ester layer was distilled under vacuum to recover excess methanol. Finally, the methyl ester layer was kept for purification and assessment.

2.5. Chemicals

Methanol (reagent grade), acetone, glacial acetic acid, iodine, potassium iodide, sodium thiosulfate, starch, diethyl ether, isopropyl alcohol, silica gel and formic acid were purchased from BDH. Potassium and sodium hydroxide, and magnesium sulfate were supplied from Merck, whereas chloroform, *n*-hexane and hydrochloric acid were supplied from Fluka. Chemicals were used without any further purification.

2.6. Purification of biodiesel over activated carbons

A chromatography column of (15 cm height and 1 cm i.d) was packed with glass wool, then a bed (2 g = 5 cm) of activated carbon was introduced into the column. Next, crude methyl esters were transferred into the column and allowed to pass through the adsorbent bed with a flow rate of (15 drop/min). Percentage yield was calculated on a weight basis with respect to the methyl ester introduced into the column (Predojevic, 2008). Silica gel was also used for the same purpose. Purification using (water washing) method was also adopted.

Table 1 Physicochemical properties of the raw oil.

Property	Test procedure	Value
Density @ 16 °C g/ml (D)	ASTM D4052-91	0.9233
Kine. Viscosity @ 40 °C mm ² /s (KV)	ASTM D445	26.50
Flash point °C (T _F)	ASTM D93	244
Pour point °C (PP)	ASTM D2500	−9
Cloud point °C (CP)	ASTM D2500	1
Acid value mg KOH/g (AV)	ASTM D664	2.82
Iodine number mg I ₂ /100 oil (IN)	Paquot, 1979	110
Refractive index @ 20 °C (RI)	D1747-09	1.470
Conradson carbon residue% (CCR)	ASTM D4530	0.35
Sapon. value mg KOH/g oil (SV)	ASTM D5555-95	201
Calculated cetane index (CCI)	Krisnangkura, 1986	49.15
Higher heating value (HHV)	Demirbas, 2008	39.27

Table 2 Characteristics of the prepared carbon adsorbents.

Sample	Yield %	IAN mg I ₂ /g	MB mg/g	PH	Acidity m mol g ⁻¹	Basicity m mol g ⁻¹
AC _{ST}	27	767	39.30	9	1.57	3.55
AC _{TH}	41	688	43.0	8	1.53	3.15
SG	–	478	–	–	–	–

2.7. Properties assessment of the purified biodiesels

Properties of the parent oil were measured according to the ASTM standards listed in Table 1. Iodine number (IN) was measured according to the Hanus method (Paquot, 1979). Higher heating value (HHV) was determined depending on equations proposed by Demirbas (Demirbas, 2008). The calculated cetane index (CCI) is based on Krisnangkura equation (Krisnangkura, 1986):

$$CCI = 46.3 + (5458/SV) - (0.225IN) \quad (3)$$

Where, SV is the saponification value and IN is the iodine number.

2.8. Regeneration of spent activated carbon

Spent activated carbon (AC_{ST}) used for the purification of crude methyl esters was regenerated to be reused for the purpose explained in (Section 2.6). Then, the yield and fuel properties of the purified methyl esters were determined and compared with those purified by the authentic (AC_{ST}), silica gel and water washing method.

3. Results and discussion

3.1. Properties of the feed stock

Each value of the measured properties was the result of at least two trials, only the mean was recorded. The average molecular weight obtained for WCO is 821. It is well known that base catalyzed transesterification (BCTE) is not suitable for oils of high free fatty acid content (>1%), for it leads to catalyst deactivation and soap formation. As a result, yield decreases (Sharma et al., 2008). However, reviewing the literature indicates little works about the production of BD from oils of high fatty acid content using BCTE (Phan and Phan, 2008; Araujo et al., 2011).

3.2. Characterization of the adsorbents

Yield, total acidity, PH, oxygen surface groups and iodine and methylene blue adsorption numbers of the produced biochars were determined and presented in Table 2. Yield of the produced carbons was specified as the ratio of the weight of final activated carbons to that of initial raw materials used for the preparation. It can be seen from Table 2 that yield AC_{ST} was lower than that produced through one step pyrolysis. This is because steam accelerates further removal of the volatiles from the structure of the feedstock. As a result, the yield decreases. Iodine adsorption number was used as a function of surface area of the produced carbons. Each 1.0 mg of iodine adsorbed equals to 1.0 m² of the activated carbon internal surface area (Egwaikhide et al., 2007). Iodine adsorption numbers of the adsorbents are listed in Table 2. It can be seen from this

table that AC_{ST} had higher surface area compared to AC_{TH}. This is because steam activation helps to increase the porous structure through further removal of volatiles. Consequently, the surface area increases. The adsorption of methylene blue is attributed to its meso porosity. MB values of the produced carbons were much lower than those of the IAN. This means that the produced carbons have micro porous structures. The values of PH showed that both AC_{ST} and AC_{TH} had a basic surface, but the surface of AC_{ST} was more basic. This was also confirmed through the titration against a (0.06 M) solution of HCl. The most important oxygen groups specified by FTIR spectroscopy for the produced AC are presented in Table 3.

3.3. Purification of biodiesel using the produced activated carbons

The main purpose of this study was to use the produced activated carbons for biodiesel purification, and comparing its results with those purified by using silica gel and water washing methods. Yields of the produced BD fuels were specified by the weight percentage of the purified BD relative to the original weight of the crude methyl esters introduced into the column. It can be seen from Tables 4 that using ACs for purification of the crude methyl esters results in higher yields compared to using SG and water washing methods. In comparison to SG, activated carbon has higher surface area. Besides, it is well known that the adsorption takes place through physical or chemical interactions between the adsorbate and the adsorbent surface. Furthermore, the oxygen groups that exist on the surface of the adsorbent play an important role in the adsorption. As for the SG, it is well known that the only groups that exist in SG are silanol groups, while many oxygen groups can be found on the surface of activated carbon. This is why, purification using ACs is better. With regard to water washing method, excessive amounts of water are added with gentle shaking to remove impurities such as glycerol, unreacted methanol and base (catalyst). Consequently, part of the esters is lost in the form of emulsion and soaps decreasing the yield. One of the disadvantages of this method is that it produces large amounts

Table 3 Fundamental IR absorption bands of the produced carbons.

Band cm ⁻¹	Possible assignment
3425–3435	OH groups in aliphatic and phenolic structures
2925	Represents aliphatic CH, CH ₂ and CH ₃ stretching modes
1726	C=O in ketones, aldehydes or carboxyl
1599	νC=O
1450	C–O Stretching vibrations, C–O–C, O–H bending modes in carboxylic acids, carboxyl, lactones, esters, and ethers.
874	O–O stretching
716	C=O stretching

Table 4 Yields and properties of biodiesel purified using the ACs.

Property	WCO			
	AC _{ST}	AC _{TH}	SG	Washing by DW
Yield%	97	95.50	93	88
Density @ 16 °C g/ml	0.8755	0.8766	0.8800	0.8920
KV @ 40 °C mm ² /sec	2.63	2.73	3.22	3.40
AV mg KOH/g oil	0.092	0.144	0.247	0.301
RI @ 20 °C	1.445	1.446	1.448	1.457
(PP) °C	-8	-8	-7	-6
T _F °C	169	169	172	175
HHV MJ/KG	40.66	40.71	40.93	41.11

of highly polluting wastewater. It also increases the size and cost of the separation equipment, resulting in yield loss, and causes an environmental disposal problem (Saleh et al., 2010). Pighinelli et al. (2011) prepared ethyl ester from sunflower oil. They used three methods for purifying the produced ethyl esters including acidified water (5% of phosphoric acid), silica gel and distillation. The yields of the produced ethyl esters obtained by using these purification methods were (84.4%, 84.6% and 92.3%), respectively. Predojevic (2008) prepared biodiesels from waste cooking. He used three different methods for the purification of the produced methyl esters including water washing method, washing by acidified water (5% H₃PO₄) and silica gel. He found that purification by the acidified water and silica gel methods resulted in higher yield (92%) compared to the water washing method (89%). Therefore, one can say, that our handling was better than those applied by the aforementioned studies; it resulted in higher yields.

For BD to be used as a fuel in diesel engines, it should meet some specifications according to the ASTM standards or European standards. Thus, after the purification of the produced methyl esters by the suggested method, some essential properties were measured, and compared to those obtained by other methods. These properties were measured according to the ASTM standards as can be seen in Table 1; fuel properties of the produced fuels are given in Table 4.

One of the most important properties of biodiesel is viscosity. This property should be low. Poor atomization of the fuel spray and less accurate operation of the fuel injectors is associated with high viscosity (Demirbas, 2009). It is obvious from Table 4 that the viscosity of the methyl esters purified using the ACs was lower than that purified by SG and water washing method. This means that the ACs is an effective adsorbent in removing impurities, such as glycerol and soaps which accompany the biodiesel during its production, compared to SG and

water washing. The values were between (2.63 and 3.40 mm²/sec). These values were much lower than those recommended by the ASTM and the European standards. Density is another important property of biodiesel. As in the case of the viscosity values, the density of the methyl esters purified using ACs were also lower than that purified using SG and water washing method. The values ranged from (0.8755 to 0.8920 g/mL). The acid value can be used as a guide in quality control of fuels. Acid value for the produced methyl esters was lower than that of the parent oil. Methyl esters purified using ACs had lower acid values than those purified by using SG and water washing method. Lower acid values of the methyl esters purified using ACs reflects the high refining degree compared to the methyl esters purified using SG and water washing method. The values ranged from (0.092 to 0.301 mg KOH/g). Refractive index (RI) values of the fuels were lower than that of the parent oil and ranged between (1.445 and 1.457). The flash point is the lowest temperature at which a fuel will ignite when exposed to an ignition source (Ghobadian et al., 2008). Flash point values of the methyl esters purified using the ACs were lower than those purified using SG and water washing method. This is because purification using ACs leads to further elimination of impurities such as unreacted triglycerides, glycerol and the catalyst, as well as higher ester content of these samples is behind this phenomenon. The pour point values ranged from (-6 to -8). Such values could be a good indicator of the fact that BD fuels prepared in this study are suitable for use in cold weather conditions prevailing in Northern Iraq in winter. The HHV values ranged from (40.66 to 41.11) million joules/Kg).

3.4. Regeneration of spent activated carbon

Some authors used adsorbents such as Magnesol, SG and ion exchangers for BD purification. Borrios and Skelton (2008) used Magnesol and ion exchanger resin for BD purification. Predojevic (2008) used SG for BD purification. He found that purification using SG resulted in higher yield and better fuel properties in comparison to water washing method. However, the problem with these adsorbents is that they cannot be recycled. Besides, it is hard to dispose of their wastes particularly at a larger scale (Saleh et al., 2010). One of the attractive characteristics of activated carbon is that it can be regenerated therefore spent activated carbon was regenerated and denoted as (AC_{SR}). Yield and fuel properties of BD purified using (AC_{SR}) are listed in Table 4. It was found that the yield and the fuel properties especially the acid value, kinematic viscosity and flash point of BD purified using the AC_{SR} were lower than

Table 5 Yield and properties of the biodiesel purified using AC_{SR}.

Property	WCO			
	AC _{SR}	AC _{ST}	SG	Washing by DW
Yield%	94	97	93	88
Density @ 16 °C g/ml	0.8865	0.8755	0.8800	0.8920
KV @ 40 °C mm ² /sec	3.10	2.63	3.22	3.40
AV mg KOH/g oil	0.195	0.092	0.247	0.301
RI @ 20 °C	1.449	1.445	1.448	1.457
(PP) °C	-7	-8	-7	-6
T _F °C	171	169	172	175
HHV MJ/KG	40.89	40.66	40.93	41.11

those purified using the AC_S as can be seen from Table 5. This can be attributed to the reduction of the active sites available for the adsorption. However, in comparison to methyl esters purified using SG and water washing method; purification using AC_{SR} resulted in higher yield and better fuel properties. Thus, it can be said that AC or AC_{SR} is a good adsorbent for the purification of biodiesel in comparison to the SG or water washing method.

4. Conclusions

Activated carbons prepared from spent tea waste used for the purification of crude biodiesel produced from waste cooking oil through base catalyzed transesterification. For comparison, silica gel and water washing were also used for the same purpose. The study showed that in general, using activated carbons for biodiesel purification resulted in higher yields and better fuel properties compared to the above mentioned methods. Moreover, the fuel properties met the specified limits according to the ASTM standards. Furthermore, spent activated carbon was regenerated and reused for the same purpose. The results indicated that regenerated activated carbon was effective to produce a biodiesel fuel of higher yield and better fuel properties compared to the other methods.

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