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Transestrification Reactions for the Production of Biodiesel from Chicken Wastes

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Abstract The objective of this work is to employ chicken fat as a feedstock for the production of biodiesel by transesterification reaction using methanol, and alkali catalyst such as KOH. The experimental part presents a method to recover fat from the chicken wastes (skin) and convert triglycerides to methyl ester. The reaction progression was checked and characterised by IR spectroscopic method. The physicochemical properties such as; pour point, flash point, specific gravity, aniline point and viscosity of biodiesel was measured. The obtained results were principally consistent with previous results of other reports and with biodiesel international standards (EN-14214) and ASTM standards for petroleum gasoil.

Keywords: Chicken fat, Transesterification reaction, Alkali catalyst, Biodiesel, FAME.

تفاعل الأسترة التحويلية لإنتاج وقود الديزل الحيوي من مخلفات الدواجن

أمل الجطيلاوي و حواء علي و عبدالرحمن فرج و موسى خليفة و *المهدي المكي
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الملخص يهدف هذا العمل الى استخدام مخلفات دهون الدجاج كمادة أولية لإنتاج وقود الديزل الحيوي عن طريق تفاعل الاسترة التحويلية باستخدام الميثانول ومركب قاعدي كعامل حفاز مثل هيدروكسيد البوتاسيوم KOH لتتحول الجليسريدات الثلاثية الى ميثيل استر. وتمت متابعة سير تفاعل الأسترة باستخدام طيف الأشعة تحت الحمراء. كما انه تم فحص الخواص الفيزيوكيميائية للوقود الناتج مثل نقطة التسحب، نقطة الانسكاب، نقطة الوميض، الكثافة النوعية، نقطة الانيلين، واللزوجة. النتائج المتحصل عليها أظهرت توافقا كبيرا مع نتائج أبحاث سابقة وكذلك مع معايير عالمية لمواصفات الديزل مثل المعيار الألماني والمعيار الأمريكي لاختبارات المواد.

الكلمات المفتاحية: دهون الدواجن، تفاعل أسترة تحويلية، عامل حفاز قاعدي، ديزل حيوي، FAME.

Introduction

In recent years, there are an international awareness on the emissions of oil-based fuels and their potential hazards on health and environment. Furthermore, the conventional energy resources such as natural gas, petroleum and coal are predicted to be depleted in the near future. These factors and others prompted the governments and researchers to look for alternative energy sources. Due to their environmental and economical benefits, biomass sources such as vegetable oils and animal fats have attracted much attention to be used as alternative energy resources. The European Union has set an objective to secure a market share for motor biofuels of 20% of the total motor fuel consumption by 2020.[1] China also has a national strategy of developing renewable energy. Consequently, this biggest developing country with rapid economic growth needs more energy in the nearest future than before.[2] The main advantages of biofuels are there renewability, biodegradability, better quality of exhaust gas emissions, and then consequently considered as environment friendly products.[3] Biodiesel as an example of alternative fuels attracts increasing attention worldwide as a blending component or a direct replacement for diesel fuel in vehicle engines. It is produced by a variety of methods, but the most commonly used method is transesterification of vegetable oils and animal fats.[4] The produced biodiesel consists of a mixture of fatty acid alkyl esters with chain lengths of C_{14}-C_{22}. In the case when methanol used as a reactant the process is called methanolysis, and the product will be fatty acid methyl esters (FAME), and when ethanol used the process is called ethanolysis and the product will be fatty acid ethyl esters (FAEE). Methanol is commonly and widely used in biodiesel production due to its low cost and availability. [5, 6] Transesterification reaction is the displacement of alcohol from an ester by another to produce fatty acid alkyl esters and glycerol. This reaction is a reversible reaction and proceeds essentially by mixing the reactants, but the presence of a catalyst (a strong acid or base) accelerates the conversion. However, it was observed that transesterification is faster when catalyzed by an alkali such as potassium hydroxide, KOH. [7] Methanolysis of triglyceride is represented in Figure 1.

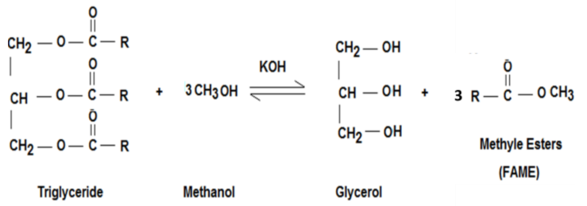

Figure 1: General equation for transesterification of triglycerides

There are many factors affect the transesterification process depending upon the used reaction conditions such as type of alcohol and alcohol to oil molar ratio, catalyst type and concentration, moisture content, reaction time and reaction temperature, and Mixing intensity. [8].

EXPERIMENTAL

Materials and instrumentation

The waste chicken skins were brought from the city Slaughter houses in the local market of Sebha, Libya. Methanol and potassium hydroxide were purchased from "Romil LTD - UK". The used water was distilled by "Gesellschaft Fur Labortechnik" distillation machine. FTIR analysis was run using Tensor 27 FTIR – Germany, sample preparation time: 30 sec. Measurement technique: single reflection ATR.

Feedstock Preparation: Fats were extracted by slowly heating up of 1000 g of waste chicken skins with continues stirring using a glass rod for 4 hour at temperature of 80 °C to avoid any degradation. This chicken fat is a mixture of solid and liquid phases at room temperature. Melted fats were then filtered to remove suspended matters and residues.

$$\text{The yield of dried extraction fats }\% = \frac{\text{Wt. of extracted oil}}{\text{Wt. of row materials}} \times 100 = \frac{202.3734\text{g}}{1000\text{g}} \times 100 = 20.24\ \%$$

Transesterification reaction

Transesterification of chicken fat with methanol over the potassium hydroxide catalyst was carried out by a batch-type reactor. The reaction was performed by reacting 50 g of melted chicken fat with 11 g of methanol containing 0.5 g of KOH dissolved in it. The reaction mixture was stirred in a 250 ml round bottom flask which equipped with a condenser. The speed of string was maintained at 500 rpm, for 2 hour at 65°C. Once the reaction is completed, two major products exist: glycerin and biodiesel. The mixture was transferred to the separating funnel. The glycerin phase is much denser than biodiesel phase and the two can be gravity separated with glycerin simply drawn off the bottom of the separation funnel. Washing operation, for purifying biodiesel from catalysts and the remaining glycerine, has been performed three times by adding hot water (70°C) to the biodiesel phase, mixing well, and draining the water from the bottom of the separation funnel. The Biodiesel which contains some water has been dehydrated in vacuum using distillation by rotary evaporator.

$$\text{Conversion rate }\% = \frac{\text{Wt. of produced ester}}{\text{Wt. of initial oil}} \times 100 = \frac{142.4262}{202.3734} \times 100 = 70.377\ \%$$

Fuel characterization

Physiochemical properties of Chicken fat biodiesel were performed according to the American system for testing of materials, ASTM. Different tests were performed on samples such as:

A) FTIR spectroscopy: One drop of biodiesel was placed on the measurement window, measured and later removed simply with a tissue and cleaning of remaining parts with a drop of solvent. System will be ready for measurement of next sample within one minute.

B) Specific Gravity: Specific gravity is the ratio of the density of the material to the density of equal volume of water. This was measured using the hydrometer. The density was calculated at 15.6°C and the value was recorded.

C) Flash point: This method covers the determination of flash point by Pensky-Martens Closed Cup tester. The sample is heated at a slow, constant rate with continual stirring. A small flame is directed into the cup at regular intervals with simultaneous interruption of stirring. The flash point is the lowest temperature at which application of the test flame causes the vapor above the sample to ignite.

D) Cloud point: After preliminary heating, the sample is cooled at a specified rate and examined at intervals of 1 °C for flow characteristics. The lowest temperature at which a cloud or haze of wax crystal appears at the bottom of the test jar when the oil is cooled under prescribed condition is recorded as the cloud point.

E) Pour point: After preliminary heating, the sample is cooled at a specified rate and examined at intervals of 3 °C for flow characteristics. The lowest temperature at which the movement of the oil is observed is recorded as the pour point.

F) Kinematic viscosity: The viscosity is determined by the Oswald viscometer.

Kinematic viscosity, $\nu = C \cdot t$

Where: t = falling time of a liquid for a particular distance through the tube of Oswald viscometer, and C = calibration constant of Oswald viscometer.

G) Aniline point: Specified volumes of aniline and sample are pleased in a tube and mixed mechanically. The mixture is heated at a control rate until the two phases become miscible. The mixture is then cooled at a controlled rate and the temperature at which the two phases separate is recorded as the aniline point.

RESULTS AND DISCUSSION: A The yield% of oil extraction from chicken's skins reaches 20% while the conversion rate of these greases to biodiesel is 70% depending on the used reaction conditions. The obtained conversion rate is good, although the target was higher. The key factor for higher yield is the water content. The presence of any traces of water interferes with the transesterification reaction and can result in poor yields and high level of glycerin and free fatty acids (FFA) in the final fuel.[5] This problem may be addressed through further investigation.

A) FTIR spectroscopy

FTIR Spectroscopy was used to investigate the changes in the spectra due to the effect of the transesterification on chicken waste oil to produce a biodiesel. The huge molecule of a tri-glycerol is cracked into the glycerine molecule and diverse FAME as a result of a transesterification reaction. As shown in figure 2 and Table 1, the differences are visible regards triglycerides (A) and the FAME (B).

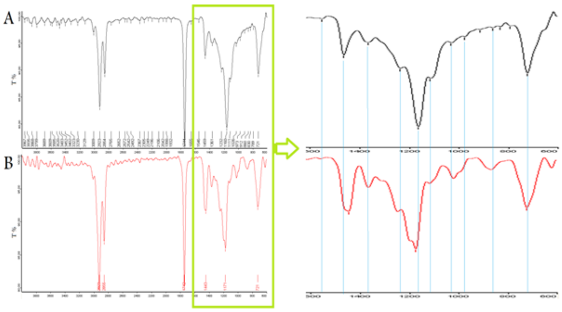

Fig. 2: Typical infrared absorbance spectra of pure chicken waste oil (A) and a pure biodiesel (FAME) (B). The magnification showing the differences in region at 600 to 1600 cm^{-1}.

Table 1: Discussion of infrared spectra of chicken waste oil compared with biodiesel.

Chicken easte oil		Biodiesel(FAME)	
Vibration (cm^{-1})	Remark	Vibration (cm^{-1})	Remark
721	-CH_2 rocking	721	-CH_2 rocking
973	-CH_2-O-	-	-CH_2-O-
1026	-O-CH_2-C	1018	-O-CH_2-C
-		1194	CH_3-O-
1232	C-CO-O-	1244	C-CO-O-
-		1443	(CO)-O-CH_3
1744	C=O Ester	1742	C=O Ester

The peak analysis of both spectra shows significant differences. All aspects regards the carbonyl groups are visible. The strong C=O vibration peak of chicken oil at 1744 cm^{-1} and C=O vibration peak of biodiesel at 1742 cm^{-1} are clear.[9] The change from ester groups to methyl ester has the strongest impact in the infrared spectrum. The ester group we are talking about is in common described as R1-C(OR)=O in chicken oils and as R1-C(OCH_3)=O in biodiesel.[10] All groups regards the CH_2-O- at 973 cm^{-1} are reduced and new signals at 1194 cm^{-1} are visible belonging to CH_3-O vibrations in the biodiesel.[10,11] The most influence as result from transesterification is to see the new signal at 1443 cm^{-1} which is definitely the methyl ester group with its deformation vibration.[12] The next visible transformations are the shift in the ester control signal from 1232 cm^{-1} to 1244 cm^{-1},as well as, the strong broad signal at 1160 cm^{-1} in chicken oil separated into two signals at 1171 and 1194 cm^{-1} in biodiesel. [12,13]

B) Physico-chemical properties

Table 2 summarize our experimental results (FAME) which were compared with results of previous research (Ref. 4), biodiesel European standard (EN-14214), and ASTM standard for pure petroleum gasoil.

Table 2: experimental results (FAME) compared with previous research results (Ref. 4), EN-14214, and ASTM for pure gasoil.

Sr. No.	Characteristics	Unit	Test Method	FAME	Ref.4	EN 14214	Pure gasoil
1	Density	g/cc	ASTM D1448	0.8830	0.864	0.862-0.900	0.830
2	Viscosity	CSt	ASTM D445	3.8	5.5	3.5-5.0	3.0-8.0
3	Flash point	^{0}C	ASTM D93	115	-	>101	>65
4	Cloud point	^{0}C	ASTM D2500	15	8	<amb.	<20
5	Pour point	^{0}C	ASTM D2500	9	5	<amb.	<15

In summary, our experimental results principally met the specifications of EN 14214 and the petroleum gasoil specification. Moreover, they were principally consistent with previous literature on methyl esters from chicken fat (Ref. 4).

CONCLUSION

Biodiesel has become more attractive recently because of its environmental benefits and the fact that it is made from renewable resources. Of the several methods available for producing biodiesel, transesterification of fats is currently one of the methods of choice. The work we performed utilized the animals' fat wastes (chicken skin) for producing biodiesel. The results obtained are optimal in terms of biodiesel yield. FTIR spectroscopy has been used to investigate the fuel production and monitoring the quality of biodiesel. Moreover, the physico-chemical properties of the synthesized biodiesel meet well with previous literatures and international standards. Thus, it is suitable for use as an alternative fuel against the petroleum diesel, either by direct use or by mixing it with oil based petroleum. In order to achieve the objective, two scopes have to be studied in future work. They are:

i) To study the effect of catalyst purity and concentration and reaction time on the transesterification process.
ii) To analyze methyl ester composition or purity by using Gas Chromatography.

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