A New and environmental friendly method for utilization of leather industry fleshings: Biodiesel

by

Selime ÇOLAK Gökhan ZENGİN Hasan ÖZGÜNAY Özcan SARI

Ege University Faculty of Engineering Department of Leather Engineering
35100 Bornova-İZMİR - TÜRKİYE

and

Hasan SARIKAHYA Levent YÜCEER

Ege University Faculty of Science Chemistry Department 35100 Bornova-İZMİR-TÜRKİYE

ABSTRACT

Leather processing is characterized by a large amount of solid and liquid waste and the removal of these wastes causes big problems for leather industry. As it is known pre-tanning processes are the stages where most of the solid wastes are produced. Approximately 55% of the solid wastes obtained in these stages originate from fleshing processes. Fleshing wastes from tanneries create major environmental problems. Despite their considerable fat content these wastes do not find important usage. Their disposal is also troublesome and costly. We have investigated the possible use of this fat in the production of biodiesel (fatty acid methyl esters) by transesterification, for use as a replacement for fossil fuels and use of the fuel in a vehicle, as well as the engine performance and emission values. Thus, it has been proved that a contaminating waste can be utilized in the production of an environmentally friendly fuel that can be used in every engine working with petrodiesel without a need for a major adjustment and change, providing economical and ecological profits.

INTRODUCTION

Processing hides and skins and converting them into leathers has long been an important industrial activity. The negative environmental impact of the processing has been regarded as an inevitable consequence of that activity. The technical methods for reducing the negative environmental impact of hide processing fall into two broad groups. The first group involves the introduction of processing technologies usually termed low-waste or cleaner technologies that can be regarded as advanced technologies in comparison to conventional methods. Mainly aimed at decreasing the effluent pollution load, they avoid the use of harmful chemicals and produce solid wastes which can be used as by-products. The second group encompasses the treatment of wastewater and the environment-friendly handling and processing of solid waste[1,2,3].

Most of the solid wastes occur in the pre-tanning stages by mechanical processes such as trimming, pre-fleshing, fleshing and shaving. The general composition of solid wastes originating from pre-tanning processes consists of natural fats, proteins, blood, water, salt and other wastes. Most of these wastes carry a high potential of reutilization.

Pre-fleshing process is applied just after deep soaking for removing flesh from hide/skin in order to improve penetration of the chemicals and hence improve the quality of the finished leather. The wastes occurred by fleshing are called pre-fleshings and consist of considerable amounts of natural fat and protein. Despite their considerable fat content these wastes do not find important usage. Their disposal is also troublesome and costly.

Majority of the worlds energy needs are supplied through petrochemical sources, coal and natural gases, with the exception of hydroelectricity and nuclear energy, of all, these sources are finite and at current usage rates will be consumed shortly[4]. Considering this fact, the studies carried out on alternative energy sources have gained concentration and speed. Amongst the studies executed in this direction, biodiesel has gained great significance in recent years.

Biodiesel is an alternative fuel obtained from renewable biological sources like vegetable and animal oils and fats[5,6]. This fuel is an environmental friendly energy source which is non-toxic and biodegradable, and which has low emission values[5,6,7]. Biodiesel can be produced from vegetable oils, animal fats, used cooking oil, and etc. through various chemical processes. The most common is transesterification; others include hydrocracking, catalyst-free supercritical method, e-diesel, pyrolysis, microemulsion, etc. Biodiesel fuel can be used instead of the petroleum fuel and when biodiesel mixed with petroleum diesel fuel, in small quantities, also seems to improve the fuel lubricity, and reduce fuel consumption. It can be used in its neat form, or as a blend with conventional diesel fuel, in diesel engines without any modifications.

Hence in the light of the above concerns, possible use of the high fat content of pre-fleshings in biodiesel production as an energy source and considering the advantages of biodiesel fuels, use of the fuel in a vehicle, as well as the engine performance and emission values was examined in this study.

MATERIALS AND METHODS

Material

Fat (released from pre-fleshings of sheep skins by boiling with water under high speed grinding), pure methanol, potassium methoxide ($KOCH_3$, 30% solution in methanol).

Method

Release of fat from fleshings and biodiesel production :

Pre-fleshing wastes obtained from a company operating in Menemen Organized Industrial Estate in Izmir-Türkiye, for Leather Industries, was processed as described in the study entitled “Utilization of Leather Industry Pre-Fleshings in Biodiesel Production”, and the extracted fat was transformed into biodiesel in accordance with the methods provided in the same study[8].

Gas Chromatography Analysis of Fat and Biodiesel

GC was used to determine the composition of the fat and the product (biodiesel). Fatty acid methyl esters were prepared according to AOCS Official Methods (AOCS, 1997)[10]. Sample (approximately 200 mg) was weighted accurately into a stoppered-glass centrifuge vial. 2 ml of n-heptane was added. Fallowed by 0.1 ml of 2N methanolic KOH was added. Then vial was closed and shaken well for 30 second centrifuge, removed two drops of the upper layer and diluted with 2.0 ml of n-heptane. Then standarts and samples were injected (1 µl) in a Hewlett Packart 6890 Series GC, equipped with a capillary column of Supelco 2380, with a length of 60 m, a film thickness of 0.2 µm and an ID of 0.25 mm. The GC oven temperature was programmed from 100^0C to 220^0C at 4^0C/min and was held at 220^0C for 15 min. The split mode injector was used at a split ratio of 100:1. The detector was a flame ionization detector (FID) and the carrier gas was nitrogen (1 ml/min). GC analysis of biodiesel was carried out by dissolving 0.5 cc of the biodiesel sample in 2.5 ml of n-heptane, and injecting 1 µl of this solution to the GC, in the same conditions as above.

Engine performance and emission tests:

The studies on the evaluation of the vehicle and engine performance of the biodiesel were carried out in the accredited R&D Test and Emission Laboratories of TOFAŞ-Bursa, FIAT’s Türkiye factory. A TOFAŞ manufactured Doblo 1,9 Asp. Pan. vehicle with Euro -1 emission level was used in the tests. The vehicle had a mileage of 12000 km and completed its running-in period before the tests were applied. The vehicle was examined and its compatibility with the tests was ascertained.

Emission and fuel consumption test:

The tests were executed under appropriate conditions and a test cycle dependent on 70/220/EEC main instruction and compatible with 98/69/EC instruction was applied so as to determine and compare the emission and fuel consumption. Emission test was carried out in accordance with “98/69 EC Emission Measurement Standard”[9]. Fuel consumption was calculated as liter/100 km taking HC, CO, CO_2 values obtained in 98/69 EC test and the kilometrage during the test into consideration.

Power test:

For the purpose of determining the effect of fuel on engine power, when the gas throttle valve was open at the maximum, the vehicle was driven at its maximum speed in the same gear as the test with chassis dynamometer was executed (4^{th} gear). When the vehicle was running at full throttle at its maximum speed, dynamometer tried to stop the vehicle at the designated acceleration. Counterforce was measured, and wheel power and wheel force was determined according to turnover or kilometer.

Acceleration test:

Acceleration test was realized by measuring the time elapsed between two speeds after running the vehicle at full throttle in the 4^{th} gear from the first speed (before 3 km/h) to the last (over 5 km/h) provided that chassis dynamometer was in place and road simulation values were put in.

RESULTS AND DISCUSSION

First of all we have searched characteristics of the crude fat obtained from pre-fleshings. The results of the chemical and GC analysis of the crude fat are shown in ***Table I*** and ***Table II*** respectively.

Table I

Properties of crude fat

Characteristics	Method	Results
Appearance	-	Pale yellow cream at 20 ^{0}C
Iodine color analize	DIN 6162	1.2
Acid value	ISO EN 3682	2.4
Iodine number	DIN 53241	50
Saponification number	ISO 3657	189
Refractive index 30^{0}C	DIN 51423	1.4630

Table II

% Fatty acid composition of crude fat

Fatty Acid	Chemical Structure	Crude fat
Myristic (C14:0)	$CH_3(CH_2)_{12}COOH$	3.05
Palmitic (C16:0)	$CH_3(CH_2)_{14}COOH$	20.59
Palmitoleic (16:1)	$CH_3(CH_2)_5CH=CH(CH_2)_7COOH$	4.60
Stearic (C18:0)	$CH_3(CH_2)_{16}COOH$	8.36
Oleic (C18:1)	$CH_3(CH_2)_7CH=CH(CH_2)_7COOH$	41.08
Linoleic (C18:2)	$CH_3(CH_2)_4CH=CHCH_2CH=CH(CH_2)_7COOH$	2.97
Others		19.35

The results showed that fatty acid compositions and the amounts were in agreement with the values obtained from the biodiesel studies carried out with tallow by Alcanatara *et al*[10]., DaNian Zheng-Milford A Hana[11], Michael S. Grabosk-Robert L. McCormick[12] and Fangrui Ma-Milford A. Hanna[13].

Table III

Properties of biodiesel from fleshing fat extract

Characteristics	Method	Results	ASTM Limits	Units
Appearance	-	Clear pale yellow		
Iodine color analize	DIN 6162	1.2		
Specific gravity	DIN 51757	0.8714		
Acid value	ISO EN 3682	0.27	0.80 max.	mgKOH/gm
Iodine number	DIN 53241	50.6		
Copper Strip Corrosion	D130	< 1a	No. 3 max.	-
Sulfur	UOP 727	0.008	0.05 max.	%mass
Saponification number	ISO 3657	197		
Volatile Substance %	DIN EN ISO 662	1.06		
Refractive index	DIN 51423	1.4488		
Viscosity		4.5	1.9-6.0	mm^2/sec.
Flash point (closed cup)		130 (+- 2 ^{0}C)	130 min.	Degrees C
Destilation		95% at 340 ^{0}C	360 max.	Degrees C

Table III indicates the characteristics of the fatty acid methyl esters (biodiesel) produced from the fat of pre-fleshings. The results meet the requirements of the international standards, and therefore the product is suitable for use as a fuel.

The results presented above driven us to evaluate the vehicle and engine performance of the fuel obtained from pre-fleshings. The studies carried out in the accredited R&D Test and Emission Laboratories of TOFAŞ-Bursa FIAT's Türkiye factory. The results of the engine performance and emission tests carried out with petroleum diesel fuel and biodiesel are given below comparatively in Table IV and Table V.

Table IV

Performance and Acceleration Test Results

	Petrodiesel	**Biodiesel**	**% Difference**
Wheel Power (Kw)	38 (106 km/h)	37.5 (106 km/h)	-1.3
Wheel Force (N)	1690(52 km/h)	1635 (50 km/h)	-3.3
Acceleration Time (sec.) 40-100 (km/h)	19.9	20.4	2.5
Acceleration Time (sec.) 60-100 (km/h)	14	14.7	5.0
Acceleration Time (sec.) 80-120 (km/h)	24.8	26.5	6.9

As Table IV reveals, although the results of the wheel force and power test with biodiesel are similar to petroleum diesel fuel performance values, a slight loss in force and power was detected. In parallel with this result, an increase in the acceleration time was observed in speed tests. Yücesu *et al*[14], Y. Guo *et al*[15] and M. Çanakçı[16], who have previously carried out performance studies with biodiesel fuels produced from different resources, stated that biodiesel shows slightly lower performance values in comparison with petroleum diesel fuel performance.

Table V

Emission Test Results

	Petrodiesel	Biodiesel	% Difference
CO_2 (g/km)	213.6	221.2	3.5
CO (g/km)	0.173	0.160	-7.5
HC (g/km)	0.4	0.32	-20
NO_x (g/km)	0.808	0.826	2.2
HC + NO_x (g/km)	0.848	0.858	1.1
Particulate matter (g/km)	0.189	0.071	-62.6
Fuel Consumption	8.1	8.0	-0.8

When the data relating to emission values are evaluated; despite the small increase in CO_2 and NO_X rates, the decrease in the rates of CO, HC and Particle released at the end of biodiesel use stand out to be at noticeable levels. Yücesu *et al*[14], Y. Guo *et al*[15] and M. Çanakçı[16], and R. N. McGill *et al*[17] have denoted a considerable decrease in emission values as a consequence of biodiesel use. In the studies they have executed by adding different amounts of biodiesel to petrodiesel, A. S. Ramadhas, *et al*[18] have also stated a significant decline in gas emission values as the biodiesel amount increases.

Although at low rates, lesser consumption values were obtained with biodiesel use when compared to petrodiesel fuel. Alongside this particular advantage, the fact that exhausts smell of biodiesel is less than the smell of traditional diesel fuels has been noted as another advantage.

CONCLUSION

The fat obtained from the leather industry pre-fleshings was used successfully for the production of acceptable quality Biodiesel and it has been proved that it can be used in petroleum diesel engines without necessitating any modification. Thus it is proved that pre-fleshing wastes from tanneries that storage and disposal are both troublesome and costly could be transformed to a fuel with low emission values and a performance close to diesel fuel providing fuel economization. Thus, a contaminating waste could be transformed into an environmentally friendly fuel, providing economical and ecological profits.

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