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Properties and emission indicators of biodiesel fuels obtained from waste oils from the Turkish industry

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HIGHLIGHTS

- Three waste oils from local Turkish industries proved enough potential for biodiesel production.
- The quality of these biodiesel fuels is enough to partially replace diesel in automotive engines.
- Indicators for main diesel emission were obtained from GC analysis and group contribution methods.
- Soot indicators predict increasing emission with unsaturation degree and molecular weight.

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ABSTRACT

Three waste oils from traditional manufacturing industries in Turkey, such as leather fat, obtained as a by-product in the leather industry, waste anchovy fish oil, derived from the fish-processing industry, and waste frying cottonseed oil from food industry, have been evaluated as alternative raw materials for biodiesel production, with potentially low life-cycle greenhouse emissions. Measured properties such as heating value, density, viscosity, flash point, acidity and cold flow properties, showed that the obtained biodiesel fuels fulfilled both the European and American quality standards and could be used to partially replace petroleum diesel in automotive engines. From gas chromatography analysis, detailed fatty acid profile was obtained, which permitted the application of group contribution methods for the estimation of thermodynamic properties (critical parameters, acentric factor) and thermochemical properties (enthalpies of vaporization and formation). This information was useful to calculate some indicators related to the most important diesel engine emissions, such as soot (main component of particulate matter) and nitric oxide emissions. Soot indicators reveal significant reduction potential with respect to fossil diesel fuels, and, among the studied biodiesel fuels, soot emissions would be lowest for the most saturated and shortest carbon-chain length biodiesel fuel. Adiabatic flame temperature, selected as the main nitric oxide emission indicator, shows small differences among the studied biofuels. Both the properties and emission indicators of the biodiesel fuels studied are within the typical ranges of other conventional biodiesel fuels.

1. Introduction

Diesel engines are used in many fields such as energy generation, transportation, agricultural applications and industrial sectors because of their high fuel economy and durability. However, diesel engines have high emission levels of particulate matter (PM) and oxides of nitrogen (NO_x), and it is difficult to reduce them simultaneously due to the existing trade-off between PM and NO_x. However, the European Union aims to introduce stricter limits on pollutant emissions from light road vehicles, particularly for emissions of oxides of nitrogen and particulates, in response to the increase in the number of light road vehicles on circulation in the recent years and the higher concern about environmental pollution. Besides aftertreatment systems (involving a significant extra-cost for vehicles) one of the most promising approaches for attaining the stricter emission limits is to employ new types of fuels such as biofuels, which have potential advantages over fossil fuels including renewability, reduction in dependency of fossil resources, biodegradability and low emission profile [1]. Among the biofuels, biodiesel has received significant attention. Hence, the production and use of biodiesel implies environmental and

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economic benefits as compared to petroleum based diesel fuels. Using biodiesel in diesel engines as pure or blended forms reduce carbon monoxide (CO), hydrocarbons (HC) and PM, whereas NO_x increases in most of the cases as reported in comprehensive review studies presented in 1998 [2] and in 2008 [3].

On the other hand, the European Commission has been fully aware of this fact and is encouraging the use of biofuels. The 2009/28/CE directive [4] promotes a step by step implementation of biofuels by progressive replacement of conventional fuels, and establishes a new objective of 10%, in energy basis, for biofuel consumption in the transportation sector before 2020. This directive also establishes minimum greenhouse gas emission savings from the use of biofuels (currently 35%) with respect to the typical greenhouse emissions from diesel and gasoline fuels. Among the biofuels with significant market penetration listed in the directive, lowest life-cycle greenhouse emissions, and thus maximum savings with respect to emissions from fossil fuels, were assigned (both as typical values and as default values) to waste-derived biodiesel fuels. Moreover, the recent proposal for a European directive, COM (2012) 595 [5], will limit the contribution of conventional biofuels (with a risk of greenhouse emissions derived from indirect land-use change) to the attainment of the target of the 2009/28/CE directive. This will encourage the market penetration of biofuels such as those derived from industry wastes, and especially of those derived from wastes from traditional manufacturing local industries, with proven low-carbon economies [6].

Hence, in the light of the above concerns, waste oils such as leather fat obtained as a by-product of the leather production processes in leather industry, waste anchovy fish oil derived from fish-processing industry and waste frying cottonseed oil from food industry can be used in biodiesel production as alternative raw materials in countries like Turkey, where these raw materials are available abundantly.

Turkey is one of the leading countries of the leather and leather products industry in both production and export. Turkish leather industry has taken a prominent place of the world leather trade with its high export productivity. There are 13 leather industrial organized zones functioning in Turkey and those are generally localized in the Marmara and Aegean regions [7]. The leather industry commonly uses hides and skins as raw materials, which are essentially by-products of animal slaughtered for using in meat and meat products industry. While processing hides/skins, substantial amounts of solid/liquid wastes are generated, and these wastes cause major environmental problems if not managed properly [8]. Pre-fleshing, fleshing, shaving and trimming are the pre-tanning stages of the leather production processes where most of the solid waste is originated. Pre-fleshing process is performed in order to remove flesh and to ease the penetration of the chemicals. Wastes of pre-fleshing process contain large amounts of fat and protein. Despite their fat content there are very few application methods to recover these wastes [9]. One way to recover the leather industry wastes is using them as feedstock in biodiesel production due to their rich fat content [10]. Thus, the pollution caused from the leather industry wastes may be reduced and more valuable products can be obtained by converting them to biodiesel for countries like Turkey where there is a developed leather industry.

Fish wastes are also an important waste resource to use in energy generation facilities as the fish processing industry generates large quantities of tissue waste and by-products. In this context, waste anchovy fish oil is produced in large quantities by fish-processing industry as by-product in Turkey. There are more than a hundred firms where fishery products are being processed and marketed in Turkey. Among these products, fish flour and fish oil are at the top in Turkey [11]. Apart from the oil obtained from the body and liver of fresh fish for feeding purposes, waste anchovy oil is produced by means of pressing method from head and viscera and stale fishes which are processed in fish-processing factories located in cities such as Trabzon, Sinop, Samsun and Rize in Black Sea region in Turkey. These fish wastes tend to be either discarded or used as fertilizers or animal food, and thus have little economic value [12,13]. This waste anchovy oil can be used in biodiesel production within the context of the European Commission directive of biofuel usage derived from industry wastes. Fish oil produced from Black Sea anchovy as source of energy consists of essential fat acids and high ratio of unsaturated fatty acids along with other essential minerals (calcium, phosphorus, magnesium) and vitamins (B12, A, D3, colin, inositol) [14].

The production of cottonseed oil, which is a product of the processing of cotton seed has increased regularly in Turkey, and it is among the most important sources of oil, followed by sunflower, peanut, soybean, sesame, poppy, rapeseed and safflower [15]. The production and use of cottonseed oil in Turkey is of great importance when compared to other oil types because of it is obtained by using domestic oil seeds at a rate of 95%. The cottonseed oil is quite dark colored oil which is obtained from cottonseeds; and which has its characteristic taste and smell [16]. The production of cottonseed oil provides a total of oil production as much as 30%, and it is used as frying oil in industrial patisseries in Turkey, which, thus, are potential suppliers of high amounts of waste frying cottonseed oil. With it is unfoaming characteristics, cottonseed oil is particularly used to make domestic sweets, which are made from the mixture of dough and egg at certain amount and are produced by frying in high temperature oil. In this context, waste frying cottonseed oil is a good choice for producing biodiesel in Turkey, because it is dumped after use, and it is currently collected from the small-scale food processing services by some registered oil collectors. However, in Turkey, only a small percentage of these waste oils (around 1% of all the waste oil), which is being estimated to be approximately 0.35 million tons per year, has been collected and used in producing soap [17]. Converting these waste oils into biodiesel prevents them from being disposed in a non-environmental way, and contributes to re-utilize such a waste energy source. Moreover, since the major cost factor in the production of biodiesel is the cost of the raw material [18], the cost of biodiesel produced out of waste oils is a lot lower than that of biodiesel from refined oils, which will make the former much more competitive than the latter. In Turkey, waste frying oils can be obtained without any cost directly from different food facilities or indirectly from licenced collectors, whereas waste anchovy fish oil and leather fat oils are sold with prices around 0.5 USD/l, which is less than half of the price of refined oils.

Leather fat is taken into consideration for biodiesel production in the west of Turkey where the Leather Industrial Organized Zones are established (with an average production of fat of around 6000 tons per year in these zones, although with seasonal differences) [19]. As for waste anchovy fish oil, 15 million liter has been produced from 150,000 ton of processed anchovy in fish processing factories located in Black Sea region of Turkey [13,20]. Finally, the production of cottonseed oil was also recorded as 900,000 ton per year in Turkey, and much of this oil is used in the food industry as frying oil, but, as mentioned above, most of the waste is dumped after use [21]. Therefore, no extensive studies have been performed yet on the analysis of these waste oils as potential biodiesel feedstocks.

The aim of this work is to explore the possibility of the use of these three waste oils derived from local manufacturing industries in Turkey as feedstocks for biodiesel production, to compare the measured properties of these biodiesel fuels and to evaluate their potential use in diesel engines through a selection of calculated thermochemical properties and emission indicators which have been proposed in the literature. Further experimental engine