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Waste fish oil biodiesel as a source of renewable fuel in Iran

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ABSTRACT

Among the renewable energy sources, the potential for biofuel energy in Iran is numerous. The Iranian government is paying considerable attention for utilization of renewable energy; especially biofuels. During recent years, fish wastes are considered as loss. Biodiesel production, manure composting, biogas production and burning of fish wastes to produce energy are different ways to utilize the fish waste in the world. Increasing demand for fissile fuels in the world, reduced fossil fuel's resources and pollution problems are the causes to introduce alternative renewable resources. Extracted oil from wastes of aquatic resources is an example of raw materials for production of biodiesel in the world. This study presents a brief introduction to the resource, status and prospect of waste fish oil as a sustainable energy source for biodiesel production in Iran. The main advantages of using waste fish oil for biodiesel production in Iran is also described. In this study, design and manufacturing of an oil extraction machine is also introduced. The fish oil was separated from fish wastes with the help of the designed oil extraction machine. Experiments showed that 53% of fish wastes was in liquid phase (mixture of water, oil and suspended solids) and the extracted oil was about 11% of the total weight of the fish wastes (using of 7 kg of wastes, about 3.71 kg liquid was extracted and 0.8 l (768 g) oil was isolated). Biodiesel fuel was then produced from the extracted fish oil after the chemical reaction (transesterification, reaction between methanol, potassium hydroxide and oil from fish waste). In the present investigation, for each liter of produced fish oil, 0.9 l biodiesel was produced. Important fatty acids like palmeitoleic, palmitic acid, stearic acid, oleic acid, linoleic acid and linolenic acid were identified for the extracted oil. The highest fatty acid ratio belonged oleic acid. These fatty acids affect the magnitude of the cetane number of biodiesel fuel.

Contents

1. Introduction

Fish oil is produced in large quantity by fish-processing industry as a by-product in Iran. This by-product has similar calorific value to petroleum distillates and is a renewable energy source. Several studies have been carried out for using fish oil as fuel for diesel engines; compared with No. 6 fuel oil, the fish oil has lower content of carbon and slightly higher content of hydrogen. The fish oil also has higher flash point but much lower kinematic viscosity. As a result, the viscosity of the blend is much lower than that of the No. 6 oil. This could reduce the requirement for preheating the fuel to make it flow easily, and reduce pump

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demands. Lower viscosity could also improve the atomization of the burner. Compared with the No. 6 oil, the 10% fish oil blend showed lower emissions of CO, SO_2 and particulates but noticeably higher emission of NOx [1,2]. According to the Food and Agriculture Organization (FAO), in 2005 the estimated world fish production was around 142 MT. Approximately 75% of this production is used for direct human consumption. The remaining 25% is destined for non-food products. For 2008, the estimated world fish production was 144 MT. The volume of waste produced by processing plants is calculated to be around 50% of the total processed fish, for which the amount of oil varies from 40% to 65%. Bio-oil has a large variety of compositions as a function of the feedstock. It can be produced from biomass based on triglycerides like soybean, palm, castor and canola, as well as animal fats, lard, poultry fat and fish oil capsules [3]. About 250,000 MT of fish processing waste is produced worldwide and could be converted into useful products such as oil. When directly used as fuel for engines either pure or by blending it with other solvents, the fish oil could cause problems, such as carbon deposits in engine, engine durability and lubricating oil contamination. Converting fish oil into biodiesel would be a better approach. Salmon oil, a by-product of salmon processing, was used as a feedstock for biodiesel production via transesterification in a two-step process. Sulfuric acid-catalyzed pretreatment was used in the first step to reduce the acid value from 12.0 to 3 mg [KOH] g $[\text{oil}]^{-1}$ and then, in the second step, KOH-catalyzed transesterification was applied. The maximum biodiesel yield of 99% was achieved using a total methanol/molar ratio of 9.2% and 0.5% (w/w) KOH. Ester loss due to the formation of emulsion during the washing and drying steps was 15% maximum. A preliminary economic analysis showed that the cost of biodiesel production from salmon oil was almost twice that produced from soybean oil [4]. The fish processing industry generates large quantities of tissue waste and byproducts which tend to be either discarded or retailed at low value for fertilizer or animal feed. Fish processing activities may generate byproducts such as: heads, trimmings (tail, fin), viscera and skin that could be a potential source of fats/oils for biodiesel production [5]. Biodiesel is commonly derived from vegetable oils and animal fats (fish and livestock) by alkali- or lipase-catalyzed transesterification reactions. Since free fatty acid (FFA) content is a critical parameter in the conversion of fish oils to methyl esters, the performance of a Fourier transform infrared (FTIR) spectroscopic method was assessed as an alternative to the conventional AOCS titrimetric method. It was concluded that the NaHNCN-based FTIR method is a flexible, viable instrumental alternative to the AOCS titrimetric procedure for the determination of FFA content of fish tissue lipids destined for biodiesel production [5].

Fish oil extracted from marine fish is rich in omega-3 polyunsaturated fatty acids. The length of the carbon chain of fish oil is frequently greater than that of general vegetable oils, which are primarily composed of palmitic acid, oleic acid, linoleic acid, and linolenic acid. Biodiesel with larger cetane number may cause the improvement of diesel engine performance and a reduction of pollutant emissions. Although there is great potential for the use of fish-oil biodiesel as transportation fuel or as a power source, research into the fuel properties of fish-oil biodiesel is rather limited [6]. The use of locally processed fish biodiesel as a heating fuel mixed with diesel fuel would be beneficial [7]. Because fish oil contains approximately 90% of the energy content of diesel fuel and is easy to process into usable biodiesel blend fuels, this clean burning bio-oil could be used to reduce dependence on imported fuel and improve air quality. Fish oil requires minimal processing to be made usable as fuel. At a cost of 25 cents per gallon for fish oil compared to $1.19 per gallon for diesel fuel, it is easy to see why fish biodiesel blend make good economic sense. Several different fuels like rapeseed oil, fish oil and frying fat have been tested in different engine types [8]. Biodiesel, a renewable, biodegradable, nontoxic, carbon neutral and environmentally benign fuel for diesel engines has been attracting considerable interest all over the world which can significantly reduce global warming and the dependence on conventional fossil fuels [9]. Biodiesel can be used to replace petrodiesel to reduce the pollutant emissions from combustion equipment. Vegetable oil, animal fat, algae, or waste cooking oil can be used as the raw oil for biodiesel production. Marine fish, such as cod, tuna, and squid, generally contain plenty of polyunsaturated fatty acids. During the manufacturing process of fish products, the viscera, fins, eyes, tails, etc., are often discarded. The discarded parts of marine fish are frequently ground into fishmeal to provide food for livestock, aquaculture, or pets and thus have little economic value. However, the crude fish oil extracted from the these discarded parts may provide an abundant, cheap, and stable source of raw oil to allow maritime countries to produce biodiesel and thus help to reduce pollutant emissions. Studies on the fuel and combustion characteristics of biodiesel produced from marine fish oil are rather scarce [10]. Several studies have allowed assessing the performance of diesel engines fueled with different types of biodiesel such as sunflower oil methyl ester, sunflower oil ethyl ester, rapeseed oil methyl ester, palm oil methyl ester and palm oil ethyl ester. There have been also engine tests using biodiesel made from soybean oil and waste frying oil biodiesel from different oil seeds and olives. Biodiesel from salmon oil is not carbon-neutral as biodiesel made from vegetable oil; however used as fuel for internal combustion engines is clearly advantageous compared to simple incineration and also with respect to diesel, marine fish, such as cod, tuna, and squid, generally contain plenty of polyunsaturated fatty acids, including C20:5 and C22:6 [11]. About 13% of the biodiesel currently produced in EU-25, countries. This is based on the estimate that the total biodiesel production in the EU-25 in 2005 is 3.2 MT. It has been the interest to also look at other residue materials, and the utilization of residual animal fat for biodiesel production has thus been focused in the study giving basis to the current article [12]. The potential for using the soapstock as raw material to produce fish-oil biodiesel was evaluated.

Waste oils from animal and vegetable sources continue to be important biomass feedstock due to the potential benefits over petroleum and some of the virgin vegetable oil based fuels. The potential for biofuel from fish waste is a function of the location and size of the processing plant, type of fuel requirements, and characteristics of the fish waste. Fish oils have higher viscosity, lower lubricity, more acidity, and higher flash point compared to petroleum diesel. The main concerns raised from earlier research for engines using fish oils were engine deposits in exhaust ducts and increased wear in parts which are constantly in contact with the oil [13,14]. Fairbanks Morse Engine Division of Coltec Industries Inc. tested crude fish oil and its blends with diesel in a medium speed-two cycle-six cylinder type engine. In comparison to the blends, the pure fish oil had lower volatility. Thermal cracking of the fish oil and blends occurred and the onset temperature of cracking decreased with increase of fish oil in the blend. When compared with 100% diesel, the initial boiling point of all fish oil blends was higher, but pure fish oil boiling point was lower than all blends and pure diesel. The calculated cetane index for measuring ignition delay was not applicable to the fish oil as thermal cracking occurred prior to the mid boiling point [15,16]. The thermal, rheological and stability properties of the salmon oil methyl esters were evaluated and reported by [17]. Despite the difference in the composition of salmon oil from that of corn oil, salmon oil methyl esters had comparable viscosity, volatility, low temperature properties, heating value, acid value, and specific gravity and better oxidative stability than that of corn oil methyl esters. Ghadge and Raheman found that to reduce the acid value of mahua oil from 34 to less than 2 mg [KOH] g $[oil]^{-1}$, the optimum methanol-to-oil and H_2SO_4-to-oil ratios were 0.32 v/v and 1.24 (w/v), respectively, at the reaction temperature of 60 °C and the reaction time of 1.26 h. After this pre-treatment, they used 0.25 (v/v) methanol-to-oil and 0.7% (w/v) KOH as a catalyst for biodiesel production. The conventional homogeneous catalysts are expected to be replaced by eco-friendly heterogeneous catalysts in the near future owing to the ease of catalyst recovery and simplifications in product purification. Thus, the development of solid catalysts has recently gained tremendous importance in view of the current economic climate e.g. increased competition and stringent pollution regulations [18]. The low cost highly effective heterogeneous catalysts derived from waste resources e.g. shrimp shell [19], and waste shells of mollusk [20] were successfully used for biodiesel production. Bio-oil has a large variety of compositions as a function of the feedstock. It can be produced from biomass based on triglycerides like soybean, palm, castor and canola, as well as animal fats, lard, poultry fat and fish oil capsules, and the major products are alkanes, alkenes, ketones, aldehyde, aromatics and carboxylic acids [21].

Some physico-chemical properties of waste fish oil (WFO), bio-oil (BO), light bio-oil (LBO) and heavy bio-oil (HBO) were determined and compared to Brazilian fuel specifications. LBO and HBO were also analyzed to determine the yields of compounds according to the carbon numbers in the chain by GC [22]. None of the MIR FFA methods has been applied to FFA determination in fish oils whereas near-infrared (NIR) spectroscopy has been used to analyze for FFA content in mackerel oil and in salmon fillets [23,24]. Quantified amounts (2000 mg kg^{-1} dry soil) of the chosen contaminant, i.e. processed fish biodiesel, heating diesel fuel, or blends of both containing 5%, 20%, or 50% biodiesel, prepared on the volume percent based method (ASTM D 6751-08, 2008), were added to the surface of previously uncontaminated soil. The biodiesel was produced through the transesterification process by a commercial biodiesel plant in Hawaii based on bulk raw fish oil from processors working in the North Pacific just off the Alaskan coast [25]. Several different fuels like rapeseed oil, palm oil, fish oil and frying fat have been tested in different engine types. Sunflower and fish oil have been converted to their methyl esters, tested in a single cylinder diesel engine and concluded that, the maximum output with both methyl esters was higher (0.11 kW, 3%) than the diesel fuel. The main reason for smoke decrease for biodiesel and blend fuels is thought to be the higher oxygen content of biodiesel [26]. The similar reductions were reported elsewhere. Many studies were also carried out for fish oil as fuel for diesel engines. Waste anchovy fish oils transesterification was studied with the purpose of achieving the conditions for biodiesel usage in a single cylinder. It can be concluded that the biodiesel obtained from waste anchovy fish can be used as a substitute for petroleum diesel in diesel engines [27–33]. Biofuels such as biodiesel are derived from biomass using biochemical, thermo-chemical, and physical and chemical extraction processes. Waste oils from animal and vegetable sources continue to be important biomass feedstock due to the potential benefits over petroleum and some of the virgin vegetable oil based fuels. Many researches investigated the chemical, thermal, and physical properties of biofuels derived from virgin and waste sources [34–83].

Considering this literature review, this study presents a brief introduction to the resource, status and prospect of waste fish oil as a sustainable energy source for biodiesel production in Iran. The main advantages of using waste fish oil for biodiesel production in Iran are also described. An oil extraction machine was designed and manufactured to extract the fish oil and biodiesel was produced from this product. Some standard specifications of the produced waste fish oil are also measured and compared with international standards (ASTM) to investigate the quality of this produced biodiesel. Producing biofuels from different sources like fish wastes can ideally replace some share of fossil fuel consumption in Iran.

2. Iran's energy status

Iran is OPEC's the 2nd largest oil producer and exporter after Suadi Arabia. Natural gas accounts for half of Iran's total domestic energy consumption, while the remaining half is predominately oil consumption. The continued exploration and production of the offshore South Pars natural gas field in the Persian Gulf is a key part of Iran's energy sector development plan. Iran has estimated 137.6 billion barrels of proven oil reserves or roughly 10% of the world's total reserves. In 2008, Iran produced 4.2 million barrels of oil per day (bbl/d) equal to about 5% of global production. Iran exported near by 2.4 million bbl/d of oil to Asia and European countries, making it the 4th largest exporter in the world in 2008. Iran's 2009 crude oil production was 3.9 million bbl/d. Iran's estimated proven natural gas reserves stand at 1045 trillion cubic feet (tcf), 2nd only to Russia in 2010. In 2008, Iran produced 4.1 tcf of natural gas and consumed 4.2 tcf. Natural gas is expected to grow around 7% annually. Iran's population is growing at a fast pace. It has doubled to 70 million people in only 30 years and much electricity is needed for growing population and economy use. Due to infrastructure problems, domestic demands and economic need to export oil and natural gas, these energy sources cannot fully meet future Iranian electric needs. Iran has substantial solar, wind, geothermal and biomass resources. An energy efficiency program using renewable energy

$$\text{1 mol Triglyceride} + \text{1 mol Alcohol} \Longleftrightarrow \text{1 mol Diglyceride} + \text{1 mol } RCOOR_1$$
$$\text{1 mol Diglyceride} + \text{1 mol Alcohol} \Longleftrightarrow \text{1 mol Monoglyceride} + \text{1 mol } RCOOR_2$$
$$\text{1 mol Monoglyceride} + \text{1 mol Alcohol} \Longleftrightarrow \text{1 mol Glycerol} + \text{1 mol } RCOOR_3$$

Fig. 2. Step by step mechanism of transesterification reaction.

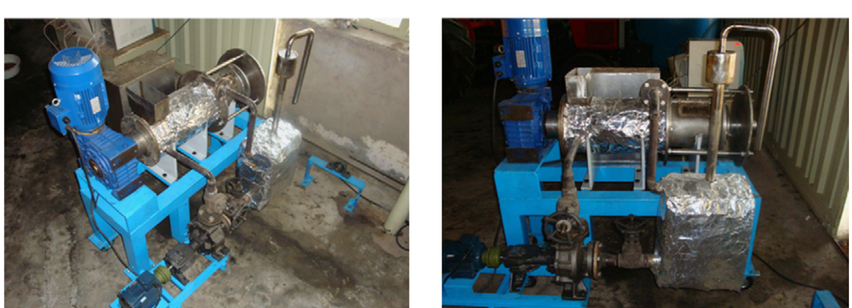

Fig. 1. Fish oil extraction machine.

can help cut electric use from conventional resources considerably and can meet all the future electric needs of Iran. Iran can meet its future electric generation goals through renewable energy and efficiency for only \$20 billion. The production of renewable energy and energy efficiency products would create thousands of jobs, help economy, reduce greenhouse gases and save Iranian oil and gas that would be available for export. Producing biodiesel from fish wastes can reduce consumption of fossil fuel in Iran [84–96].

3. Materials and methods

There is abundant fish waste in local fish market, either in coastal towns or in metropolitant cities in Iran. The moisture content of these fish wastes is about 65%. Biodiesel production, manure composting, biogas production and burning of fish wastes to produce energy are different ways to utilize the fish waste in the world. This amount was 299,128 t (Persian Gulf), 32,533 t in Caspian Sea, the total rate in 2003 reached 441,836 t.

In this study, after designing and manufacturing of an oil extraction machine (Fig. 1), waste fish oil was separated from fish wastes. Experiments showed that 53% of fish wastes was in liquid phase (mixture of water, oil and suspended solids) and the extracted oil was about 11% of the total weight of the fish wastes (using of 7 kg of wastes, about 3.71 kg liquid was extracted and 0.8 l (768 g) oil was isolated).

Biodiesel fuel was produced from the fish oil after the chemical reaction (transesterification, reaction between methanol, potassium hydroxide and oil from fish waste). For each liter of oil, 0.9 l biodiesel was produced.

Biodiesel is typically produced through the reaction of fish oil with methanol in the presence of catalyst to yield glycerin and methyl esters. This process for making biodiesel is relatively simple. The process is known as transesterification, step by step mechanism of this reaction has been shown in Fig. 2. Process of biodiesel production from waste fish oil has been indicated in Fig. 3. At the first step, the

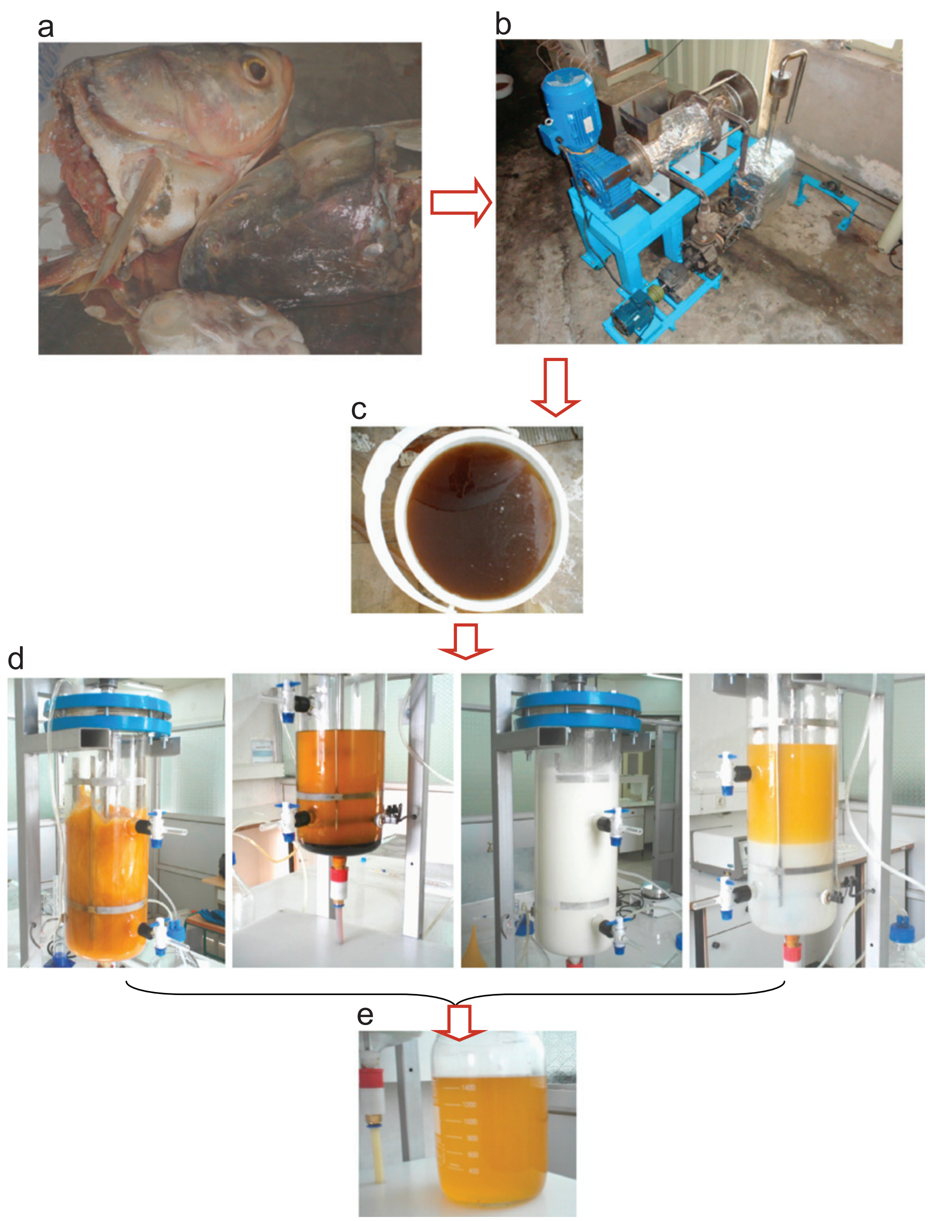

Fig. 3. Biodiesel production process from fish wastes: (a) fish wastes, (b) fish oil extraction, (c) fish oil, (d) transestrification reaction, and (e) produced biodiesel.

Table 1
Biodiesel fuel specifications based on ASTM D6751.

Property	Test method	Specification	Measured	Units
Flash point, closed cup	ASTM D93	130 Min	164	°C
Water and sediment	ASTM D2709	0.050 Max	–	volume %
Kinematics viscosity, 40 °C	ASTM D445	1.9–6.0	4.717–4.205	mm^2/s
Sulfated ash	ASTM D874	0.020 Max	–	wt%
Sulfur	ASTM D5453	0.0015 Max	–	wt%
Copper strip corrosion	ASTM D130	No. 3 Max	–	–
Cretan number	ASTM D613	47 Min	–	–
Cloud point (°C)	ASTM D2500	–	–	–
Carbon residue	ASTM D4530	0.050 Mass	–	wt%
Acid number	ASTM D664	0.80 Max	–	mg KOH/g
Free glycerin	ASTM D6584	0.020 Max	–	wt%
Total glycerin	ASTM D6584	0.240 Max	–	wt%
Phosphorous content	ASTM 4951	0.001 Max	–	wt%
Distillation temperature	ASTM D1160	360 °C Max	–	% distilled

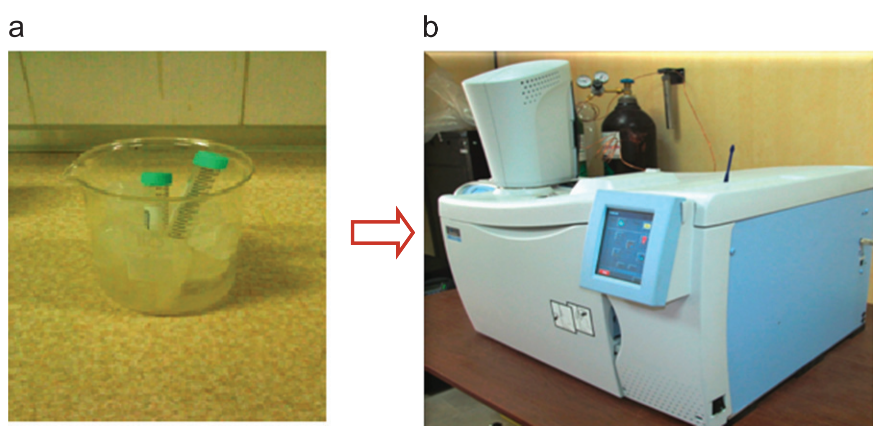

Fig. 4. (a) Samples and (b) gas chromatography (GC) analyzer.

Table 2
Parameters used in biodiesel GC analysis.

Gas Chromatograph: Perkin Elmer Clarus 580 GC			Column: Select Biodiesel CP9080 30 m × 0.32 mm × 0.25 μm film	
Inlet temperature: 250 °C			Mobile phase: helium gas (purity 99.999)	
Mobile phase flow: 1 ml/min			Detector:	FID 250 °C
Split flow:	50 ml/min		Air flow:	450 ml/min
			Hydrogen flow:	45 ml/min
Column temperature program:			Volume of material injected:	0.5 μl
Hold (min)	Temp. (°C)	Rate (°C/min)		
2	60	–		
–	210	10		
10	230	5		

processed waste fish oil was fed into the system. The existing water in the reaction at higher temperature levels resulted in triglyceride hydrolysis and free fatty acid formation. Free fatty acids neutralized the catalyst led to soap formation. Therefore, it can be implied that the existence of water and free fatty acids caused soap production. For performing the tests, the catalyst of potassium hydroxide (1% oil weight) and alcohol to oil volumetric ratio of 1:4 was applied. Since waste oil was used for biodiesel production, the color of resulting mixture was dark brown during the early stages of reaction turning to a lighter color at the later phases of the reaction. The reaction was conducted for 2 h at the temperature of 60 °C, agitation speed of 300 rpm and at the ambient pressure. The reason for selecting the temperature value of 60 °C, was that, the temperature of reaction had to be below the boiling temperature of the methanol (64 °C). Biodiesel produced contains no sulfur or particular matter that contributes to air pollution. Sulfur and PM have been responsible for black smoke and sour odor problems commonly attributed to dirty diesel fuel. Biodiesel has greater lubricity than petroleum diesel. After production of biodiesel, some biodiesel standard specifications were measured. It was noticed that these specifications are matched with international standards (ASTM) (Table 1).

4. The chemical composition of waste fish oil

The weight proportions of the fatty acid compositions of the biodiesel were analyzed using a gas chromatography (GC) analyzer (Claus 580 GC model, Perkin Elmer Co., USA), (Fig. 4). The parameters used in biodiesel GC analysis are indicated in Table 2. The GC–MS analysis of waste fish oil showed the main composition of fatty acids to be the followings: 1.07% muriatic (C14:0), 20.91% palmitic (C16:0), 6.81% palmeitoleic (C16:1), 0.69% heptadecanoic

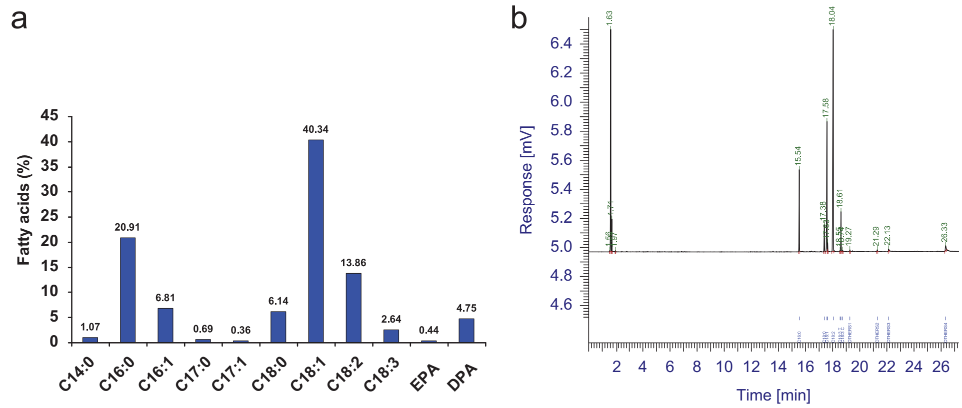

Fig. 5. (a) Important fatty acids of waste fish oil and (b) determination of the yields of fish oil compounds according to the carbon numbers in the chain by GC.

Table 3
Comparison of biodiesel produced from rapeseed oil, fish oil and waste oil.

Spec.	Standard method of test	Waste oil	Rapeseed oil	Fish oil	Unit
Flash point	ASTM D92	176	170	164	°C
Kinematics viscosity	ASTM D445	4.73	4.01	4.205–4.717	mm^2/s
Density	ASTM D1298	80	900–930	867–869	kg/m^3

(C17:0), 0.36% heptadecenoic (C17:1), 6.14% stearic (C18:0), 40.34% oleic (C18:1), 13.86% linoleic (C18:2), 2.64% linolenic (C18:3), 0.44% eicosapentaenoic (EPA) and 4.75% docosahexaenoic (DHA) (Fig. 5). These fatty acids affect the amount of cetane number of diesel fuels.

Biodiesel produced from rapeseed and waste oil and their specification were compared with fish oil (Table 3). The results proved that flash point of fish oil is lowest than others, kinematics viscosity of fish oil is lower than waste oil and upper that rapeseed oil. The comparison of oils' density shows that rapeseed oil has the highest density while the lowest density belongs to the waste oil.

5. Future prospects

There is a great potential of waste fish oil as a sustainable source for production of biodiesel. Research for producing biofuels from fish oil is in the beginning stages and there is a substantial need for more research to study the other economic issues related to biofuels. There is also a considerable potential for utilization of fish oil as biodiesel in Iran. Producing biodiesel from the fish oil can ideally replace about 5% of total diesel fuel consumption in the first step in transportation sector. There is no doubt that a substantial need for more research work to study the other economic issues related to biodiesel production from waste fish oil.

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