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Characterization of the liquid products obtained from Tunisian waste fish fats using the pyrolysis process

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ABSTRACT

The use of organic wastes as new renewable energy sources is becoming necessary to achieve the growing energy demand in Tunisia. In this work, the pyrolysis of abundant waste fish fats provided by a canned Tuna factory was examined in a laboratory fixed-bed reactor. The main objective was to analyze the properties and the composition of the produced bio-oil using in order to implement the suitable valorization strategy. Therefore, high heating value, viscosity, density, flash point, acidity index, moisture content and ash content measurements as well as FTIR and GCMS analyses were carried out to characterize the pyrolytic oil obtained during waste fish pyrolysis at 500 °C.

The obtained results revealed that waste fish fats can be considered as important feedstock for biofuel production. In particular, the bio-oil characterization showed the presence of many organic compounds such as alkanes, alkenes, alkynes, cyclic hydrocarbons, carboxylic acids, aldehydes and alcohols. These compounds could be used as a valuable and sustainable chemicals source. Moreover, the bio-oil properties indicated a good calorific value (~9391 kcal/kg) compared to Tunisian Diesel and European biodiesel specifications. In contrast, higher acidity (~103 mg KOH/g sample) and viscosity (~7 cSt) compared to conventional fuels were obtained. These properties limit the direct use of bio-oils as alternative fuel in a Diesel engine. An efficient mixture with fossil fuel may be a promising solution to improve the fuel properties.

Hence, pyrolysis seems to be an eco-friendly process to recover the fish fatty wastes in Tunisia. The implementation of such management strategy will help Tunisian agri-food industries to reduce their environmental impact and fossil fuel consumption and to promote the renewable energy use.

1. Introduction

The major problems facing the world today are soaring fossil fuel prices, depletion of energy resources, climate changes and air pollution. Consequently, biofuel productions from biomass have become more attractive with the potential to offset fuel mitigation and to reduce greenhouse gas (GHG) emissions [1]. Among various biomass resources, organic wastes are a promising green feedstock due to their abundance and their rising production with human population increase. However, great efforts are required to convert them into renewable fuels, a suitable choice to reduce their harmful impacts into the nature and to decrease the world's fossil fuel dependence [2].

Energy and environmental constraints have encouraged many developing countries like Tunisia to develop the use of renewable energy. In fact, Tunisian fossil fuel reserves are modest and the national energy balance was moved from a precarious balance between 1995 and 2000 to a deficit state which incites the renewable energy development [3]. In addition to the energetic context, waste management represents a major challenge in Tunisia since 6 million tons/year of organic waste was produced between 2008 and 2009 [4]. This organic waste can be considered as important feedstocks for bioenergy production.

Several studies were performed to identify the available bioenergy feedstocks in Tunisia. Chouchene et al. have evaluated the performance of olive mill residues during combustion tests [5]. Elmay et al. have investigated the combustion performance of different date palm residues [6]. Recently, Jeguirim et al. have characterized four Tunisian biomass species: industrial by product (Pine Sawdust), agro-industrial by product (Olive Solid Waste), agricultural residue (Date Palm Trunk) and seaweed (*Posidonia oceanica*) to assess their eventual utilization for energy recovery [7]. These previous investigations have showed promising issues for the energy recovery of dry biomasses. However, several constraints were identified for the wet biomasses such as residues from agrifood, meat and fish industries. In this regard, pyrolysis can be considered as an alternative conversion method to reduce wet waste

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Table 1
Summary of waste animal fats pyrolysis studies: operating conditions and products yield.

Reference	Feedstock	Reactor type	Reaction conditions	Mass balance
[10]	The animal (lamb, poultry and swine) fatty wastes, used for pyrolysis feed, were obtained from various meat factories in Tunisia.	A fixed-bed reactor heated by an electric furnace	Sample mass: 200 g Temperature: 400–550 °C Heating rate: 5–15 °C/min	Pyrolysis conditions: (500 °C, 5 °C/min) Liquid yield: 58–77.9 wt.% Gas yield: 20.3–40.5 wt.% Solid yield: 1.5–1.8 wt.% Organic fraction: 45.8–61.6 wt.% Aqueous phase: 12.2–21.5 wt.%
[15]	Industrial waste fish fats	A fixed-bed reactor	Temperature: from 300 to 500 °C Heating rate: 10 °C/min	Liquid yield: 71.29% (wt.) Organic fraction: 17.08 wt.% Aqueous phase: 54.21 wt.% Catalytic pyrolysis: The best bio-oil yields (72 wt.%) was obtained using Al_2O_3/Na_2CO_3 as catalyst.
[16]	Waste fish oil (WFO) collected from waste treatment unit of a fishery industry in Brazil, after flotation in the aerobic treatment unit followed by separation in a centrifuge. The sample was used as received without any pre-treatment.	Continuous pilot plant tubular reactor	Sample mass: 10 kg Temperature: 525 °C Feed rate: 3.2 kg/h	Liquid yield: 72.83% Gas yield: 15.85% Solid yield: 11.32% Light bio-oil yield: 35.86% Heavy bio-oil yield: 34.83% Oily sludge yield: 2.14%
[14]	Lard produced by Sobeys in Toronto and obtained from a retail outlet.	A tubular fixed-bed vertical microreactor	Temperature: 500–800 °C Carrier gas (N_2): 10–70 cm^3/min Steam to lard mass ratios: 0.5–2.0	Liquid yield: 55.6–78.3 wt.% Char yield: 29–31 wt.% Gas yield: 31–34 wt.% Liquid yield up to 61 wt.% obtained at 600 °C, residence time of 1.5 s and packing particle size of 1.7–2.4 mm.

volume and toxicity, and to upgrade bio-oil production [8,9]. Therefore, Belhassen-Trabelsi et al. have studied the pyrolysis of waste animal fats (lamb, poultry and swine) collected from different Tunisian meat factories [10]. Authors have concluded that fatty wastes are valuable sources for biofuel production and lead to a higher bio-oil yield with an important calorific value.

Generally, waste animal fats obtained from the food industry include fish waste, poultry waste, beef tallow, yellow grease and brown grease [11]. The recovery of the triglyceride materials (fats and vegetable oils) obtained from these wastes is usually realized through transesterification process [9]. Nevertheless, this recovery method has several drawbacks. The main obstacles are the excessive alcohol use, the acid index change, the solid content, the biodiesel purification and the heavy equipment for industrial scale [12,13]. Consequently, pyrolysis technology seems to be more efficient in converting waste animal fats into alternative liquid fuels [8,14]. As shown in Table 1, few studies have examined the pyrolysis of waste animal fats at laboratory scale. These studies indicated that biofuel production via the pyrolysis of waste animal fats could be a valuable solution to reduce their environmental impact.

Among the abundant waste animal fats in Tunisia, fish wastes represent a huge bioenergy potential of and especially bio-oils. In fact, the fish production was evaluated to 109,000 tons in 2012 with 18 fish processing plants that have used 13,000 tons of fish in 2010 [17]. During the product process, about 50 to 75% of the total fish becomes unused waste. The amount of oil presented in this waste varies between 40% and 65%. Fish wastes obtained from the agri-food industries are subject to strict environmental regulations. Sanitary landfills and effluent treatment ponds are no longer authorized due to the generated disagreeable odor [18,19]. Therefore, the implementation of a management strategy has become a prominent necessity. Currently, the major part, particularly obtained from fat containers, is released into the nature generating many environmental problems or in wastewater collecting system blocking sewage piping, although national regulations prohibit such actions.

The fish wastes are mainly constituted of triglyceride that can be used as feedstock for biofuel production [15,16]. Fish biodiesel was tested as a partial and/or full in many countries such as Canada, India, Taiwan and Japan. As an example, Ocean Nutrition Canada has produced biodiesel from residual fish oils in 1999. The produced oil is used for producing heat and water vapor in the manufactory and distributed via local subcontractors [21].

The aim of this present work is to evaluate the potential of the waste fish fats obtained from a fat container of a Tunisian tuna factory for biofuel production. Therefore, the bio-oil produced during the waste fish pyrolysis is characterized using different analytical techniques. The obtained properties and composition will help to define the suitable strategy for Tunisian waste fish recovery.

2. Materials and methods

2.1. Materials

In this study, waste fish fat from Tunisian food industry was used as raw materials for the pyrolysis process. The sample was obtained from the downstream part of the fish processing chain of Thon Sidi Daoued (ABCO) Factory located in northern part of Tunisia. This waste consists on a very heterogeneous mixture with fatty compounds, spine and water.

2.2. Pyrolysis procedure

The pyrolysis experiment (Fig. 1) was carried out in a stainless fixed bed reactor (L: 30 cm; Ø: 15 cm). During the pyrolysis test, 500 g of waste fish fats was placed in the reactor and the temperature was increased up to 500 °C at a rate of 5 °C/min under 0.3 l/min nitrogen flow. After the pyrolysis reactions, the condensate vapors were collected using refrigerant cooled by circulating of cold water using a cryostat. Then, the organic fraction or bio-oil from the aqueous fraction was separated by simple decantation using a separatory funnel. The bio-oil and aqueous yields are calculated as follows:

$$\text{Liquid fraction } (\%) = \text{The amount of liquid collected} / \text{total amount of initial feedstock} \times 100$$
$$\text{Bio-oil or organic fraction } (\%) = \text{The amount of bio-oil collected} / \text{total amount of initial feedstock} \times 100$$
$$\text{Aqueous fraction } (\%) = \text{The amount of bio-oil collected} / \text{total amount of initial feedstock} \times 100.$$

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