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Biodiesel production from tannery fleshings: Feedstock pretreatment and process modeling

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HIGHLIGHTS

- Biodiesel production from tannery pigskin fleshings.
- Waste fat deacidification and its mathematical modeling.
- Extraction of free fatty acids by alkali extraction agent.
- Evaluation of extraction efficiency and determination of losses of triglycerides.

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ABSTRACT

During raw hide processing, tanning industries generate large quantities of wastes containing a considerable amount of fat which can be converted into biodiesel. A typical representative of such wastes is fleshings – which however, usually contains a significant amount of free fatty acids, proteins and other impurities. Pretreatment was suggested as a means of processing this acidic feedstock, thereby enabling the reduction of the free fatty acid content under the limit value of 0.5% w/w when the alkali catalyst is then appropriate for transesterification. The feedstock pretreatment process involved the refining melting of fresh pigskin fleshings with subsequent extraction using a methanol or methanol solution with an equimolar amount of alkali i.e. tetramethylammonium hydroxide, isopropylamine and cyclohexylamine. A mathematical model of the pretreatment process was proposed, verified and used in further simulation calculations – which confirmed that deacidification employing methanolic alkali solutions is more efficient than pretreatment with pure methanol; in addition, the free fatty acids can be removed to the demanded level in just one step (fat initial acid value = 20 mg KOH/g, mass ratio of methanol to oil = 1.5). The fat pretreated by the suggested procedure was used for alkali catalyzed transesterification. The prepared biodiesel met most of the EN 14 214 requirements with respect to the limitations caused by the used fleshings fatty acid profile.

1. Introduction

The increasing demand for energy is growing due to the ever-greater industrialization of societies coupled to the ballooning growth in the worlds population; therefore, it is inevitable for human existence [1]. Biodiesel – as a renewable, non-toxic and biodegradable fuel, has been considered in recent years as an alternative to diesel fuel [2]. As a chemical substance, it can be defined as a mixture of fatty acid methyl esters (FAME) in long-chain fatty acids. Biodiesel is usually produced by the transesterification of vegetable oils and animal fats with a short-chain alcohol – typically methanol, usually catalyzed by alkali or acid catalysts [3,4].

However, the high price of vegetable oils makes biodiesel production economically disadvantageous because nearly 75% of the price of biodiesel is made up by the price of this feedstock [5]. From this point-of-view, the production of biodiesel has perspectives from other economically acceptable feedstocks such as waste frying oils, beef tallow, pork lard or tannery waste fats (fleshings), which make biodiesel production economically profitable [6,7]. On the other hand, such feedstock often contains a significant amount of free fatty acids (FFAs), which form the major obstruction to the direct conversion of waste fats and oils into biodiesel by the most common method, i.e. transesterification catalyzed with inorganic alkali catalysts (e.g. KOH, NaOH and similar bases), because the catalyst is spent on the neutralization of FFAs and thus the

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conversion of the transesterification reaction is not high enough [8,9]. The recommended FFA content in a feedstock suitable for effective alkali transesterification should be less than 1 mg KOH/g, which corresponds to 0.5% of FFAs [10]. Nevertheless, biodiesel can also be made using acid catalysts (e.g. sulfuric, phosphoric acid) which are also able to catalyze the esterification of the FFAs; however, the transesterification process is too slow and the acceleration of this reaction requires a large excess of methanol [8]. Therefore, the utilization of acid catalysts is more suitable as a first step in the pretreatment of the acidic waste fats which leads to the esterification of the FFAs into esters. After reducing the FFA content in the feedstock, the alkali catalyst may be used for the subsequent transesterification of triglycerides into biodiesel [10].

It should be noted that waste fats and oils – as well as crude vegetable oils and animal fats, contain notable quantities of accompanying substances (impurities) apart from the FFAs – the most important additional compounds are proteins (especially in the case of waste fats), water, oxidation products and phosphatides [11]. To make the feedstock suitable for biodiesel production by means of the common transesterification reaction catalyzed by homogeneous alkali catalysts, these impurities must also be removed from the feedstock, or their content must be significantly reduced. Currently, there are two main methods for the pretreatment of fats and oils commonly used on the industrial scale – namely, physical and chemical refining [12].

Degumming is the first step in the refining process, the purpose of which is to reduce phospholipids below the value of 5 mg/kg of phosphorus prior to further processing (by using a physical or chemical procedure). During this process, the hydratable phospholipids are especially eliminated; nevertheless, the content of non-hydratable phospholipids – i.e. the calcium or magnesium salts of phospatidyl ethanolamine and phosphatidic acid can also be reduced [12]. Degumming is usually performed by means of one of the following methods: degumming with water, acid (phosphoric or citric acid) or enzymes (phospholipases) as well as also using semi-permeable membranes [12–15].

The degumming process is followed by further refining. With regard to physical methods, the most common procedure is steam refining. Steam refining means the elimination of the free fatty acids from the feedstock using vacuum distillation with hot steam (200–270 °C) as the stripping gas (0.5–2 wt.%) and under low pressure (0.2–0.5 kPa) [16]. Replacing the steam with nitrogen allows one to obtain a more stable deodorized oil, a better quality distillate and lower losses of neutral oil [17]. Krishnamurthy et al. [18], showed that up to 82% of free fatty acids were removed at 162–288 °C using nitrogen as a stripping gas. Other authors [19,20], found suitable conditions for refining beef tallow and some vegetable oils using a stream of nitrogen at 50–270 °C and under a pressure of 0.013–0.79 kPa, or 220–240 °C and under a pressure of 0.2–0.4 kPa, respectively. Extraction by solvents is another option for physical refining. This method is often used for the treatment of waste fats from slaughterhouses which contain a high content of FFAs. When methanol was used as an extraction agent in multistage extraction (i.e. cross-flow), the content of FFAs in slaughterhouse fat was decreased from 1.6% to a value below 0.1% at 60 °C [21]; however, the authors give no information on the molar ratio of methanol to fat. During the extraction of palm oil by a mixture of carbon dioxide and dimethyl ether in a ratio of 1:1, the level of FFAs decreased from 4.2% to 0.2%, as was also reported by Drescher et al. [21]. Other possible extraction agents that can be used for physical refining are, polyethylene glycols, dimethyl ether, ethane, propane, etc. [21].

Chemical (or alkali) refining is the most frequently used industrial method for the deacidification of fats and oils [22], which allows the removal not only of the FFAs but also of slime substances, phospholipids and pigments [23]. Deacidification is carried out by the addition of alkali to the oil or fat after the degumming step, thereby the precipitation of the FFAs occurs – resulting in the formation of alkali soaps, which are subsequently removed from the neutral fat by centrifugation. The most widely used alkali for alkali deacidification is sodium hydroxide, since it is a strong alkali and easily able to neutralize the FFAs [24]. However, the chemical deacidification of fats and oils leads to great losses of neutral oil as a result of hydrolysis or the formation of occlusions in the soaps. The resulting soaps are able to hold up to 50% of the neutral oil – which significantly reduces the yield of refined fat and oil [25]. Let us note that in the case of biodiesel production, deacidification can also be performed via esterification of the FFAs with methanol; as was mentioned above.

The literature provides only a limited number of studies dealing with the processing of tannery fats (i.e. fleshings) into biodiesel. Fleshings constitute up to 60% of overall tannery wastes [26]. As a result, their utilization is beneficial from the waste management point of view; nevertheless, fleshings are often not recovered or their utilization is not effective [1,27,28]. The estimated amount of fleshings generated by the tanning industry worldwide is around 3.8 million tons annually [29]. They can be obtained either before or after the liming treatment, being termed as green fleshings (or pre-fleshings) and limed fleshings, respectively [30]. The raw fleshings usually contain a high amount of water, FFAs, protein and inorganic salts [28,31]. İşler et al. in [1], reported the production of biodiesel from fleshings using sodium hydroxide as a catalyst; however, the study provides no details on how the fleshings were treated prior to transesterification. Colak et al. [32], reported in their study that they obtained fat from sheep pre-fleshings by boiling the feedstock with water under high speed grinding. Thereafter, the fat was separated without further refining (the FFA content was 1.2%) and was then used for the production of fatty acid methyl esters by using methanol and potassium methanolate (30% in methanol) as a catalyst. The FAME yield achieved was 95%. Alptekin et al. [27], used sulfuric acid and methanol for the pretreatment of the acid fleshing oil. After the reduction of the FFA content from 12.15% to below 1%, they performed the transesterification reaction with various alkaline catalysts (i.e. CH_3ONa, CH_3OK, NaOH and KOH) and methanol. Crispim et al. [31], described the production of biodiesel from limed fleshings – where the fat was obtained by washing them with hot water (90 °C) and was subsequently refined by extraction using *n*-hexane. The fat so obtained was deacidified by means of FFA esterification. However, as stated by the authors, the suggested pretreatment requires further optimization steps to reduce investment and energy costs. Ramos et al. [33], used esterification for the reduction of the FFA content in fat extracted from fleshings, using methanol in the presence of sulfuric acid after washing with hot water (60 °C) and extraction with *n*-hexane to remove proteins. This was followed by two-step transesterification with methanol and KOH as a catalyst. Ong et al. [6], used tannery fats with a high share of FFA transesterification under supercritical reaction conditions (nitrogen 12 MPa, methanol to oil ratio of 40:1, temperature 250–325 °C) without prior refining for the production of biodiesel. Getahun and Gabiyye [34], reduced the FFA content in fleshings from 12.33% to 1.5% by esterification with methanol in the presence of sulfuric acid (10 wt.%) at 60 °C for 1 h. Thereafter, the transesterification reaction catalyzed by KOH, reached an immediate FAME yield of 97 %. Kolomazník et al. [35], proposed the refining melting process as a suitable pretreatment step for acidic tannery fats with subsequent transesterification with a strong organic catalyst like tetramethylammonium hydroxide (TMAH), which simultaneously serves as an esterification agent of FFAs instead of the commonly used strong mineral acids. The refining melting operation allowed