Hydrophobization of bleaching clay used for purification of waste frying oils

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Abstract. The paper presents the results of research on the possibility of carrying out the hydrophobization process of bleaching clay Jeltar 100 and the usage of such modified sorbents for purification of waste frying oils. The hydrophobization process was carried out with the usage stearic acid solutions with organic solvents. The hydrophobization degree of modified sorbent was determined. Utility properties of the hydrophobic sorbent were evaluated in contact with waste frying oils. It has been proved that the properties of the sorbent Jeltar 100 (raw material) after the hydrophobization process are improved. The density of frying oil after the purification process decreases. The acid value of the purified oil decreases significantly when the hydrophobic Jeltar 100/5 (material after modification) was used. The greater increase is observed in iodine value for oil purified by sorbent Jeltar 100/5. Peroxide value of oil after its purification increases to the value obtained for waste frying oil, however, in the case of the sorbent Jeltar 100/5 increase in this parameter is reduced. It has been found that the hydrophobized sorbent absorbs a smaller amount of liquid products from crude oil than the raw sorbent. The hydrophobization process improves both the adsorption and mechanical properties of the sorbent Jeltar 100. Hydrophobic bleaching clay has better dispersion in volume of purified oil that results in improvement in oil regeneration.

1. Introduction

About 157 tons of the oil is produced per year [1]. Depending on the geographic region different plants are used to make oil. In Asia palm oil is the most common. Both North and South Americas are predominated by the soy oil. While in Europe most popular oils are the sunflower and the rapeseed oil. Vast majority of produced oil is used to cooking purposes, mostly to high temperature treatment such as deep frying. Due to the high temperature during frying process multistage reactions of the triglycerides occurs that cause oil degradation [2]. The amount of the waste frying oils produced in industrial frying processes is so vast that they are causing a serious danger to the environment. This kind of pollutions is similar to the petroleum pollution. It is important to acknowledge that the waste frying oils are mixture of different types of oils and fats that in addition it unfavourably influences the way of its processing [3,4]. However, even so overcharged waste oils contains enough valuable triglycerides to use them as a raw material for biodiesel production after cleaning [4-11].

This way of use of the waste frying oil seems to be attractive in the light of an European Union directives [12,13] concerning gradually increase of share of the biofuels in fuel market. Polish law guarantees implementation of the European Union directives and they are assuming increase share of the alternative fuels which make waste cook oil an interesting biofuel raw material [14 - 15]. In favour of the waste frying oils as component of biofuel speaks social attitude that condemn use of the whole...
some grain and oil seeds as a raw material to obtain biofuels [16-17]. Using waste frying oil as a biofuel component is also recommended for the economic reasons, because price of obtained biofuel is lower than the price of similar quality fuel synthesized from for example rapeseed oil [18–19].

As was mentioned before using of waste frying oil as the biofuel component hence requires its purification from harmful products created in frying process. Detailed guidelines of quality requirements and methods of research of liquid bio components are specified by proper ordinances and standards [20–22]. The adjustment of oil properties to the bio components requirements is not an easy task and research still continues to gain new methods of the purification to achieve required level of clearing of waste frying oil. The most common methods of purification mentioned in literature are alkali neutralization, vacuum drying, use of the desiccants or the adsorbents [23–26].

Use of the adsorbents for the oil purification is often a subject of studies. Its effectiveness is examined as an individual material and as mixture of different adsorbents. Results of studies show that selection of the type and amount of purification material should be preceded by quantitative and qualitative analysis of the pollutants. In addition it was found that level of the oil purification and types of removed pollutants strongly depends on sort of the used adsorbents and the conditions of process [27]. Therefore different types of the adsorbents are used for example: synthetic silica, bleaching clay, activated carbons and silica gel. The effects of the use of the adsorbents in different conditions are still current topic of many researches. Activated carbon and bleaching clay deserve special attention [4, 24-26, 28]. Activated carbon is the adsorbent with special abilities such as huge specific area, developed microporous structure, good reactivity of surface and finally vast adsorption capacity. Bleaching clay is very effective in removal of the peroxides. Research [27] show that during experiments effectiveness of bleaching clay was over 80% while active carbon have lowest peroxide removal between 36.2 to 64.2%. Other research also indicates that bleaching clay is good for the waste frying oil clearing. Selectivity of different sorbents causes that especially well for purification process is mixture of activated carbon and bleaching clay [29].

Unfortunately the activated carbons used for the removal of pollution from the solutions are characterized by high water absorption. It may be unfavourable during the regeneration process. In case of powder materials such as bleaching clay unfavourable phenomenon of wetting is common and can causes agglomeration that leads to decrease of the specific area and blocking of the active centers lowering its ability to adsorb substances especially polar compounds. Therefore in this application an important feature of sorbents may constitute resistance to the water. Water resistance of sorbents can be changed by means of the hydrophobization process [30 - 33]. The change of the hydrophobic properties of these sorbents, which is applied during production filters for removing oil and organic pollutants were done also [28, 34].

The hydrophobic sorbents are less cohesive and have wide application in processes where hydrophobic character of its surface is improving operation. Hydrophobic fine particles are used in industries such as chemical, metallurgy, architecture, agriculture, sugar companies, in production of paints, varnishes, rubber and plastic and also in coal mining [35 - 41].

The hydrophobization process of bleaching clay Jeltar 100 can lead to production of less amount of the solid waste during the industrial oil purification process, moreover new features of the sorbent make its storage and dosage easier. The topic of the study is actual and the obtained results could have a potential to contribute to improvements of waste frying oil purification from harmful products.

2. Materials and methods

2.1. Materials

Bleaching Clay Jeltar 100. Bleaching Clay Jeltar 100 produced by chemical company „Siarkopol” Tarnobrzeg sp. z o.o., with composition show in Table 1, is an example of the material with ability to active and passive purification. It is grey, odorless fine powder, pH 2.9-3.5. Density of product is 2400 kg.m$^{-3}$, bulk density is about 400-600 kg.m$^{-3}$ [42].
Table 1. Composition of bleaching clay Jeltar 100 [42].

| Component                  | Content (% w/w) |
|----------------------------|-----------------|
| Acid activated bentonite   | 50 ÷ 100        |
| Cellular fibers            | 0 ÷ 15          |
| Activated carbon           | 0 ÷ 10          |
| Perlite                    | 0 ÷ 10          |
| Non-activated bentonite    | 0 ÷ 50          |

Main component of bleaching clay is bentonite. Bentonite is clay rock made mostly of montmorillonite, mineral belonging to the silicate group. This material is characterized by huge water sorption amounting 500 [% min] in Enslins scale [43]. Acid activated form is characterized by more developed porous structure, therefore have greater specific surface. Acidic character favours the adsorption of most of the polar compounds, unfortunately low pH also favours creating free fat acids and diols during oil purification. To reduce this undesirable effect causing acid value to rise only part of the bentonite present in bleaching clay is activated by acid [44]. Activated carbon is beneficial for improving acid value, anisidine value and it is decreasing amount of polar compounds in waste frying oil [45]. Perlite is mixture of oxides, mostly silica oxide. Due to its porous structure is used to passive purification of solid particles with diameter greater than 1 μm [4]. Cellular fiber adsorbs colorants significantly brightening the oil [46].

Waste rapeseed frying oil. Waste rapeseed frying oil was obtained in 26th October 2016 from the typical gastronomic point and it is characterized by average level of the wear adequate to this type of facility. Compared to the fresh rapeseed oil waste oil have much darker color, visible impurities form food processing such as dark particles at the bottom and characteristic, unpleasant odor. Modifier. Methyl alcohol or diethyl ether stearic acid solutions were used as modifiers. Industrial modifier was chosen for research as they, according to the author, guarantee good contacting of sorbent grains with a hydrophobizing preparation [47]. Stearic acid is used in mining production plants for the production of anti-explosive dust.

2.2. Methods
2.2.1. Hydrophobization process.

Bleaching clay Jeltar 100 was modified to add hydrophobic abilities. During the hydrophobization process a commercial modifier, stearic acid was used. The method of Jeltar 100 hydrophobization with the use of stearic acid was carried out with the use of methyl alcohol or diethyl ether stearic acid solutions. The concentration of these solutions was chosen in such a way that after evaporation of the solvent, the content of stearic acid in a solid material was equal to 5%. Stearic acid concentration was selected during laboratory research as lowest amount of the modifier that causes visible changes in hydrophobic character of the modified sorbent. Hydrophobization was carried out by mixing stearic acid solutions with the Jeltar 100 in a laboratory evaporator, at an increased temperature. After solvent evaporation sorbents was drying twice for two hours in the atmospheric dryer at 378 K. The detailed descriptions of the conducted hydrophobization processes can be found in the author’s earlier works [48]. Acquired sorbent after modification was marked as: H-5-me (modified by methyl alcohol stearic acid solutions.) and H-5-et (modified by diethyl ether stearic acid solutions).

2.2.2. Evaluation of the hydrophobization degree by “floating on water” test.

In this work a relative evaluation of the hydrophobization degree of the analyzed materials was based on a simple experiment – the so-called “floating on water” test [49-50]. The experiment consisted in placing a small amount of material (about 2 grams) on the surface of the water in a beaker. The hydrophobization degree of materials modified in the work was evaluated on the basis of the material amount floating on the water surface for a specified period of time. Figure 1 a present the photographs of the “floating on water” test for the materials, obtained: immediately after placing the
samples on the water surface, after 2 minutes and after 5 hours for H-5-me sample. The pictures were taken 15 seconds apart, except last one on the bottom right that was taken after 5 hours.

![Figure 1. The photographs of the “floating on water” test for: a) H-5-me, b) for raw material.](image_url)

Part of the modified bleaching clay marked as H-5-me immediately sunk, but water remain transparent, and more of the material was still floating on the surface compared do raw bleaching clay. (Figure 1b). Another part of sorbent sunk after about 2 minutes, rest of H-5-me (about 50%) was floating for over 5 hours until observation was terminated. Results of the “floating on water” test for the H-5-et sample was similar to the result for H-5-me. Research show, that solvent does not affect hydrophobisation process of the bleaching clay.

### 2.2.3 Waste frying oil purification.

The aim of waste frying oil purification was comparison of the effectiveness of the process carried out whit raw bleaching clay Jeltar 100 and modified material marked as H-5-me. The amount of the removal of the products created during frying was measured. To 200 grams of waste frying oil (in two experiments) 20 gram of sorbents was added (raw bleaching clay and H-5-me). Mixture gain deep dark color. It was heated to the 378 K and it was intensively mixed for 20 minutes. In the next step material was separated from oil by the laboratory centrifuge at 4300 rpm for 20 minutes. Visual assessment found that separation was very good. Oils were decanted and marked as oil – ru (after raw bleaching clay treatment) and oil – me (after H-5-me treatment). Used sorbents was dried in 378 K to specify the amount of water in material.

### 2.2.4 Analysis of oil properties.

To examine change in properties of the purified oils following values was measured: oil density, acid value (L.K), peroxide value (L.N), iodine value (L.I). In addition organoleptic evaluation and water impregnability of materials was checked. All measurements were conducted based on Polish Standards [51–54].
Organoleptic evaluation of oils- Waste frying oil and oils obtained after the purification with raw bleaching clay and modified material H-5-me was evaluated in terms of color (Figure 2) and smell.

![Figure 2. The photograph of oil samples – from left waste frying oil, oil - ru (after raw bleaching clay treatment) and oil - me (after H-5-me treatment).](image)

Waste frying oil is dark with unpleasant odor after food that was fried in it. Also suspended dark solid particles are present. Waste frying oil purified by raw bleaching clay Jeltar 100 (oil – ru) was lucid, have straw yellow color, and delicate scent of food that was prepared in it. Oil purified by modified bleaching clay H-5-me was similar to the oil purified by raw bleaching clay which mean, that hydrophobization process does not affect ability of sorbent to change color and smell.

*Oil density* - oil density was measured in the pycnometer in temperature 294 K. Density of water in temperature 294 K was set as 998.02 kg.m⁻³. Results were summarized in Table 2.

| Oil                  | Density (kg.m⁻³) |
|----------------------|------------------|
| waste frying oil     | 917.07           |
| oil - ru             | 915.28           |
| oil - me             | 915.79           |

*Acid value* – acid value was measured according to Polish Standard [51]. Sample blank determination was conducted twice. After adding one drop of titration color changed to pink (fuchsia) what was interpreted as zero value of blank sample.

*Iodine value* – Morgosche’s method was selected to measure value of iodine value based on Polish Standard [52]. Sample blank determination was 32.0 cm³.

*Peroxide value* – peroxide value method was based on the Polish Standard [53]. Sample blank determination was zero.

Measurements were summarized in Table 3.

| Materials         | LK (mg KOH.1 g⁻¹ oil) | LI (g I₂.100 g⁻¹ oil) | LN [mEq O₂.100 g⁻¹ oleju] |
|-------------------|-----------------------|------------------------|---------------------------|
| waste frying oil  | 0.87                  | 3.37                   | 0.25                      |
| oil - ru          | 0.86                  | 4.40                   | 1.93                      |
| oil - me          | 0.68                  | 4.87                   | 0.86                      |
Lowest acid value was obtained from the oil purified with modified bleaching clay H-5-me. Indication of iodine value in the purified oils was higher comparing to this one for waste frying oil which is desirable effect. In case of modified bleaching clay H-5-me increase was greater than in case of raw bleaching clay. Oils purified by both bleaching clays have higher peroxide value, but in case of H-5-me peroxide value is about two times lower comparing to raw material. Other research describes cases in which peroxide value was increased [56].

Impregnability - impregnability is meant as weight loss before and after drying in material from the separation in the laboratory centrifuge. Figure 3 shows photo of sorbent after oil purification and separation.

![Figure 3. The photograph of used bleaching clay after oil regeneration.](image)

Used bleaching clay is dark, muddy substance. Used sorbent was weighed and dried in atmospheric dryer for 4 hours in temperature 378 K. After that sorbent was weighed again. Impregnability was defined as difference in masses according to equation (1).

\[
\text{Impregnability} = \left( \frac{mp - mk}{mp} \right) \times 100\%
\]  

where:
mp – mass of sorbent before drying,
mk – mass of sorbent after drying.

In case of raw sorbent impregnability was measured as 1.12% while modified bleaching clay impregnability value was 0.32%. Acquired results favour bleaching clay with hydrophobic abilities. Modified bleaching clay is easier to separate from oil. It might be stated that hydrophobization process lowers impregnability of used bleaching clay.

3. Result discussion
In paper hydrophobization process of bleaching clay Jeltar 100 was conducted by stearic acid in organic solvents. Concentration of stearic acid at 5% level was considered as minimal amount of modifier to achieve the required hydrophobic abilities. Research show that there is possibility of using different of stearic acid solvents to acquire good level of hydrophobization.

After hydrophobization bleaching clay Jeltar 100 performance characteristics are not deteriorating. Organoleptic evaluation of oil purified by raw bleaching clay and modified material H-5-me is similar in both cases, oil density decreases similar as well. It means that hydrophobization process do not influence on sorption abilities of bleaching clay Jeltar 100 relative to products created during frying that are responsible for oil density.

Impregnability favours hydrophobic bleaching clay. In the industrial scale of the oil purification it will lead to smaller amount of the solid waste.

Acid value of purified oil decreases significantly in case of modified material H-5-me. In case of raw bleaching clay acid value is similar to the waste frying oil. It might be caused by acidic character
of bleaching clay form acid activated bentonite that increases acid value. Releasing of acidic compounds might be difficult after hydrophobization process.

Iodine value of the purified oils increases which is desired effect. Greater increase of this parameter is obtained using hydrophobic sorbent, which means that hydrophobization improves sorption abilities of bleaching clay relative to the compounds created during thermal treatment of oil that are blocking unsaturated bonds in fatty acids.

Peroxide value of oil purified by raw bleaching clay Jeltar 100 increased significantly which means increase in amount of oxidation products in oil marked as oil – ru. Hydrophobization of material decreases this effect, therefore oil purified by modified bleaching clay (oil-me) have lower peroxide value.

4. Conclusions
Research show, that there is possibility to improve hydrophobic abilities of bleaching clay Jeltar 100 by stearic acid in organic solvent. Hydrophobization process conserves most of the characteristics utility parameters of the material, furthermore some of properties are improved such as density, acid value and iodine value.

Bleaching clay Jeltar 100 after hydrophobization have smaller water adsorption capacity, and it is easier to separate than raw bleaching clay which can lead to creating less of the solid waste in industrial-size processes of the oil purification.

Hydrophobic bleaching clay has better dispersion in volume of purified oil that results in improvement in oil regeneration. In addition is it worth to mention, that adding hydrophobic abilities to bleaching clay with huge impregnability such as Jeltar 100 lowers cohesive forces in material and prevents from agglomeration which facilitates its storage and dosage.

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5. References
[1] Tonsil, http://www.clariant.com/en/Innovation/Innovation-Spotlight-Videos/Tonsil, 2017
[2] Chwiałkowski W 2006 Zeszyty Naukowe AE, Kraków 710
[3] Skrzyńska E and Kmiec K and Stankiewicz R, 2011 Technical Transactions, Chemistry, P.K. 10, 235
[4] Cooke B S, Adsorbent treatment of frying oils and the impact on health and nutrition, 3rd Euro Fed Lipid Congress, Edinburgh 2004
[5] Refaat A A, 2010 Journal of Environmental Science & Technology 7 183
[6] Hoissain A B M S and Boyce A N, 2009 Bulgarian Journal of Agricultural Science 15 312
[7] Zhang Y Y , Dub M A, McLean D D and Kates M, 2003 Bioresource Technology 89 1
[8] Wu H, Zong M-h, Luo Q and Wu H-Ch, 2003 Prepr. Pap.-Am. Chem. Soc., Div. F Fuel Chem., 48 533
[9] Lim B B P, Maniam G P and Hamid S A, 2009 European Journal of Scientific Research 33 347
[10] Buczek B, Czepirski L, 2004 Inform 15 186
[11] Saifuddin N, Raziah A Z and Nor Farah H, 2009 E-Journal of Chemistry 6 S1 485
[12] Dyrektywa 2003/30/EC Parlamentu Europejskiego i Rady UE z dnia 8 maja 2003 roku w sprawie wspierania użycia w transporcie biopaliw lub innych paliw odnawialnych, Official Journal of the European Union, L 123/42
[13] Dyrektywa 2003/96/EC Parlamentu Europejskiego i Rady UE z dnia 27 października 2003 w sprawie przebudowy wspólnotowych ram opodatkowania produktów energetycznych oraz energii, Official Journal of the European Union, L 283/51
[14] Rozporządzenie Rady Ministrów w sprawie Narodowych Celów Wskaźnikowych na lata 2011–2016, Projekt z dnia 19.03.2010 r, (www.mg.gov.pl/node/10711
[15] Ustawa z dnia 6 grudnia 2008 r. o podatku akcyzowym, Dz.U. z 2009 r. Nr 3, poz. 11, z późniejszymi zmianami
[16] Baier S, Clements M, Griffiths Ch and Ihrig J J, 2009 Biofuels Impact on Crop and Food Prices: Using an Interactive Spreadsheet, Board of Governors of the Federal Reserve System, International Finance Discussion Papers, 967
[17] Weyerhaeuser H, Tennigkeit T, Yufang S and Kahrl F, 2007 Biofuels in China: An Analysis of the Opportunities and Challenges of Jatropha Curcas in Southwest China, ICRAF Working Paper 53
[18] Szlachta J J, 2006 Inżynieria Rolnicza 11 463
[19] Marczak P, 2010 Wykorzystanie tłuszczu zwierzęcego jako biopaliwa – wybrane zagadnienia, Kancelaria Senatu, Biuro Analiz i Dokumentacji, Dział Analiz i Opracowań Tematycznych, OT-589
[20] Rozporządzenie Ministra Gospodarki i Pracy z dnia 19 października 2005 r. w sprawie wymagań jakościowych dla biokomponentów oraz metod badań jakości biokomponentów, Dz.U. 216, poz. 1845
[21] Rozporządzenie Ministra Gospodarki z dnia 22 stycznia 2009 r. w sprawie wymagań jakościowych dla biopaliw ciekłych, Dz.U. 18, poz. 98
[22] PN EN 14214:2004 Paliwa do pojazdów samochodowych. Estry metylowe kwasów tłuszczowych (FA FA ME) do silników o zapłonie samoczynnym (Diesla). Wymagania i metody badań
[23] Felizardo P, Neiva Correia M J, Raposo I, Mendes J F, Berkemeier R and Bordado J M, 2006 Waste Manage. 26 487
[24] Predojević Z J, 2008 Fuel 87 3522
[25] Cvengros J and Cvengrosova Z, 2004 Biomass Bioenergy 27, 173
[26] Dias J M, Alvim-Ferraz M C M and Almeida M F 2008 Fuel 87 3572
[27] Tańska M, Rotkiewicz D and Bańczek N, 2012 Nauka Przyroda Technologie 4 6
[28] Buček B and Chwitalkowski W, 2005 Żywoność. Nauka. Technologia. Jakość 4 85
[29] Integrated Pollution Prevention and Control, Reference Document on Best Available Techniques in the Food, Drink and Milk Industries August 2006
[30] Duong Do D, 1998 Adsorption analysis: Equilibria and kinetics, Imperial College Press
[31] Thomas W J and Crittenden B, 1998 Adsorption Technology and Design, Elsevier Science & Technology Books
[32] Yang R T, 2003 Adsorbents: Fundamentals and application, John Wiley & Sons
[33] Kerry F G, 2006 Industrial gas handbook: gas separation and purification, Taylor & Francis Group, LLC
[34] Lee C H, Johnson N, Drelich J and Yap Y K, 2011 Carbon, 49 669
[35] Malicka-Soczka A, Domka L and Kozak A, 2010 Physicochemical Problems of Mineral Processing, 44 151
[36] Krysztafkiewicz A and Jesionowski T, 2003 Przemysł Chemiczny 82/8-9 844
[37] Grzeszczyk S and Podkowa P, 2010 Cement Lime Concrete 15 340
[38] Domka L, Wąsicki A and Kozak M, 2003 Physicochemical Problems of Mineral Processing 37 141
[39] Ciesielczyk F, Krysztafkiewicz A and Jesionowski T, 2006 Physicochemical Problems of Mineral Processing 40 255
[40] Stanisławska A and Werner A, 2006 Przemysł Chemiczny 85/8-9, 1318
[41] Hu Z, Zen X, Gong J and Deng Y, 2009 Colloids and Surfaces A: Physicochemical and Engineering Aspects 351 65
[42] „Jeltar 100” - Safety Data Sheet 2010, Materiały wewnętrzne ZCh "Siarkopol" Tarnobrzeg sp. z o.o., http://www.zebiec.pl/mineraly/bentonit/bentonit-g-zebiec, July 2017
[43] Brooks D, Berbesi R and Hodgson A, 2013 Optimization of Bleaching Process. Edible oil processing, The AOCS Lipid Library, Vernon Hills IL
[44] Chwitalkowski W 2008 Zeszyty Naukowe Uniwersytetu Ekonomicznego w Krakowie 767
[45] Liu L, Gao Z Y, Su X P, Chen X, Jiang L and Yao J M, 2015 ACS Sustainable Chem. Eng, Hangzhou 3 432
[47] PN-G-11020, 1994 – Pyl kamienny przeciwwybuchowy
[48] Vogt E, 2008 Polish Journal of Chemical Technology 10 49
[49] Vogt E, 2012 Cement Lime Concrete 3 160
[50] Fuerstenau D W and Williams M C, 1987 Colloids and Surfaces 22, 87
[51] [50] PN-ISO [PN-EN ISO 660:2009 Oznaczanie liczby kwasowej i kwasowości
[52] PN-EN ISO 3961:2013 Oznaczanie liczby jodowej
[53] PN-EN ISO 3960:2012 Oznaczanie liczby nadłenkowej
[54] PN-EN ISO 6885:2016 Oznaczanie liczby anizydynowej
[55] Mizerski W, 2005 Małe tablice chemiczne, Adamantan, Warszawa
[56] Enweremadua C and Ruttob H, 2019 Combustion, emission and engine performance characteristics of used frying oil biodiesel, Renewable and Sustainable Energy Reviews, Pretoria 2010 14 863