Journal of KONBiN 2022
Volume 52, Issue 4
DOI 10.2478/jok-2022-0046

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PRELIMINARY STUDIES ON THE PURIFICATION OF BLEACHING EARTH FROM SLACK WAX RESIDUES IN THE ADSORPTION REFINING BY LOW-TEMPERATURE PYROLYSIS PROCESS

Badania wstępne nad oczyszczaniem ziemi bielącej z pozostałości gaczu parafinowego w procesie rafinacji adsorpcyjnej metodą pirolizy niskotemperaturowej

Abstract: *The essence of the low-temperature pyrolysis process presented below is the processing of contaminated bleaching earth, resulting in a purified bleaching earth, high calorific oil with an average level of 45.5 MJ / kg and synthesis gas that can be used to heat the reactor. For research purposes, a proprietary low-pressure reactor with a system of direct cooling of hydrocarbon vapors was used. The main advantages of the presented method are the limitation of technological processes to a minimum and the ease of automation by reducing the entire cycle to one device.*
Keywords: slack wax, bleaching earth, low-temperature pyrolysis.

Streszczenie: *Istotą przedstawionego poniżej procesu pirolizy niskotemperaturowej jest przetworzenie zanieczyszczonej ziemi bielącej, w wyniku czego uzyskuje się oczyszczoną ziemię bielącą, olej o wysokiej wartości opałowej na średnim poziomie 45,5 MJ/kg oraz gaz syntezowy, który można wykorzystać w celu grzania reaktora. W celach badawczych wykorzystano reaktor niskociśnieniowy z bezpośrednim układem chłodzenia par węglowodorowych własnego projektu. Do głównych zalet przedstawionej metody można zaliczyć ograniczenie procesów technologicznych do minimum oraz łatwość automatyzacji poprzez sprowadzenie całego cyklu do jednego urządzenia.*

Słowa kluczowe: gacz parafinowy, ziemia bieląca, piroliza niskotemperaturowa.

1. Introduction

Spent bleaching earth (SBE) is usually deposited in a landfill, however, due to high disposal costs and environmental impact, it is highly recommended to reuse this material [10]. The solutions used so far are aimed mainly at the recovery of material adsorbed on bleaching earths, like paraffins or oils [13, 12], while the residues of such a process remain useless. Various regeneration technologies are increasingly used as part of the adsorbent recovery process. This technology uses the adsorbed material as a supplementary source of thermal energy consumed during the process [8].

The recovery of vegetable oil from SBE requires appropriate extraction processes. The extraction method that is used to recover the oil involves carrying out the process in the shortest possible time and with the minimum amount of consumable solvent. A short extraction time is needed to minimize the potential degradation of active ingredients and to reduce the electrical energy consumption [11]. Among the various extraction technologies used to recover vegetable oils from spent bleaching earth are Soxhlet extraction, membrane technology, subcritical water technology and supercritical fluid extraction (SFE).

The oil adsorbed in the SBE can be extracted using a Soxhlet extractor, where hexane is used as the solvent [5]. The extraction process begins by placing the sample on an extraction thimble holder filled with hexane until the solvent exceeds the flow level, the siphon releases the solute in the extraction thimble holder, transferring a portion back to the distillation flask, which then delivers the extracted oil to a clean flask. The extraction process is continued until all the oil has been extracted. The extracts obtained from the process are filtered and the solvent is removed under reduced pressure and temperature in a rotary evaporator. In this extraction method, it is very important to choose the right solvent, as the polarity of the solvent directly affects the compounds to be dissolved. After extraction, the oil with partial solvent content undergoes separation, which requires a considerable amount of energy. At the refining stage, the addition of lye leads to saponification, which can retain part of the oil comprising about 50% of the free fatty acid content. As a result of the process, highly polluted sewage is obtained, for which large amounts of water and chemicals are used, which has a negative impact on the environment.

Semipermeable barriers that separate two phases and prevent the transport of various substances are called membranes [2]. The main advantages of the extraction process using membrane technologies are: low energy consumption, higher separation efficiency, reduction of the number of processes, improvement of end product quality and reduction of polluted waste water emissions. Many researchers in Japan, Germany, America and India have proposed the use of the membrane as an alternative and reliable treatment method that takes into account the drawbacks of the conventional refining of vegetable oil [15]. Oxidation can be avoided due to the mild operating conditions which is the main advantage of oil processing with membrane technology.

Subcritical Water Technology (SWT) is an alternative method of palm oil recovering from SBE using water instead of an organic solvent [1]. The extraction of vegetable oil takes place in the reactor tube. The reactor must be airtight and should not be filled with water, to exclude the influence of hydrostatic pressure. The extraction operating temperature ranges from 180°C to 280°C, and the pressure value for saturated steam is reached [3]. The obtained extracted product is separated into water, solid and oil phases. The processes of centrifugation and vacuum filtration are used to separate the individual phases, and then, using petroleum ether, the residual traces of oil from the water phase are eliminated.

Supercritical fluid extraction (SFE) is another method used to recover vegetable oil from contaminated bleaching earth. This technology is a clean and environmentally friendly alternative method using harmless carbon dioxide (SC-CO2) as the solvent in the extraction process [4]. With this method, a good quality of recovered oil can be obtained [6]. Supercritical fluids (SCF) are widely used in various fields such as food, pharmaceutical, chemical and fuel industries due to the absence of toxic substances in the final product [14]. In a supercritical extraction process, the mobile phase is subjected to temperature and pressure near or above the critical point, which improves the solvation capacity [17]. The exclusion of organic solvents from the process reduces the problem of their storage in the laboratory, which is a major advantage of using supercritical fluids during extraction. The critical temperature and pressure for carbon dioxide are respectively 31.1°C and 73.8 bar [16]. In the supercritical state, it has high diffusion coefficients, low viscosity and high solvation power. Supercritical CO2 exists as a liquid solvent. Optimum solubility of contaminated bleaching earth in SC-CO2 is obtained at 82.7 MPa and 80°C [11]. It has been shown that under such conditions vegetable oil is obtained at a lower cost than oil obtained in the conventional liquid extraction process [7].

Low-temperature pyrolysis is a method of purifying spent bleaching earth obtained in the paraffin purification process. The bleaching earth treatment process takes place in a controlled environment without oxygen access and with temperature controlled throughout the pyrolysis cycle. The technology of low-temperature pyrolysis is also used in research on the ecological processing of plastic waste, where as a result of the process, oil and pyrolysis gas are obtained. Both process products are a high-energy source that can be used as part of the pyrolysis cycle and in the case of pyrolysis oil, it can be an additive to commercial fuels [9].

This article presents a method for purifying bleaching earth from paraffinic slack wax. Paraffinic slack is obtained in the initial stage of crude oil processing by using two-stage atmospheric and vacuum distillation, one step of furfurol extraction and Di-Me evaporation process at the final stage.

Depending on the further destination of the obtained paraffin, the following purification methods are commonly used to ensure adequate purity and product properties corresponding to the industrial application:

- adsorption refining with bleaching earths,
- hydrogen refining in the presence of a catalyst.

The presented processes aim to reduce the amount of undesirable polar components, such as: polycyclic aromatic hydrocarbons, aromatic hetero compounds or resins, and to obtain products that meet the required criteria of chemical purity, e.g. in terms of very low sulfur content, as a few ppm. The method of processing is selected depending on the application and designed properties of the final product.

Paraffins are used extensively in various applications. In the engineering industry, they are used, among others in products used as dust suppressants, impregnants, lubricant components, abrasion resistance enhancing components or anti-corrosive agents. Obtaining paraffin wax and paraffin with the appropriate purity is necessary especially for their use in anti-corrosion and lubrication products, where any particles significantly affect the operational properties, durability and safety of the equipment in use.

2. Low-temperature pyrolysis of bleaching earth

The main objective of the research conducted on the low-temperature pyrolysis process was to recondition the bleaching earth used in the slack wax purification process. Additionally, the slack wax contained in the contaminated bleaching earth was converted into pyrolysis oil with a high content of petroleum products and pyrolysis gas.

For the test 249.078 g of contaminated bleaching earth was measured on a laboratory scale and placed inside reactor. The test bench is shown in Fig. 1

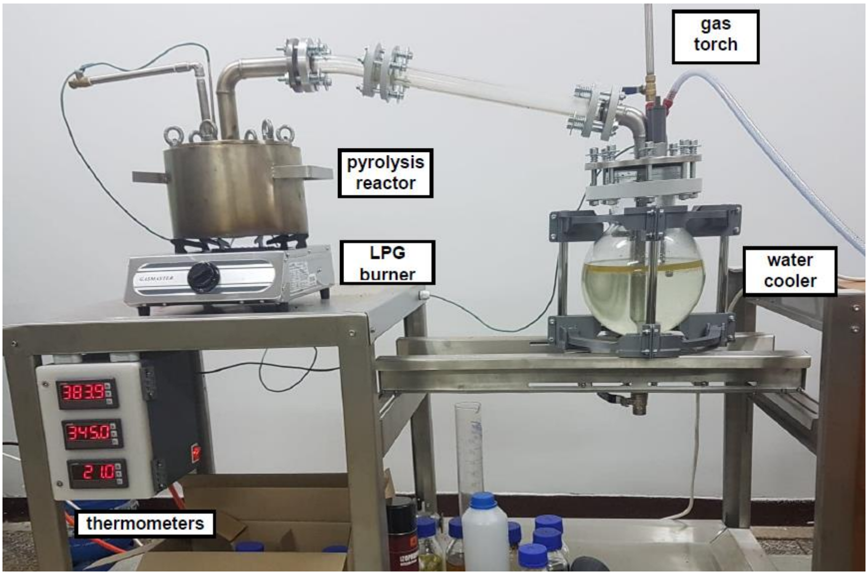

Fig. 1. Low-temperature pyrolysis reactor

The reactor consists of:

- thermally insulated batch chamber with a capacity of 2 l,
- LPG burner with a heating power of 3 kW,

- vapor cooling system (water cooler with discharge of finished gas and oil products),
- control cabinet (process control).

<u>Preparation of the charge</u>

Figures 2a and 2b show contaminated bleaching earth before and after the crushing. The process was carried out manually with a hammer and low force. High force during this stage would lead to compacting the soil into a lumps and adversely affect the pyrolysis process.

a)  b) 

Fig. 2. Batch preparation: a) contaminated bleaching earth before crushing process b) contaminated bleaching earth after the crushing process

<u>Process</u>

The process involved the thermal decomposition of hydrocarbons contained in the so-called bleaching earth without oxygen share. Pyrolysis resulted in gaseous, liquid and solid products and whole process took place in the temperature range from 320 to 480°C in a sealed and airtight installation at low pressure. The emitted gases and hydrocarbon vapors ware cooled directly in water. Due to the difference in density, the oil accumulated above the water surface.

The pyrolytic reactor is equipped with two temperature sensors. The first, designed to indicate the temperature of the feedstock, was placed in the lower part of the reactor, while the second, dedicated to indicating the temperature of the hydrocarbon gases, is located in the upper part of the reactor. An additional temperature sensor was placed in the hydrocarbon steam cooling system.

The process was completed after approximately 6 hours, reaching the following parameters during the cycle:

- the maximum temperature of the hydrocarbon vapor was 360°C,
- the maximum batch temperature was 463°C,
- water temperature in the cooling system was 21÷23°C.

After the entire process had been carried out and the installation had cooled down, a preliminary analysis of the obtained products was performed.

3. Results

As a result of the pyrolysis process, initially loose bleaching earth was obtained without lumps of slack paraffin. Figure 3 present the bleaching earth after the pyrolysis cycle.

Fig. 3. Bleaching earth after low-temperature pyrolysis

After the pyrolysis process, the weight of bleaching earth without slack wax contamination was 175.469 g, but also 66.984 g of oil and 6.625 g of pyrolysis gas were obtained. Gas flow measurement was performed using the DPM37S-V0L6-A2 flow meter. Figure 4 shows a sample of the acquired oil.

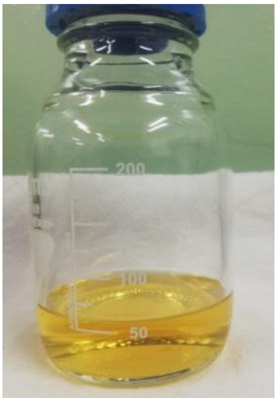

Fig. 4. Oil sample after pyrolysis

The obtained oil was initially tested for its calorific value. Three equal samples weighing 0.5 g each were prepared and tested on IKA C600 calorimeter (Fig. 5).

Fig. 5. Calorimeter IKA C600

As a result of the calorific value tests, the following results were obtained:

I. 44 811 J/g
II. 46 343 J/g
III. 45 477 J/g

The average result from 3 trials was: 45 543 J/g

Figures 6, 7 and 8 presents a visual comparison of the bleaching earth granulation depending on the process carried out. Figure 6 shows the bleaching earth before the paraffin refining process, Fig. 7 shows the bleaching earth after the paraffin refining process, and Fig. 8 shows the earth cleaned as a result of the pyrolysis process.

Fig. 6. Bleaching earth

Fig. 7. Bleaching earth after the paraffin refining process

Fig. 8. Purified bleaching earth after the pyrolysis process

4. Conclusions

As a result of the pyrolysis process conducted with 249.078 g of contaminated bleaching earth; 175.469 g of purified solid fraction, 66.984 g of pyrolysis oil and 6.625 g of gas were obtained. It can be assumed that the aim of the conducted research was fulfilled, as the purified bleaching earth obtained in the process showed physical properties comparable to virgin material in preliminary tests. To confirm the suitability of the purified bleaching earth for reuse, it is necessary to carry out additional detailed tests.

After preliminary analysis of the obtained results of calorific values at an average level of 45.5 MJ/kg, it can be concluded that the obtained pyrolysis oil shows high energy potential. A detailed petrochemical analysis should be performed to determine the suitability of the pyrolysis oil for heating and internal combustion engine applications.

Pyrolysis is an effective technology that makes it possible to process various wastes containing oil and its derivatives. Using this technology offers the possibility of partial recovery of products in the form of oil, gas and solids which can be reused.

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