Investigation the possibility of using non-woven materials from recycled fibers for open oil spills clean up.

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Abstract

Manufacture of textile and ready-made products generates a significant amount of solid waste. A major part of it is deposited in landfills or disposed of uncontrollably. This is slowly degradable volume waste causing problems for environmental protection. The aim of this work is to investigate the possibility of using non-woven materials from waste fibers for open oil spills clean up and their subsequent recovery.

In the present study are used two types of non-woven materials obtained by methods in which seamlessly are utilized waste fibers. Thus, real textile products are produced (blankets) with which are covered and removed spills by adsorption. These products are produced by two methods as the strengthening of the covering from recovered fibers is made by entanglement as soon as needles of special design pass through layers (needle-punching) or by stitching with thread (technology Maliwatt).

Regardless of the random nature of the fiber mixture, investigated products are good adsorbents of petroleum products. The nature of their structure (a significant void volume and developed surface) leads to a rapid recovery of the spilled petroleum products without sinking of the fiber layer for the sampled times. Used non-woven materials can be burned in special conditions.

Introduction

Hydrocarbons come in the aquatic environment from a variety of natural and artificial sources. Maritime transport contributes to this in the utmost. Most of the emission of oil are due to the performance of standard operations, and smaller part of incidents.

When oil is spilled on the surface of water, it disperses rapidly and after a few hours the stain typically begins to break apart and form narrow sectors parallel to the wind direction.

Consequently, the oil will be dispersed over a huge area with large differences in thickness of the floating layer in a short time. This is one of the main reasons that impede the use of any techniques for dealing with spills.

When oil spreads, moves and fragmens, it undergoes some physical and chemical changes collectively known as atmospheric destruction. This process is performed under the action of natural forces, such as evaporation, dispersing, dissolving and precipitation and leads to the disappearance of oil from the water surface. On the other hand, the formation of the water-oil emulsion and the concomitant increase in viscosity as the oil absorbs water up to four times its weight promote its resistance.

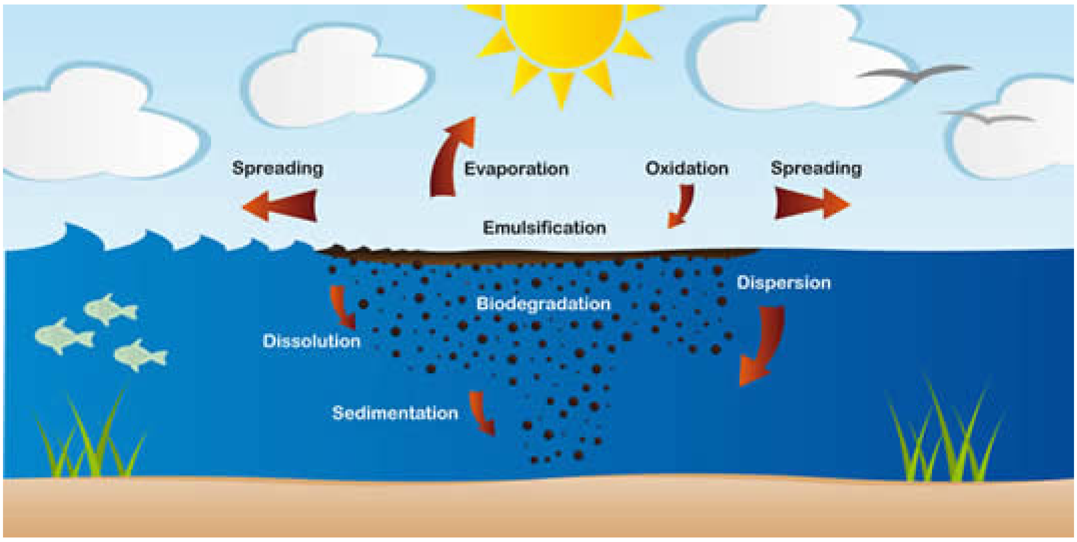

Fig.1. Fate of oil spilled at sea showing the main weathering processes [1]

When oil falls in the water, a layer (oil film) is formed on the surface which breaks the exchange of energy between the atmosphere and the seas. Its low surface tension, low gas permeability and other negative qualities adversely affect the physical and chemical conditions in the ocean. Incoming volatile petroleum products, medium- and heavy distillate fractions lead to flora and fauna destruction in the sea basin, contamination animals with carcinogenic hydrocarbons that subsequently by indirect way fall into human body [2].

Methods for cleaning up oil spills

There are several methods which can help limit the damage from the spill and oil to be cleaned. The most commonly used techniques include collection and recovery, dispersion, bio-processing and incineration.

Collection and recovery is the first measure to be applied in the presence of spill. Long floating plastic or rubber enclosures (booms) are placed around the oil spot. They detained it and do not allow to extend or move to the coast. Once limited, oil can be removed through various defractors (dividers) [3]. The enclosures vary greatly in design and construction, but usually all contain the following key elements: surface part to prevent or reduce the overflow; underwater "skirt" to prevent or reduce leakage of oil under the facility;

flotation by air or some floating material; facility to absorb longitudinal forces (chain or wire) to ensure stability and to withstand the influence of winds, waves and currents [4-7].

The operation of all types of enclosures is influenced largely by the conditions on the water surface - waves, direction of movement, tides, temperature, pH, salt content, etc. Most of the enclosures perform well in calm seas with smooth, long waves [8].

Use of sorbents to clean up oil spills

Sorbent materials are appropriate in some cases because of their ability to collect and completely remove spilled oil products. Placing the sorbents in the spill facilitates the change from liquid to semi-solid phase and removal of the oil together with the sorbent is much easier. Good sorbents must be hydrophobic and oleophilic, to have a high degree of absorption and retention for a long period of time on the surface of the water, to allow the extraction of oil and finally absorbed oil to be able to be reused or recycled [9].

Spilled oil removal by sorbents can be used in turbulent or fast-flowing water [3]. Sorbents are used in difficult to access places, such as along the coast, where it is impossible to use defractors or vacuum devices and can serve as enclosures (sorbent booms) [3].

Sorbents absorb oil through the mechanisms of absorption or adsorption and because they have a certain porosity, oil is collected by capillary action. Adsorbents attract the oil to the surface, but do not allow to penetrate into the material. They have developed surface and affinity to oil products. Often both the techniques -collection and sorption are combined [10].

The adsorption of aqueous solutions is carried out as a result of the gradual increase in the concentration of substances on the surface of the adsorbent. At adsorption of aqueous solutions the degree of retention of certain components is determined by the difference in the energy of the interaction of the adsorbent with the molecules of water (hydration) and the extractive matter.

It is precisely based on the competition of the processes of hydration and adsorption that determines the ability of the adsorbents to remove organic and inorganic substances from aqueous systems. For the adsorption of organic substances are generally used carbon porous materials (activated carbon, coke, synthetic polymers).

Recycling of textile waste

There are many reasons that require recycling of wastes from textile products and processes. They include preservation of resources, reducing the need for landfills and payment of fees, supply of raw materials at low cost [11].

Recovery and recycling of textiles is of great benefit not only for the economy but also for the environment - textile materials are a problem for landfills because synthetic fibers degrade slowly and woolen during decomposition produce methane, which is one of the main culprits for the global warming. In addition, thus is reduced the need for new resources, pollution which is unavoidable in the processing of new materials is avoided [12].

Needlepunching is the oldest process for the preparation of non-wovens. In this process, the fibers are transferred into the depth of the wadding by needles with special design and are intertwined. Thus a product is yielded with a three-dimensional structure, with high density and durability, resistance to mechanical impact, which is a prerequisite for its widespread use for household and technical purposes [13].

Stitch-bonding is a method for the production of textile sheet materials, which is performed by the respective machines, by stitching and reinforcement of the base material (mat, foil, tissue, system filaments or a combination thereof), as arranged in a row needles form simultaneously stitches with or without broaching filaments [14].

Physical-mechanical properties depend significantly on machine-technical parameters of the process and can be easily controlled.

Materials and methods

Seawater differs freshwater by the content of dissolved ions. Water in the world's oceans has an average salinity around 3.5%. Due to the added weight of the salts relative weight of seawater at the ocean surface is 1.025 g/ml, while fresh water reaches a maximum of 1.000 g/ml.

There were used non-woven materials obtained by needlepunching and stitch-bonding method with parameters listed in Table 1 with a size of 5 x 5 cm.

Table 1. Used materials.

Materials	**Type**	**Composition**	**Parameters**
Material 1	stitch-bonding type Maliwatt	Wool 15% Cotton 18% Viscose 20% Polyester 17% PAN 30% Stitch fiber - polyester 100%	Step of stitching: 2.12 cm Length of thread in 1 cm: 3.74 cm Number of stitches in 1 cm: 3.2
Material 2	stitch-bonding type Maliwatt	Wool 5% Cotton 20% Viscose 17% Polyester 23% PAN 35% Stitch fiber - polyester 100%	Step of stitching: 0.7 cm Length of thread in 1 cm: 3.26 cm Number of stitches in 1 cm: 3
Material 3	needle punched	Wool 20% Cotton 20% Viscose 20% Polyester 20% PAN 15% Polyamide 5%	Frequency of needle-punching: 500 min^{-1} Depth of needle-punching: 12 mm Projection density: 15 needles/cm
Material 4	needle punched	100% recovered wool	Frequency of needle-punching: 800 min^{-1} Depth of needle-punching: 10 mm Projection density: 50 needles/cm

Material 1

Material 2

Material 4

Material 3

Fig. 2. Photos of the materials used

For the experimental work was used seawater taken from the Black Sea in the Bourgas area. Two types of oil were used - mineral motor oil OMV Austroil SAE 15W/40 and waste motor oil collected from oil change workshop. A methodology has been developed in a laboratory using different amounts of pure mineral and waste oil in static conditions and agitation and residence time of the samples in the suspension from 10 to 30 min in beakers of 600 ml in which are placed 100 ml of seawater and 2 ml oil. The degree of sinking is determined after a period of 48 hours.

The used materials are characterized by determining the thickness, area and volume weight, air permeability. Retention and extraction of oil from the suspension is determined by weight after drying 4 hours at 105^{o} C with blasting.

Results and discussion

Used stitch - bonding materials (type 1 and 2) have a smaller thickness, and needlepunched, particularly from recovered wool have a greater one.

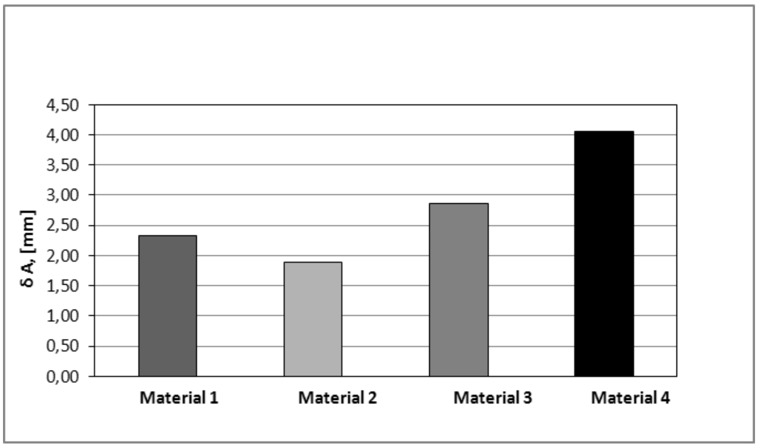

Fig. 3 Thickness of used fibrous sorbents

Stitch-bonded materials on the other hand are more voluminous and porous, with a large amount of open pores due to insufficient entanglement of the fibers in the volume of the product.

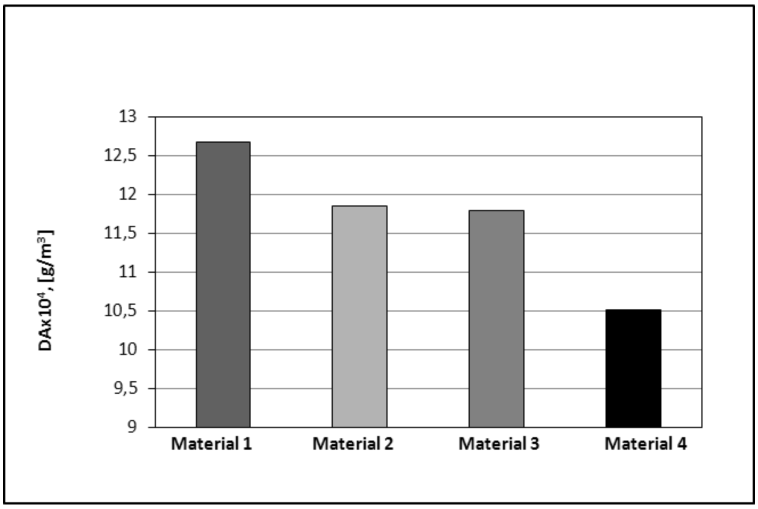

Fig. 4 Volume density of used nonwoven samples.

Results in terms of mass per unit area in the samples indicate that the amount of fibers in the needlepunched samples is greater, therefore, they have more developed fibrous surface as a result of which a greater sorption capacity can be expected.

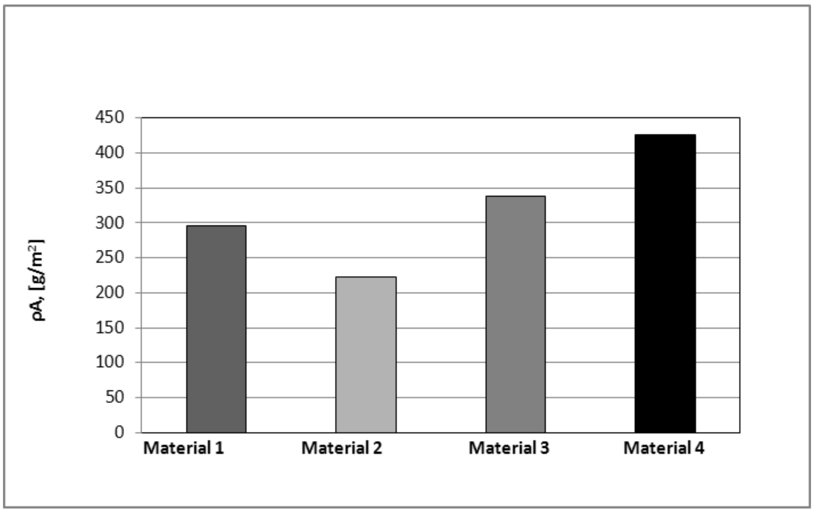

Fig. 5 Mass per unit area of used nonwoven samples.

The results for air permeability, that show the porosity and free volume of the device and from there the included air in it, indirectly indicate the ability of the product to be retained on the surface of the water and to sorb as long as possible the contamination (Figure 6).

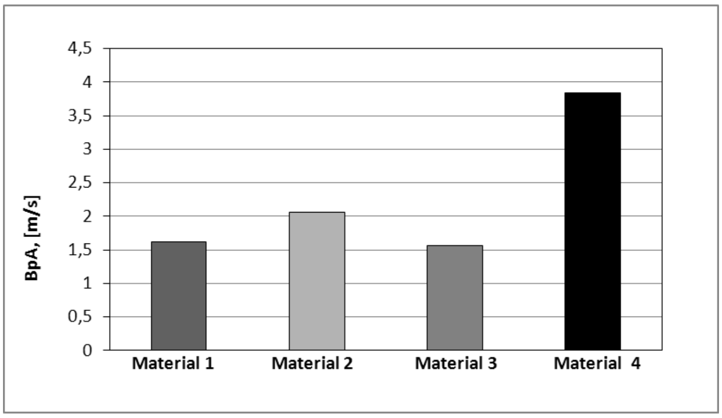

Fig. 6. Coefficient of air permeability of used nonwoven samples

Based on these preliminary analyzes, it can be assume that material 4 (100% recovered wool) will be most appropriate for sorption of oil products, especially taking into account the properties of wool fibers.

The rate of uptake of oil by the fibrous sorbents, also depends on the type of nonwoven material, its composition, but also on the conditions of the experiment - under static conditions or agitation, at imitation of wool as well as the type of pollutant itself - clean motor or waste oil. It can be seen from the below presented Figures 7 and 8.

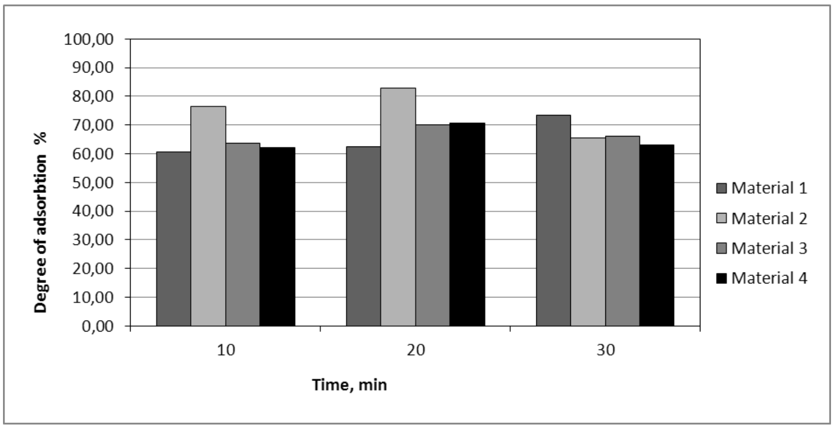

Fig. 7 Degree of adsorption of pure oil under agitation depending on the residence time of the sample in suspension.

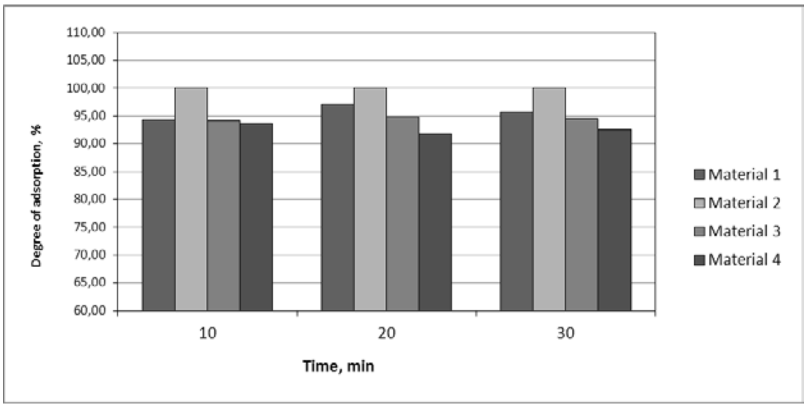

Fig. 8 Degree of adsorption of pure oil under static conditions depending on the residence time of the sample in suspension.

It was found that the amount of sorbed pollutant under dynamic conditions is less, than under static conditions. Stitch-bonded products adsorb a larger amount of pollutant, due to the large volume and mixed composition.

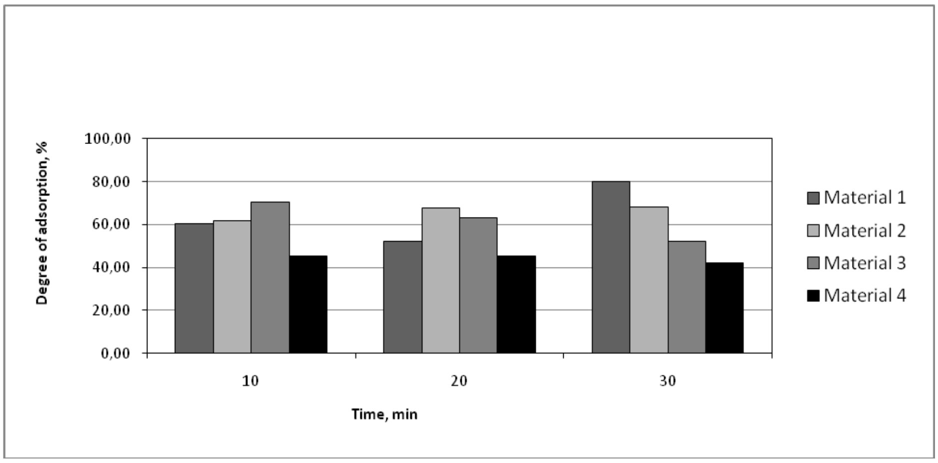

Fig. 9 Degree of adsorption of waste oil under agitation depending on the residence time of the sample in suspension.

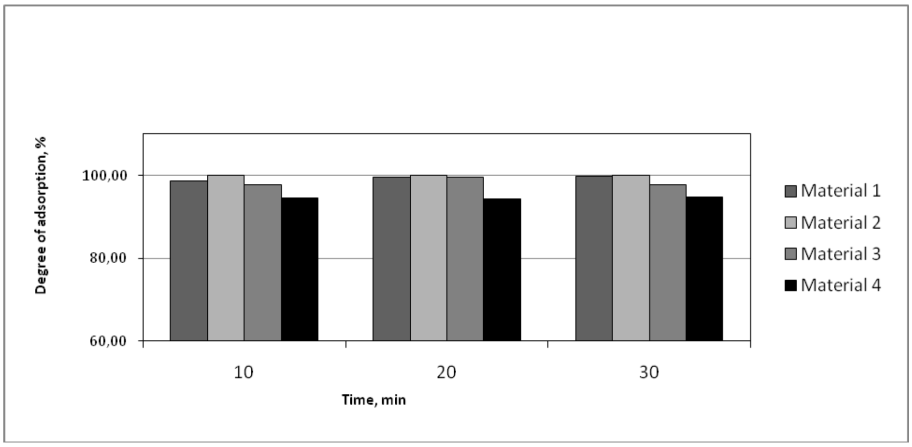

Fig. 10 Degree of adsorption of waste oil under static conditions depending on the residence time of the sample in suspension

In this case stitch bonded material 1 and needle punched material 3 showed better ability to adsorb waste oil as working with or without agitation, but the trend for greater efficiency of the sorbent under static conditions remains. This is shown in Figures 11 and 12, wherein the samples stay in the suspension.

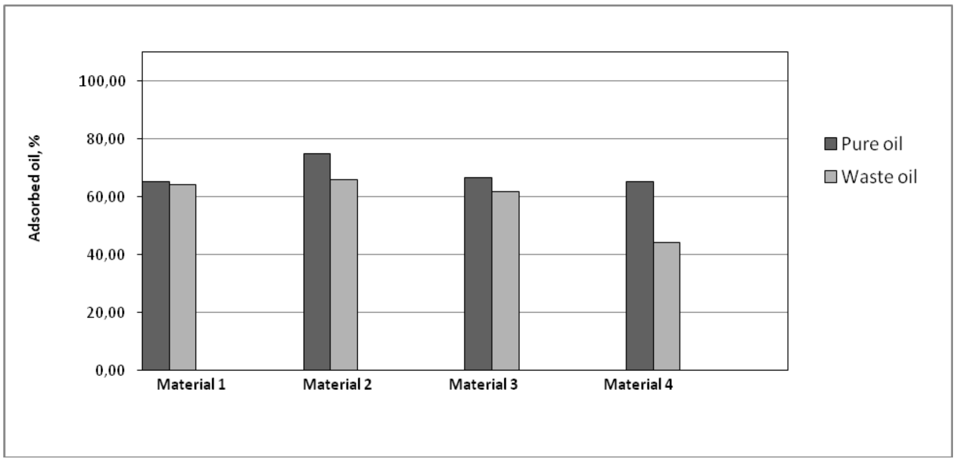

Fig. 11. Adsorbed pollutant at agitation according its type

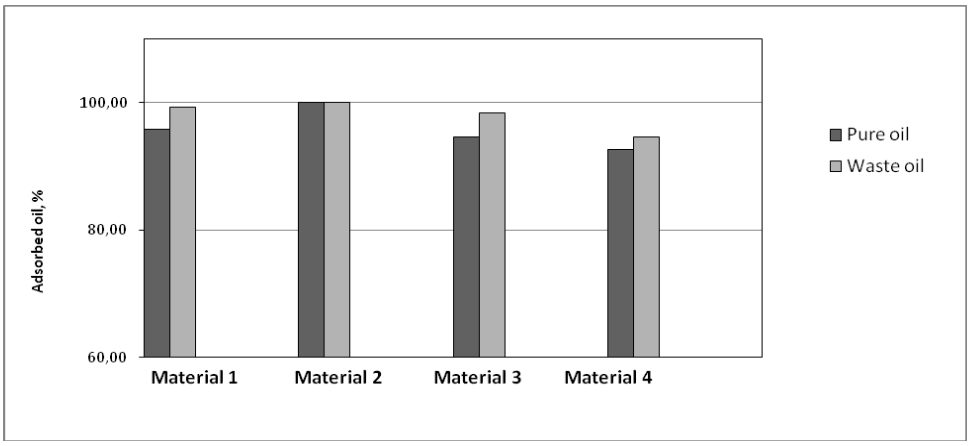

Fig. 12. Adsorbed pollutant under static conditions according its type

Generally, materials showed better ability to retain pure oil regardless the operating conditions. Stitch-bonded materials are effective sorbents whatever the conditions of the experiment. In all cases, material 2 (stitch-bonded type Maliwatt and a composition of състав Wool 5%, Cotton 20%, Viscose 17%, Polyester 23%, PAN 35%, Stitch fiber - polyester 100%), is most effective at the tested conditions, probably due to the reduced content of hydrophilic fibers in the mixture, and the larger content of PAN and PET. Samples with the lowest bulk density retain a small amount of oil, due to the presence of air in the pore volume which impedes the penetration of the suspension into the volume of the fibrous sorbent. This is confirmed by the the results obtained of air permeability - samples with the highest coefficient of air permeability absorb least oil products.

On the other hand, retention of the material on the surface of the suspension and its sinking, depends precisely on the enclosed air in the system. At this stage of the study, samples of any kind do not sink after a stay in static and dynamic conditions after 48 hours.

An analysis of the calorific value of different materials after saturation was provided in a certified laboratory. The test was performed according to BSS ISO 1928. The obtained results are presented in Table 2.

Table 2. Results from combustion of waste samples

Material	Heat of combustion, kcal/kg	
	Unprocessed material	Processed material
Material 1	5754 ± 30	30 015± 30
Material 2	7399 ± 30	31 452± 30
Material 3	7260 ± 30	31 361± 30
Material 4	8122 ± 30	34 365± 30

Conclusions

As a result of tests carried out it has been found that the stitch-bonded nonwoven materials have better ability to retain oil in comparison to needle-punched, because of the greater amount of free fibrous surface.

The use of waste fibers mixtures with a higher content of PAN is more effective for absorbents of petroleum.

After use of the sorbents, their calorific value increases and therefore can be used as an energy source. But due to changing the code of the waste they have to be burned in special facilities, such as tunnel kilns.

Depending on the fiber composition, textile sorbents sink after different periods of stay in the water due to the amount included hydrophilic fibers, but these studies continue in order to provide prescription for the way and time of use of non-woven blankets from regenerated fibers.

Obtained sorbents can be used in enterprises of petrochemical and oil industry and for wastewater treatment from petroleum products.

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