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Properties of Fibrous Petroleum Collectors Obtained from Polystyrene Waste Material by Treatment with Water Vapour

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Abstract

Properties of fibrous petroleum collectors obtained by non-isobaric thermal treatment of various kinds of polystyrene raw material with water vapour were studied. It was shown that these sorbents possess high sorption capacity with respect to petroleum products and can be used as the filtering material in the process of water purification from petroleum products. It was established that fibrous sorbents possess not worse characteristics than the commercial analogues do.

Key words: non-isobaric thermal treatment, water vapour, polystyrene, petroleum collectors, filtering material

INTRODUCTION

Timely and efficient purification of soil and water sources from petroleum and petroleum products is important ecological problem; its solution would ensure a reduction of the negative technogenic effect on the environment. Various petroleum sorbents are successfully used to remove petroleum pollution; a special position in efficiency among these sorbents is occupied by synthetic fibrous materials [1]. Various polymers including polystyrene are used as a raw material to obtain these polymers. It is known that polystyrene fibres (PF) and their mixtures with the fibres of different nature may be used to fill booms and sorptive mats. The petroleum capacity of these fibres is not less than that of polypropylene and polyethylene fibrous materials that are traditionally used for these purposes [2]. Substandard PF that does not meet the standard requirements for use as optical pipes or fillers

of reinforced plastics is suitable as petroleum sorbent [3]. As a result of the deposition of photocatalytic additives on PF, fibrous material intended for fine purification of air and water from various impurities including organic ones was obtained [4]. It is promising also for water purification from dissolved petroleum products.

Independently of the method of fibre spinning (pressing through filament extrusion device, electrostatic filament spinning *etc.*), it is necessary to transform the polymer into thermoplastic state, solution or melt [3, 5]. In some cases it is necessary to use organic solvents in large amounts to make polymer solutions [6]. This defines the complicated and multistage nature of the technologies of polymer materials and often their substantial ecological hazard. It is known that the technologies of sorbents intended for collection of petroleum and petroleum products must be characterized by high purity from the ecological viewpoint, provide the production of the sorbents of differ-

ent types in one technological cycle, be distinguished by the minimal consumption of deficient raw materials and energy resources *etc.* [1]. It should be noted that the industrial production of PF is aimed at processing high-quality raw material of definite composition. As a rule, household and industrial wastes of polystyrene plastic foam are inhomogeneous and contain foreign inclusions, which hinders their processing according to known technologies. In this connection, the development of ecologically safe methods of obtaining fibrous sorbents for collection of petroleum and petroleum products from polymer wastes is of high practical importance.

The goal of the present work was to study sorption properties of fibrous polystyrene sorbents obtained during non-isobaric thermal treatment of polystyrene wastes with water vapour.

EXPERIMENTAL

Fibrous sorbents from various kinds of polystyrene raw materials were obtained according to the scheme (Fig. 1).

Foamed polystyrene was obtained from the beads of PSV-S grade (OST 301-05-202-92 E) according to the industrial technology. Polystyrene waste material was crushed household foam plastic waste (thermopressed foamed polystyrene with particle size 5–10 mm). A mixture of foamed polystyrene and wood wastes (aspen bark and the outer part of birch bark) was used to obtain wood-polystyrene fibrous (WPF) sorbent. The content of wood wastes of the fraction 0.5–1.5 mm in WPF was varied from 10 to 60 mass %.

Polystyrene fibre was obtained by means of non-isobaric thermal treatment under the following conditions: temperature $(115 \pm 5)^\circ\text{C}$, pressure of the mixture of air with vapour 3.0 MPa, treatment time 30 s. Wood-polystyrene fibrous sorbents were obtained at a temperature of $(125 \pm 5)^\circ\text{C}$, vapour pressure 3.0 MPa for 60 s.

To determine the properties of the materials, PF and WPF sorbents were dried to the air-dry state at a temperature of $(20 \pm 2)^\circ\text{C}$. Petroleum-absorbing capacity (PC), oil capacity (OC), water uptake (WU), floatability and

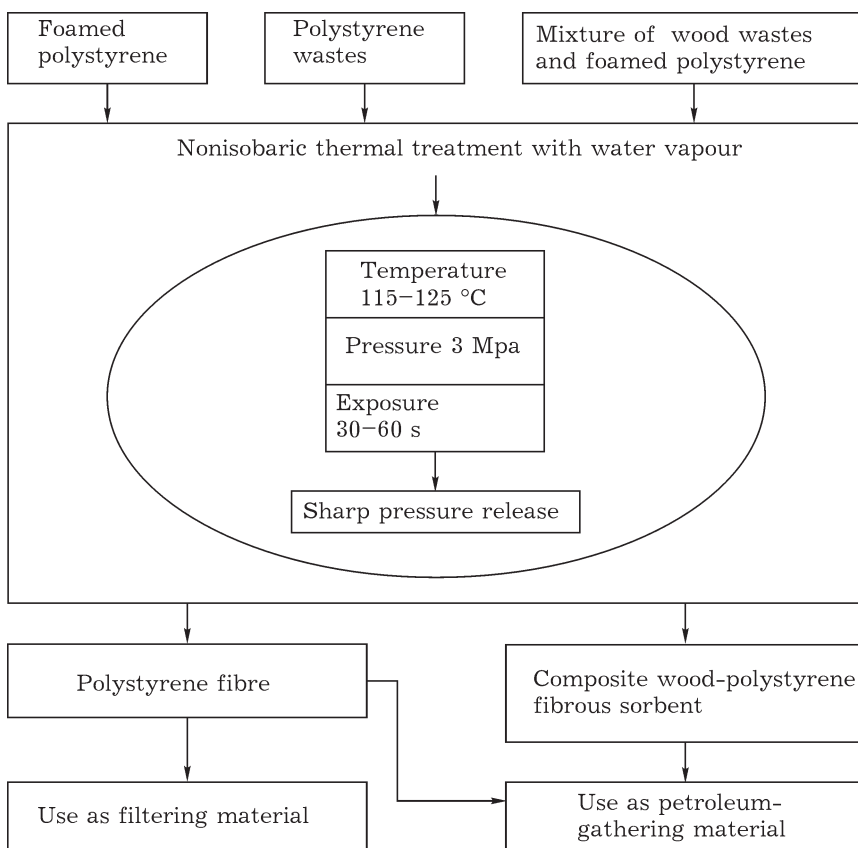


Fig. 1. Scheme of obtaining polystyrene fibrous materials for different purposes.

press ratio were determined according to procedures described in TU 214-10942238-03-95. Petroleum capacity and oil capacity were determined with respect to crude oil from the Tyumen deposit ($\rho = 0.85 \text{ g/cm}^3$) and used motor oil ($\rho = 0.89 \text{ g/cm}^3$).

Investigation of water purification from fine petroleum products was carried out with the help of a model filtering column (inner diameter 10 mm) filled with PF to the height of (500 ± 2) mm. Water-oil emulsion was prepared by ultrasonic dispersion (with a UZDN-2T disperser, at the frequency of (400 ± 2) kHz) of industrial oil I-20A in water. Water-petroleum emulsion was prepared in a similar way using crude oil from the Tyumen deposit. Emulsions with oil (petroleum) concentration 20 and 100 mg/L were used. The emulsions were self-flowing through the layer of filter at the top of the column. The filtrate was collected in a receiver; the residual content of petroleum products in purified water was determined according to OST 38.01378-85. Filtration was stopped when breakthrough was achieved.

RESULTS AND DISCUSSION

The material obtained from foamed polystyrene or wastes of household foam plastics is polydisperse fibre with filament diameter 0.5–1.0 mm and 5.0–30 mm long. The thickness and length of filaments of the fibre are almost independent of the kind of initial raw material. WPF sorbents are clumpy masses composed also of the fibres of different diameters (0.25–1.0 mm) and length (2–10 mm). Some filaments in the mass of PF and WPF sorbents are formed as bundles.

It was established that the following conditions are optimal for obtaining PF: temperature $(115 \pm 5)^\circ\text{C}$, pressure of the mixture of air with water vapour 3.0 MPa, treatment time 30 s. The yield of the final product is $(97 \pm 2)\%$. It is unreasonable to carry out the process at lower temperatures because the resulting fibre contains large number of undestroyed conglomerates (up to 30 % at 90°C). Similar effects are observed with a decrease in treatment time (below 30 s) and pressure reduction (below 3.0 MPa). An increase in treatment temperature above 120°C , treatment time longer than 30 s and

pressure above 3.0 MPa causes a decrease in the yield of fibrous product due to chemical destruction of initial material [8].

For obtaining WPF sorbent, it is reasonable to raise temperature to $(125 \pm 5)^\circ\text{C}$, treatment time to 60 s to provide maximal garneting of wood particles. The yield of final product is 95–98 %. Wood particle garneting provides rather high strength of polystyrene and wood fibre adherence, so that the process can be carried out without chemical binders [7].

It should be noted that non-isobaric thermal treatment (or “explosive autohydrolysis”) is traditionally used to treat wood raw material [9]. However, it is used for the first time to obtain polymer fibre. The process of fibre formation does not require preliminary transformation of the polymer into the thermoplastic state, which simplifies the technological flowchart substantially.

The characteristics of the polymer fibre of PF and WPF sorbents for collection of petroleum and petroleum products are presented in Table 1. The samples PF-1 and PF-2 were obtained from foamed polystyrene and the wastes of household foam plastics, respectively. One can see that the properties of PF sorbents are weakly dependent on the kind of initial polymer raw material. The introduction of wood fillers into PF provides an increase in petroleum and oil absorbing capacity though for wood fillers themselves thermally treated with water vapour under the conditions of WPF preparation, these parameters are three times lower as average in comparison with the fibrous composite sorbents obtained. It should be stressed that without thermal treatment the absorption of petroleum (oil) by aspen bark and the outer layer of birch bark is 0.5 (0.6) and 1.3 (2.5) g/g, respectively.

WPF sorbents have high absorption capacity with respect to petroleum and motor oil at 0°C , unlike PF sorbents. This is due to the ability of aspen bark and birch bark, components of WPF, to exhibit better retention of petroleum with high viscosity. It should be noted that the ability of WPF sorbents to absorb petroleum and petroleum products at 0°C is much higher than that of known industrial fibrous sorbents. This is especially valuable feature, in view of the fact that the capacity of many known fibrous petroleum-collecting agents with

TABLE 1

Properties of PF and WPF sorbents for gathering petroleum and petroleum products

Sorbents	Wood filler	PC*, g/g	OC*, g/g	WU, g/g	C _{pres} , %	Floatability (200 h), %
PF-1	no	6.7/6.0	6.9/6.8	12.7	90	100
PF-2	no	6.8/6.0	6.7/6.5	12.6	90	100
WPF	20 % aspen bark	7.4/9.3	8.3/10.3	8.2	83	100
WPF	20 % birch bark	7.6/10.1	8.7/10.9	8.7	85	100
Aspen bark**		2.2/3.6	2.8/3.9	6.5	30	90
Birch bark**		1.9/2.5	3.2/3.9	5.0	35	100

Note. PC is petroleum capacity, OC is oil capacity, WU is water uptake, C_{pres} is press ratio.

* Values for 20 °C are in numerator, values for 0 °C are in denominator.

** Conditions of non-isobaric thermal treatment of wood fillers with water vapour are similar to the conditions of obtaining WPF sorbents.

respect to petroleum products decreases by an order of magnitude at temperatures below 4 °C [1]. In addition, WPF sorbents are characterized by lower water absorption than PF, which increases the efficiency of their application to collect petroleum and petroleum products from water surface.

It follows from the data shown in Fig. 2 that an increase in petroleum capacity of WPF sorbents and a decrease in their water-absorbing capacity are characteristic of a broad range of wood filler concentrations and depends on the concentration of wood filler.

For WPF sorbent with birch bark, a substantial increase in petroleum capacity is observed with an increase in birch bark content from 10 to 60 mass %. These sorbents possess higher pe-

troleum-absorbing capacity than sorbents filled with aspen bark (see Fig. 2, curves 1, 2).

With aspen bark as filler, WPF sorbents exceeding PF in petroleum capacity are to contain wood material not more than 40 mass %. Maximal absorption is exhibited by WPF sorbents containing 20 mass % aspen bark and 30 mass % birch bark.

With an increase in the concentration of wood filler, water absorption by WPF sorbents decreases substantially, likely due to a decrease in void volume and lower water-absorbing capacity of aspen bark and birch bark (6.5 and 5.0 g/g, respectively) [7]. The most substantial decrease in water absorption by WPF is achieved using aspen bark as filler (see Fig. 2, curve 3).

In the experiments on petroleum and oil collection, no expansion of the studied PF and WPF was detected, which reduces the risk of destruction of the formed conglomerates during mechanical gathering from the surface to be purified. Regeneration of collected petroleum and oil may be carried out by mechanical pressing. The degree of petroleum recovery from fibrous conglomerates is not less than 90 % for PF sorbents and 80 % for WPF sorbents (see Table 1). These parameters of the studied sorbents are not worse than those of industrial analogs [1]. Repeated absorption of petroleum products does not exceed 10 %, so it is reasonable to use the studied sorbents only once.

It is possible to utilize used PF and WPF sorbents similarly to utilization of synthetic materials: either use the residues in road construc-

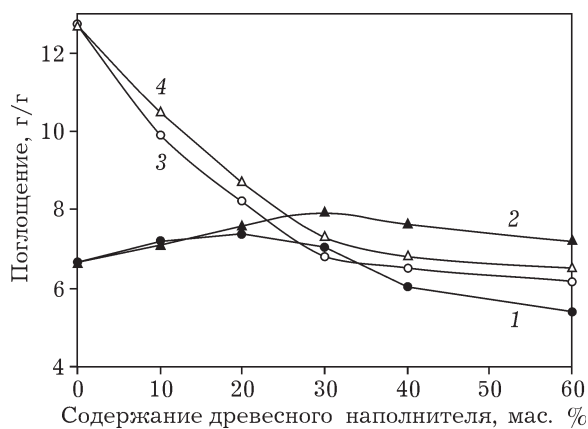


Fig. 2. Effect of wood filler content on petroleum capacity (1, 2) and water uptake (3, 4) by WPF sorbents: 1, 3 – aspen bark, 2 – outer layer of birch bark.

TABLE 2

Effect of PF and WPF solvents compaction on petroleum absorbing capacity

Sorbents	Petroleum capacity, g/g			Petroleum capacity in sporadic packing, g/g
	after compaction, kg/m ³			
	100	150	200	
PF-2	9.8	10.9	10.1	6.7
WPF (20 % aspen bark)	9.5	10.5	9.7	7.4
WPF (20 % birch bark)	9.7	10.8	9.9	7.6
Ekosorb	8.3	10.0	12.5	6.9
IRVELEN	8.0	9.9	11.6	7.2

Note. PF-2 was obtained from wastes of household foam plastics. Ekosorb, IRVELEN are reference samples.

tion or burn them in high-temperature sets up like Fakel *etc.* [1].

It was established that PF and WPF sorbents are characterized by 100 % floatability for a long time staying in water after petroleum accumulation, which creates a time reserve for the removal of used sorbents from water surface (see Table 1).

Preliminary compaction of PF and WPF sorbents promotes as increase in their petroleum capacity (Table 2). This allows substantial increase in the efficiency of gathering petroleum and petroleum products with the studied sorbents packed in special mats, booms *etc.*

It follows from the data shown in Table 2 that PF-2 and WPF sorbents compacted to 100 and 150 kg/m³ exceed the reference samples in petroleum capacity. One can see that it is unreasonable to compact the sorbents above 150 kg/m³ because this causes a decrease in petroleum capacity.

In addition to gathering spills of petroleum and petroleum products, PF may be used as filtering materials to purify water from finely dispersed petroleum products.

Table 3 shows the results of filtering of model water-oil emulsions of different concentrations through a layer of PF-2 prepared from the wastes of household foam plastics.

One can see that the use of PF as filtering material allows a substantial decrease in oil content in purified water during primary filtration; the best effect is achieved when water with higher oil content is filtered. It should be noted that the studied fibres are not worse in the efficiency of purification of emulsion containing 20 % oil than polymer fibres described in literature. For example, the use of sipron as filtering charge to purify water containing 10–20 mg/L petroleum products allows one to decrease the concentration of admixture to 5–7 mg/L [10]. It follows from the presented

TABLE 3

Water purification from industrial oil admixture by filtering through polystyrene fibre

Filter packing density, kg/m ³	Filtering rate, m/h	Oil content in purified water, for initial oil content, mg/L	
		20	100
		50	3.1
100	2.8	5.5/10.6	15.6/22.3
150	2.4	4.8/9.8	10.3/20.4
200	2.0	3.7/8.8	10.1/20.4
250	0.7	3.8/9.2	10.1/21.1
300	0.3	3.7/9.1	10.1/21.3

Note. Here and in Table 4: data for single use of the fibre are shown in numerator, for repeated use – in denominator.

TABLE 4

Water purification from petroleum admixture by filtering through PF and industrial fibrous filters

Filtering material	Petroleum content in purified water, for initial petroleum content, mg/L	
	20	100
PF-2	3.2/9.1	9.7/20.7
Ekosorb	4.0/5.5	9.9/12.1
IRVELEN	3.5/5.3	9.5/10.7

Note. For designations, see Table 3.

data that filtration rate and residual concentration of oil in water decrease with an increase in the density of filter packing. The packing density of 250 kg/m³ for PF is critical because it leads to a sharp decrease in filtration rate. The packing density of 200 kg/m³ may be considered optimal because in this case, with good filtering rate, the lowest concentration of admixture in water is achieved. No compaction of fibre layer by the flow to be filtered is observed during filtration. Therefore, there is no increase in the hydrodynamic resistance in the layer of filtering material, which would cause a decrease in the efficiency of its operation.

We also studied the efficiency of the use of PF-2 to filter water-petroleum emulsions in comparison with industrial materials Ekosorb and IRVELEN. The density of filter packing for all materials was 200 kg/m³ (Table 4).

One can see that the use of PF-2 as filtering material allows substantial decrease in petroleum content of water during primary filtration. Similarly to the case of filtration of oil-water emulsion, the best effect is observed for purification of water with petroleum content 100 mg/L. PF is not worse than industrial analogs in the efficiency of water purification from petroleum during primary filtration.

It was established that after filtration up to 65 and 60 % of absorbed oil and petroleum, respectively, drain from PF within 4 h due to gravity. Subsequent use of these filtering materials (with residual oil and petroleum) leads to increased concentration of impurities in pu-

rified water (see Tables 3 and 4). It should be noted that repeated use of industrial samples in water purification from petroleum provides lower content of pollutant in water (see Table 4). This is due to the fact that up to 85 % of collected petroleum drains out of these materials within 4 h, which increases the efficiency of repeated filtration. So, it is reasonable to use PF as one-time filtering material.

The use of WPF sorbents as filtering charge is of no practical significance because water-soluble substances from wood filler are transferred into purified water.

CONCLUSION

It is demonstrated that fibrous sorbents with good sorption capacity with respect to petroleum products can be prepared by means of nonisobaric thermal treatment with water vapour from various kinds of polystyrene raw materials. The resulting PF and WPF sorbents are not worse in their characteristics than industrial analogs. Polystyrene fibre can also be used as filtering material for water purification from dispersed petroleum products.

The developed method of obtaining fibrous sorbents is single-stage, is characterized by short duration (30–60 s) and does not require preliminary transformation of the polymer into the thermoplastic state. The absence of chemical reagents ensures its ecological safety.

REFERENCES

- 1 Kamenshchikov F. A., Bogomolny E. I., Udaleniyе Nefteproduktov s Vodnoy Poverkhnosti i Grunta, Moscow–Izhevsk, 2006.
- 2 US Pat. No. 4070287(A), 1978.
- 3 Perepelkin K. E., Proshloye, Nastoyashcheye i Budushcheye Khimicheskikh Volokon, Moscow, 2004.
- 4 ER Pat. No. 17983117A1, 2007.
- 5 RU Pat. No. 2179600 RU, 2002.
- 6 RU Pat. No. 2349369, 2009.
- 7 Veprikova E. V., Tereshchenko E. A., Chesnokov N. V., Kuznetsov B. N., *Zh. SFU. Khimiya*, 1 (2011) 27.
- 8 RU Pat. No. 2428530, 2011.
- 9 Gravitis Ya. A., *Khim. Drev.*, 5 (1987) 3.
- 10 Tarnopolskaya M. G., *Voda i Ekol.*, 3 (2005) 74.