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Utilization of petroleum residues under microwave irradiation

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HIGHLIGHTS

- Applied porous carbon sorbents possess high value of microwave irradiation adsorption.
- Breakdown processes occur initially on the surface of carbon sorbent and then in the bulk of the material.
- Microwave irradiation energy enough for active C–H bond cracking.
- Hydrogen is a main gas product of tar conversion under MWI.

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ABSTRACT

This paper presents the results of tar conversion under microwave irradiation (MWI). It is established that carbon adsorbents produced from natural mineral row possess by high microwave energy absorption coefficients; which characterized by high value of dielectric losses. Non-liner dynamics of carbon adsorbents heating at different current density from 80 till 200 $\mu A/cm^2$ indicates that plasma generation occurs during microwave irradiation. It is found that the mechanism of tar conversion which preliminary adsorbed in the pores of the carbon sorbents under microwave irradiation and convective heating is different. The C–H bond is mainly activated and decomposed under microwave treatment with predominant formation of hydrogen. In case of C–C bonds, they are mainly subjected to thermolysis under convective heating and methane is the main product of degradation. To confirm the difference in the mechanism of tar destruction under microwave influence and convective heating the experiments with individual hydrocarbons adsorbed in the pores of hydrophobic sorbents were carried out.

1. Introduction

The development of effective utilization methods of petroleum residues and pollutants is one of the most important ecological problems of considerable current interest. Petroleum and petrochemical industries have a strong ecological impact because of the release of harmful hydrocarbon pollutants into the natural environment. Crude oil, oil sludge, tars, and other harmful and toxic substances are environmental hazards [1–5]. It is well known that the enormous volumes of oil and petroleum products are spilled in emergencies at oil-field facilities, oil storage tanks, petroleum pipelines, refineries, and petrochemical plants and also at oil-consuming facilities-sea and river ports, railroad junctions, automotive fleets, gasoline stands, etc. [6]. Nowadays methods based on microwave technologies are developed as effective approach for liquidation of petroleum contaminants and pollutants [7–9].

Sorption by hydrophobic carbon sorbents is the most effective and most commonly used method for the fixation and absorption of petroleum products in the removal of oil spills from the surface of water areas and also in the purification of polluted soils and other solid surfaces. These sorbents based on peat, fossil coal, or renewable biomass are manufactured using well known technologies [10–14]. In this case, problems related to the collection and utilization of sorbents with absorbed petroleum products decrease the effectiveness of this method. The development of effective approaches to the utilization of anthropogenic emissions and industrial wastes is the problem of considerable current interest.

Last decade the steady tendency of microwave irradiation applying to different chemistry fields is become more visible. The results of these works are controversial and there are associated with the formation of more or less dispersed metal-containing catalytic active components [15,16]. The positive effect of microwave irradiation was observed in stimulation of dry reforming of methane in presence of platinum and rare earth components deposited on the Al-containing oxide catalysts [17,18].

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In this works were obtained higher content of synthesis gas compared to its equilibrium concentration under microwave irradiation. This effect was explained by higher temperatures on the metal-containing active centers compared to the average temperature of the reaction zone of the reactor. Also positive effect was obtained when using microwave irradiation for the preparation of Fe–C catalyst for the reaction of oxidative decomposition of hydrogen sulfide into elemental sulfur [19]. It was found that under microwave irradiation formed nanosized particles of magnetite with average size of 3–5 nm on the catalyst surface, are very active. Previously was determined that carbon materials have a high coefficient of absorption of microwave radiation substantially higher than many inorganic materials [20,21]. The complex permittivity of soot ω was measured at various frequencies in the following work [22]. It was established that using the irradiation with wave length 8 mm and a current density 10 W/cm^2 the carbon soot particles are heated up to 800 °C at 5–10 with [23].

Using of microwave radiation proved to be very effective for the decomposition of organophosphorus compounds, pre-adsorbed in the pores of the carbon sorbent with high values of dielectric losses [9]. It was shown that in the presence of several carbon sorbents obtained on the basis of natural coal, while the microwave radiation dynamics of the temperature rise characteristic of the plasma [23].

This approach can be considered promising for its use to the speed of decomposition of heavy hydrocarbon feedstocks to high-speed disposal of oil spills.

Here, we report the results of studies on the high speed degradation of petroleum residues and pollutants adsorbed in the pores of carbon sorbents under the action of microwave radiation.

2. Experimental section

For performing the high-speed destruction of petroleum residues and pollutants, they were adsorbed in the pores of carbon sorbents. After that the sorbents with a petroleum product adsorbed in the pores were loaded in a reactor and processed under the action of microwave energy (2.45 GHz) at an induced temperature of 300–600 °C in a flow of argon Ar or CO_2 during 10–15 min. The principle scheme of laboratory MWI unit presents on Fig. 1. The following sorbents were used in the studies: finely dispersed hydrophobic sorbents based on wood waste (WWS), flax chaff (FCS) [7,8], and hydrophilic sorbents based on gas coal (GCS), and (crushed sorbents with irregularly shaped particles) brown coal (BCS) [14,19,23]. Table 1 summarizes the physicochemical and structural characteristics of the carbon sorbents. At first step, different carbon sorbents were tested for the ability to absorb microwave energy. It was necessary for determining the applicability of various carbon sorbents to the high-speed destruction of petroleum residues and pollutants. For this purpose, we investigated the kinetics of heating of sorbent samples under the following optimized microwave treatment conditions: the current density $I = 200$ mA and a power of 540 W [19,23,24].

An M-140 magnetron (1) (oscillation frequency, 2.45 ± 0.05 GHz), was applied as a microwave radiation source; an ac power supply with a voltage of 220 V (50 Hz) was employed, and the voltage was regulated with a laboratory adjustable ratio autotransformer. The carbon sorbents with tar adsorbed in the pores were placed in a quartz flow reactor (4) which was fixed at ceramics base (3) arranged in the waveguide (2) of a microwave unit and supplied with a tungsten–rhenium thermocouple (5), which was placed in a metal casing for microwave radiation shielding. The waveguide is connected to the MWI adsorption chamber (6) (U-shaped vessel), in which due to the flow of water is realized the absorption of the residual irradiation. The correctness of the measurement of the temperature change dynamics in microwave irradiation tests was evaluated using γ-alumina as a reference substance; the results of measurements were compared with published data on the temperature measured with the aid of an IR remote sensing thermometer (Condtrol IR-T4).

During the irradiation, the reactor was purged with argon or carbon dioxide at a flow rate of 8–12 cm^3/min. These experiments were carried out at constant average temperature of reaction zone 300 or 600 °C induced by irradiation. The temperature of reaction zone was also measured by the tungsten–rhenium thermocouple connected with independent temperature-measuring device during the experiments. Check measures were carried out while short deactivation (switch off) of magnetron. The purging gas after the reactor passed through a microseparator (7) cooled at −50 to −70 °C and entered a receiver, then it was supplied to a chromatograph for analysis (8). After the completion of the experiment and the cooling of system, the sorbent was removed and analyzed to determine the residual amount of tar in it. Several comparative tests on the destruction of tar in an electric furnace with convective heating were also carried out. A quartz reactor with a sorbent and tar adsorbed in its pores was placed in the furnace heated to 300 or 600 °C and exposed for 10–15 min. after reaching a specified temperature as in the experiments with the use of microwave energy. After completion of the experiment and the cooling of the system, the sorbent was unloaded and analyzed to determine the residual tar content. The determination of the residual tar content of carbon sorbent samples was performed using accelerated solvent extraction followed by the analysis of the resulting extracts by high performance liquid chromatography. An ASE200 automated extractor from Dionex was used for the extraction of the samples. Chromatographic analysis was carried out on a GIL-SON instrument with a UV2000 detector. The solvent was hexane–isopropanol in a ratio of 95:5; the extraction cell temperature was 90 °C; the pressure was 200 atm.; and the extraction time was 30 min. A Zorbax Sil analytical column with $L = 250$ mm, an inside diameter of 4.6 mm, and a stationary phase particle size of 5 µm was used; the mobile phase (eluant) was hexane–isopropanol in a ratio of 95:5; the eluant flow rate was 2 mL/min; the injected sample volume was 20 µL; and the wavelength was 254 nm. Standard solutions of initial tars with concentrations from 0.1 to 0.001 mg/mL were used for calibration. The purging gas was

Table 1
Main characteristics of carbon sorbents.

N/N	Sorbents	A^d, wt.%	Fe content, wt.%	Pore volume, cm^3/g			ε	$\tan\delta$
				V_Σ	W_s	V_{ma}		
1	WWS	2.5	0.56	1.29	0.27	1.02	2.10	8.6
2	FCS	13.4	1.39	2.52	0.23	2.29	2.07	8.2
3	GCS	25.1	2.05	0.97	0.48	0.49	3.31	12.7
4	BCS	24.0	1.85	1.00	0.47	0.53	3.24	9.4

Note: WWS is the wood waste sorbent; FCS is the flax chaff sorbent; GCS is the gas coal sorbent; BCS is the crushed brown coal sorbent; γ is the apparent density; A^d is the mineral matter content (ash content); V_Σ is the total pore volume; W_s is the volume of sorbing pores; V_{ma} is the volume of macropores; ε is the dielectric constant; and $\tan\delta$ is the dielectric loss tangent.