Development of energy-efficient techniques and technology for environmentally friendly microwave processing of oil sludge

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Abstract. Methods of processing hydrocarbon-containing waste, such as chemical, biological, thermal, physico-chemical, filtering and settling, centrifugation at low efficiency and a wider range of other disadvantages. One of the promising technologies in the oil industry is considered to be microwave heating of hydrocarbon compounds to reduce viscosity during transportation, separation of stable emulsions during primary oil refining, and utilization of drilling oil sludge and petrochemical production wastes. The results of the development of energy efficiency low-temperature technology for environmentally friendly microwave processing of hydrocarbon-containing waste are presented. Studies on a mathematical model showed that at a frequency of microwave radiation equal to the resonant frequency of water molecules, the field strength needed to break the emulsion is 2-100 V/m. For comparison, we note that microwave generators with a power of 50-100 kW are used for heating, respectively, the electric field is more than 10000 V/m, i.e. 100 times higher than required. The time required for phase separation imposes unacceptable requirements on the flow rate. In the studied microwave processing mode due to the resonant interaction of water dipoles with an electromagnetic field, the exposure time is determined by the value of 10-9-10-10 seconds. With these parameters, the temperature of hydrocarbon-containing waste, as shown by calculations on the mathematical model, remains practically unchanged. Due to short-term (microsecond) processing, this technology can be used in the process stream of primary processing and oil refineries, which will significantly reduce the amount of waste generated.

1 Introduction

In the Russian oil industry, up to 25 million cubic meters of solid and liquid wastes are generated annually, which are accumulated in 5000 drilling sludge pits. Only 10% of sludge pits are liquidated annually in the industry. Oil-containing wastes pollute surface and underground waters, soil and vegetation cover, and atmospheric air. In countries with a hot

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climate, the negative impact on the biosphere of waste generated during the extraction, transportation, processing, storage of hydrocarbons is multiplied.

Most common methods for oil sludge processing, that are currently used, such as thermal (obtaining bituminous residues by burning) [1-4], physical (mixing and physical separation of oil sludge by filtration, settling, centrifugation) [5-8], physicochemical (using reagents changing physicochemical properties, followed by separation) [9], chemical (extraction, curing using additives, treatment with hydrophobic reagents) [10-14], biological (microbiological and bio-thermal decomposition using special hydrocarbon-oxidizing bacteria) [15-20], with low efficiency and high cost, have a number of other disadvantages, the main of which are the burning of “useful” hydrocarbons, large amounts of carbon dioxide and other toxic gases formation, low productivity, and the inability to use at low temperatures, inapplicability to hardly stratified highly viscous oil sludge.

In addition, they cannot be used in oil refineries, which are one of the sources of oil sludge, the processing of which in the technological stream of oil refining, i.e. “in-place”, could significantly reduce the amount of waste generated [21]. To reduce these shortcomings, integrated oil sludge processing schemes are used, combining different methods based on their composition and properties characteristics.

In connection with the above, it is relevant to develop a fundamentally new, energy-efficient technology for the environmentally friendly processing of oil sludge.

Currently, one of the promising technologies in the oil and refining industries is considered to be high-frequency and super high-frequency processing of hydrocarbon compounds to reduce viscosity during transportation, stable emulsions separation during primary oil refining, drilling oil sludge and petrochemical waste utilization [22-23]. In this case, emulsion phases’ separation occurs mainly due to heating. For example, in [24] the following information is given: due to medium dielectric losses, the energy of electromagnetic waves is converted into thermal energy, as a result, the temperature rises and the viscosity of the liquid decreases. Imperial Petroleum Recovery Corp. Company (USA, Stafford) has successfully applied microwave separation for the processing of difficult-destroyed stable emulsion oil sludge. The emulsion oil sludge enters the unit at a temperature of 26–65 °C, then is subjected to microwave treatment to create differences in surface tension and phase viscosity, which accelerates the subsequent separation of the emulsion into phases by centrifugation and sedimentation. The degree of oil recovery at this facility is about 98%. Increased installation performance is achieved by parallel placement of several modules.

In [25], a laboratory machine for the processing of hydrocarbon-containing wastes and the results of experimental studies is presented. Thermal transformers are used to efficiently convert microwave energy into heat.

It should be noted that in the proposed options, the thermal effect is ultimately used, which does not allow talking about energy efficiency, taking into account losses in the transmission of electricity, the efficiency of the transformer, microwave generator and transmission line (antenna-feeder devices) and losses during the reverse conversion of microwave energy into heat.

A patent search [26–32] also showed that microwave energy is used to process oil sludge by heating.

Microwave processing parameters at the final stage have to be studied experimentally, but the frequency, power of the generator, and exposure time must be determined by at least rough calculations, because, firstly, there are several hundred varieties of oil and oil sludge, and secondly, microwave generators are produced only for several fixed frequencies, the most accessible of which are 0.91 and 2.4 GHz, which, incidentally, explains their indiscriminate use in practice.
The main goal of our work is to develop energy-efficient low-temperature technologies for environmentally friendly oil sludge waste microwave processing.

To achieve this goal, the following tasks were solved:
1. A critical analysis of the literature on existing oil sludge processing methods.
2. Theoretical basis for the possibility of low-temperature oil sludge microwave processing.
3. Experimental verification of the adequacy of mathematical models for the study of low-temperature sludge waste microwave processing.

2 Methods

In the most general form, the relationship between the parameters of the electromagnetic field and the medium with which it interacts is described by Maxwell's equations.

According to the first Maxwell equation

\[ \text{rot} \mathbf{H} = J_{\text{neq}} + \frac{\partial \mathbf{D}}{\partial t} \]  

the magnetic field \( \mathbf{H} \) in the medium is excited by conduction currents \( J_{\text{cur}} \) and a change in time of the electric displacement vector \( \mathbf{D} \), which in the general case is determined by two components

\[ \mathbf{D} = \varepsilon_0 \mathbf{E} + \mathbf{P} \]  

where \( \mathbf{E} \) is the electric field strength, V/m; \( \mathbf{P} \) – matter polarization - a phenomenon associated with a limited displacement of bound charges in a dielectric or electric dipoles rotation, usually under the influence of an external electric field.

Then the time variation of the electric displacement vector \( \mathbf{D} \) (displacement current density \( \frac{\partial \mathbf{D}}{\partial t} \)) is determined by the formula

\[ \frac{\partial \mathbf{D}}{\partial t} = \varepsilon_0 \frac{\partial \mathbf{E}}{\partial t} + \frac{\partial \mathbf{P}}{\partial t} \]  

and relates to the change in time of the electric field, as well as to the polarization of the substance, i.e. with the movement of bound charges. An important practical conclusion follows from this: in an oil-water emulsion, it is necessary to create an electric field strength \( \mathbf{E} \) sufficient to break the bound charges, which will lead to the destruction of the globules at the corresponding electromagnetic field frequency. It can be assumed that the maximum displacement current density, ceteris paribus, will be at the resonant frequency of the natural vibrations of the bound charges and electric dipoles, which are water molecules.

The resonance frequency of water molecules is known and is 30 GHz [33].

To determine the minimum microwave field strength, we proposed a simple model connecting the electric field strength with the known dipole moments of coupled charges and electronic, atomic, and relaxation (orientational) polarizability [34].

\[ p = \alpha E_0 \]  

where \( p \) is the dipole moment of water molecules and hydrogen-carbon bonds, oxygen-carbon bonds present in oil-water and oil-water emulsions, Cl m; \( \alpha \) — polarizability, m3; \( E_0 \) is the amplitude of the electric field, V / m.

Whence \( E_0 = p/\alpha \). Since the parameters \( p \) and \( \alpha \) are different for different molecules and bonds, we choose the maximum value \( p_{\text{max}} = 11.12 \times 10^{-30} \) and the minimum \( \alpha_{\text{min}} = 0.48 \times 10^{-30} \), which will determine the minimum electric field strength necessary for breaking the
emulsion, equal to 23.1 V/m. We take $E_0$ equal to 100 V/m and evaluate the heating temperature under normal conditions, using our model of heating multicomponent mixtures\cite{35}.

$$T(r) = T_0 + S_0 \sum_{i=1}^{n} k_i F_{ei} \frac{e^{-2\alpha_i r}}{2\alpha_i} \exp \left( \frac{4\pi \alpha_i}{\lambda_{ami}} t \right) \frac{a_i^2}{1 - 1}$$

(5)

where $T(r)$ is the temperature of the reservoir, $^\circ$C; $r$ is the distance from the source, m; $T_0$ - initial formation temperature, $^\circ$C; $\alpha_i$ is the attenuation coefficient of the electromagnetic field in water, oil and sand, respectively, dB/m; $k_i$ is the volume fraction of water, oil and sand in the total volume of the mixture, respectively; $S_0$ is the Poynting vector in vacuum; $F_{ei}$ is the energy transmission coefficient in the $i$th medium (1 - water, 2 - oil, 3 - sand), $\lambda_{ami}$ - thermal conductivity coefficient of the $i$-medium, W/(m K), $a_i^2 = \lambda_i / (\kappa \rho_i)$ is the thermal diffusivity of the $i$-medium; $t$ is the time, s.

The calculation results are shown in the graph (Fig. 1).

![Fig. 1. The dependence of the temperature of the heating surface of the emulsion for 1s](image)

A computational experiment was carried out for a frequency of a microwave generator of 10 GHz, an initial emulsion temperature of 20 $^\circ$C, an emulsion water content of 40%, and $E_0 = 100$ V/m. It can be seen from the graph that the temperature of the emulsion on the surface rose by 2.4 $^\circ$C in 1 s.

It should be noted that the model reflects the ideal case when the processing is carried out by electromagnetic action during plane electromagnetic wave normal incidence on the boundary of the oil sludge with constant electrophysical parameters. In low-temperature processing, when the effective exposure time can be nanoseconds, the restriction on the rate of oil sludge flow is practically removed. It is not difficult to ensure that the vast majority of the emulsion enters the microwave field for at least a few nanoseconds. In this case, the emulsion temperature from microwave energy action will not practically increase.

For experimental verification of the obtained results, an assembly \textit{t} was developed (Fig. 2), containing a power supply unit 1, a microwave generator 2, an amplifier 3, a circulator 4, an emitting antenna 5, a microscope with a video camera 6, a computer 7 with a video camera control program. The test sample of oil sludge is applied to the glass and placed on the object table, microwave energy is fed through the waveguide to the surface of the sample. In the process of microwave processing, video is recorded.

![Fig. 2. The structural diagram of the experimental assembly](image)
3 Results and Discussion

Figure 3 shows frames showing changes during processing for 2 minutes, in Fig. 4 - location of globules of oil-water emulsion before and at the end of processing.

![Figure 3](image_url)

**Fig. 3.** Destruction of globules during processing.

Marked areas show globules before and after destruction.

![Figure 4](image_url)

**Fig. 4.** The location of the globules of the oil-water emulsion a) before the start of and b) at the end of treatment.

The output power of the microwave signal is 2 W, the frequency is 10 GHz, the electric field strength is 20-30 V/m.

First of all, we note that when considering video frames, it has to be taken into account that the thickness of the oil sludge layer on the glass is fractions of a millimeter, and the size of the globules is nanometers, so globules of several layers are visible in the figures.

The experimental results confirm the calculated data, and the microwave radiation power is practically at the lower limit of the power necessary for the destruction of globules. Therefore, globules of only certain sizes are destroyed. This is explained by the fact that, firstly, the surface tension force depends on the globules size, and secondly, microwave radiation frequency is 3 times less than the water molecules resonant frequency. When calculating the minimum electric field strength, we did not take into account the surface tension force. To overcome it, it is necessary to increase the radiation power. Thus, low-temperature separation of the emulsion is possible due to the breaking of chemical bonds under the influence of an electromagnetic field, rather than heating. It is to be noted that, ceteris paribus, if the field strength is increased 100 times, the surface will heat up to 600 °C in 3 minutes, which is unacceptable for reasons of safety and the possibility oil sludge coking. In addition, heating in the stream also becomes problematic since for heating only the surface to 60 °C, it takes about 30 s, and this at a power of 50 kW ($E_0 = 10,000$ V / m) and under conditions close to ideal. In fact, the contradiction between the requirements of uniform heating in volume and ensuring the necessary flow rate is
insurmountable. Therefore, emulsionphases' separation by microwave heating has its significant, rather unavoidable, disadvantages.

4 Conclusions

Low-temperature separation of the emulsion will eliminate the disadvantages of existing methods, such as the burning of “useful” hydrocarbons, the formation of large volumes of carbon dioxide and other toxic gases, low productivity, the inability to use at low temperatures, and inapplicability to hard-to-decompose high-viscosity oil sludge. In addition, this technology and equipment can be used in the process stream of oil refineries, which will significantly reduce the amount of waste generated.

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