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Removal of a liquid paraffin film from a water surface by short pulses from a CO_2 laser

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Abstract. **The process of removal of a liquid paraffin film from a water surface irradiated by 40 – 270-μs pulses from a CO_2 laser is studied experimentally and theoretically. It is found for the first time that the mass of removed paraffin can exceed that of paraffin located in the region irradiated by the laser pulse. A theoretical model is proposed which explains the results obtained.**

Keywords: *paraffin films, water surface, short pulses.*

1. Introduction

In accidents accompanied by the spread of petroleum products over a water surface, petroleum is removed, as a rule, by mechanical methods (see, for example, [1]). Because these methods cannot be applied to thin petroleum-product films of thickness less than 100 μm, it was proposed to use laser radiation for their removal. The burning or evaporation of the films by laser radiation was studied in papers [2, 3]. The films can be also removed from the water surface due to the laser-induced boiling up of water at the film – water interface [2] and the ejection of the film substance by the vapour pressure.

The use of a CO_2 laser for the removal of thin films due to boiling up of water seems most acceptable because radiation at 10.6 μm is much more strongly absorbed by water (absorption length being ~20 μm) than by petroleum products (absorption length being in the region ~100 – 200 μm). Therefore, in the case of films of thickness lower than 100 μm, the radiation from a CO_2 laser is mainly absorbed by water, and petroleum products are ejected due to boiling up of water at the water – film interface. The methods based on the evaporation or burning of petroleum require large energies and are less efficient. Water at the water – film interface can be rapidly heated using repetitively pulsed lasers.

The properties of petroleum depend substantially on its fractions. In thin films, light fractions are evaporated rather rapidly, whereas to develop a theoretical model, it is desirable to use in experiments a material having stable properties. It is known that the physical and optical properties (at a wavelength of 10 μm) of paraffins at 60 °C are close to those of petroleum. Experiments with paraffin films can give quantitative data for the development of models for physical processes determining the efficiency of the laser-induced removal of petroleum products from the water surface.

This paper is devoted to the experimental and theoretical analysis of the regimes of removing paraffin films from the water surface irradiated by 40 – 270-μs pulses from a CO_2 laser.

2. Experimental results

We used in our experiments a repetitively pulsed, fast-flow, transverse-discharge CO_2 laser described in Ref. [4]. The laser had a maximum average power of 1 kW, a pulse repetition rate of 0.1 – 350 Hz, a pulse energy of 0.1 – 8 J, and a pulse duration of 20 – 500 μs. We used a stable three-pass laser resonator with the output-mirror reflectivity $R = 40\,\% - 92\,\%$. The scheme of the experiment is shown in Fig. 1. The laser beam was directed with a metal mirror and was focused with a KCl lens on the surface of water poured in a cell and covered by a paraffin film of the known thickness. An organic glass diaphragm with the diameter of a hole exceeding the laser-beam diameter by 2 – 4 mm was placed 15 – 30 mm over the cell.

As mentioned above, the film absorbs a smaller part of laser radiation (a 100-μm thick film absorbs about 30 % of radiation). The rest of the pulse energy is absorbed in a thin water layer of thickness about 20 μm, resulting in the

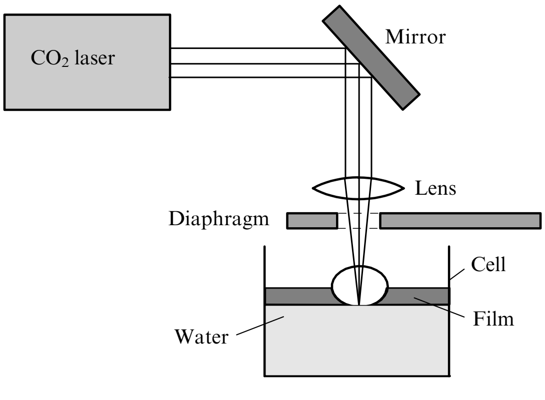

Figure 1. Scheme of the experiment on the removal of a paraffin film from the water surface.

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boiling up of water. A vapour cushion formed due to boiling expands under the action of its pressure upward and along the radius from the spot centre, dispersing the paraffin film. This process will continue until the development of instability will result in the decomposition of the film into separate drops. The paraffin drops colliding with the diaphragm are deposited and solidified on it. It is evident from this scheme of the paraffin-film removal that this effect has a threshold. If the radiation energy density is insufficient to produce the boiling up of the surface layer of water, the paraffin film will not be ejected.

We used in our experiments highly purified paraffin V-2 with the melting temperature 52 – 54 °C. To obtain a homogeneous paraffin film, solid paraffin was placed in water heated to 70 – 75 °C; after melting, paraffin covered the water surface by a homogeneous film. The total area of the paraffin film on the water surface was 25 cm^2. The film was irradiated at different sites by several ($N = 10 - 50$) pulses with a pulse repetition rate of 0.5 Hz, so that the total irradiated area was 5 – 7 cm^2. During the time between pulses (2 s), the homogeneity of the paraffin film was restored over the entire water surface. After irradiation, the cell was cooled and solidified paraffin was mechanically collected and weighed. The removed paraffin mass m_e was determined as a difference between the initial and final paraffin weight. The measurements were performed at different values of the energy E and different durations τ_p of the laser pulse. The laser spot diameter was varied from 3.5 to 8 mm.

Fig. 2 shows the dependences of m_e on the energy density E/S in a laser spot for a paraffin film of thickness $H = 87$ μm for different pulse durations τ_p. One can see that the threshold ratio E/S, at which the removal of the paraffin film begins, decreases with decreasing τ_p, whereas the removed paraffin mass increases by several times for the same ratio E/S. Therefore, the efficiency of film removal increases with decreasing the laser pulse duration. One can clearly see this from the dependences of the removed paraffin mass per 1 J cm^{-2} on the energy density in Fig. 3. This figure shows that short pulses with a relatively low energy density are most efficient.

Another important result demonstrated in Fig. 2 is that the removed paraffin mass for $E/S > 3$ J cm^{-2} is, as a rule, two – three times larger than the mass m_{ei} of a directly irradiated paraffin film m_{ei} ($m_{ei} = HNS\rho$, where N is the number of laser pulses, S is the laser spot area, and ρ is the paraffin density.)

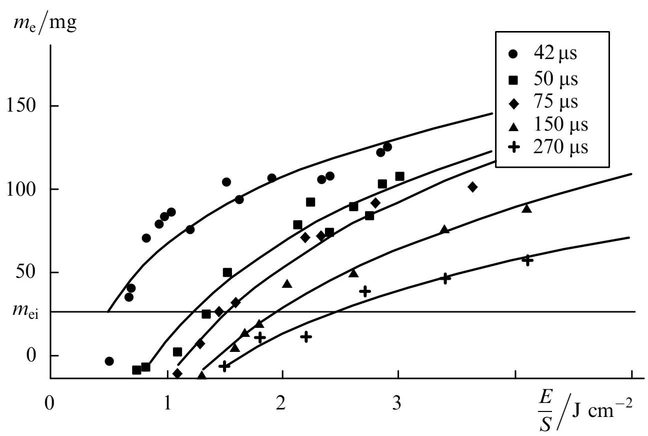

Figure 2. Dependences of the removed paraffin mass m_e on the energy density E/S in the laser spot for different durations of the laser pulse, $S = 0.1$ cm^2, $N = 50, H = 87$ μm.

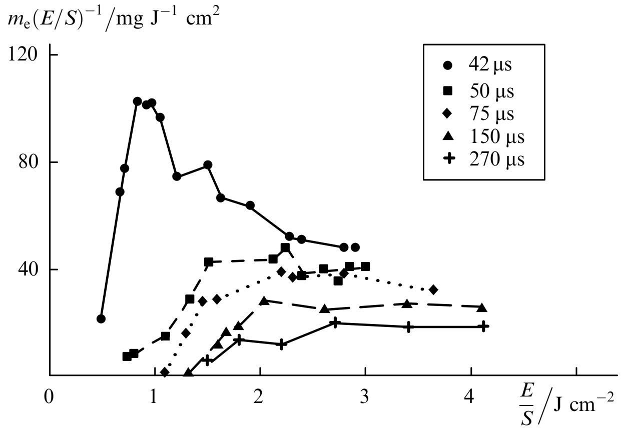

Figure 3. Dependences of $m_e(E/S)^{-1}$ on the energy density in the laser spot for different durations of the laser pulse, $S = 0.1$ cm^2, $N = 50$, $H = 87$ μm.

The dependences of m_e on E/S for paraffin films of different thickness are shown in Fig. 4. One can see that the removed paraffin mass ceases to change with decreasing the film thickness (for $H = 65, 44$, and 22 μm) beginning from some value of E/S, and the saturated value of m_e is proportional to the film thickness. Note that for any thickness of the film and $E/S > 1.5$ J cm^{-2}, the removed paraffin mass substantially exceeds m_{ei}.

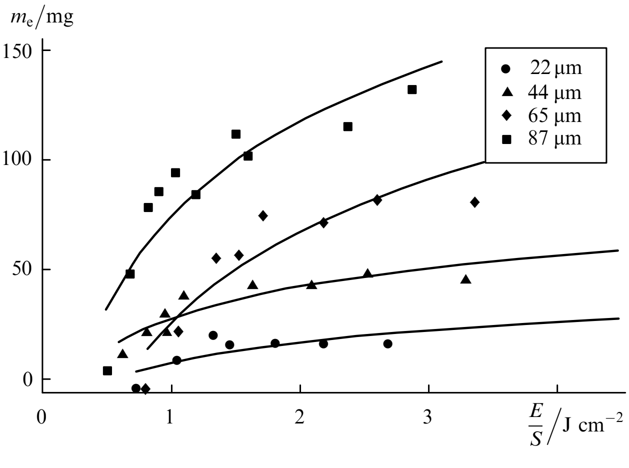

Figure 4. Dependences of the removed paraffin mass m_e on the energy density in the laser spot for different thickness of the paraffin film, $S = 0.1$ cm^2, $N = 50, \tau_p = 42$ μs.

By varying the laser spot size and retaining the total irradiated film area constant (S_{tot} = const = SN), we found that the removed paraffin mass increased with decreasing laser spot size when the laser energy density was constant. The efficiency of the paraffin film removal also depends on the distribution of the energy density in the laser spot. We measured the inhomogeneity of the energy distribution in the laser spot from an indentation produced by the laser beam on the organic glass. The inhomogeneity varied from 30 % to 80 %. The paraffin film was removed more efficiently when the distribution of the energy density was more homogeneous. When the initial temperature of water was lowered from 75 to 57 °C (at temperatures lower than 52 – 54 °C, the paraffin film solidified), the value of m_e decreased by half and became close to m_{ei}. This can be explained by the fact that an additional energy is required for heating water to the boiling temperature, as well as by a change in the properties of the paraffin film at lower temperatures.

3. Numerical simulation

To calculate the dynamics of petroleum film lift, we developed numerical one-dimensional and two-dimensional programs, which take into account the shape of a laser pulse, the spatial and time dynamics of heating of the surface layer of water, the heat conduction and boiling up of water.

It is assumed in the one-dimensional approximation that a paraffin film (of thickness H and density ρ) subjected to the action of the water vapour remains flat. The dynamic equation, which takes into account the inertia of the paraffin film and the counteraction of the external pressure p_0, has the form

$$\frac{d^2h}{dt^2}=\frac{1}{H\rho}(p-p_0), \tag{1}$$

where h is the thickness of a vapour interlayer. The pressure in the vapour interlayer can be determined from the equation of state for an ideal gas

$$p=\frac{m}{\mu_w}\frac{RT}{Sh}. \tag{2}$$

Here, m is the vapour mass under the paraffin film; μ_w is the molar mass of water; T is the vapour temperature in kelvins; $R = 8.31$ J mol^{-1} K^{-1} is the gas constant. A change in the vapour mass is determined from the solution of the heat conduction equation in the surface layer of water

$$\frac{dm}{dt}=\frac{S\kappa_w}{r}\frac{\partial T}{\partial z}\bigg|_{z=0}, \tag{3}$$

$$c_w\rho_w\frac{\partial T}{\partial t}=e(t)S\exp\left(-\frac{H}{\Lambda}\right)\exp\left(-\frac{z}{\Lambda_w}\right)+\kappa_w\Delta T, \tag{4}$$

$$T|_{z=0}\leqslant T_{\text{boil}}. \tag{5}$$

Here, the coordinate axis z is directed deep inside the water layer; $e(t)$ is the laser power density; r is the vaporisation heat; Λ, Λ_w are the absorption lengths in paraffin and water, respectively; $c_w, \rho_w, \kappa_w, T_{\text{boil}}$ are the heat capacity, density, heat conduction, and boiling temperature of water, respectively. The system of equations (1) – (5) with the initial conditions $h(0) = 0$, $p(0) = p_0$, $m(0) = 0$, and $T(0) = T_0$ determines the solution of the one-dimensional problem.

In the two-dimensional calculation program, we used the approximation of the axial symmetry of a laser beam. The height of the film lift depends on the radius. The system of equations (1) – (5) is valid at each point. The vapour mass and its volume are summed over the total boiling surface and it is assumed that the vapour pressure under the removed film is the same at any point. Both in the one-dimensional and two-dimensional case, the acceleration of a liquid film was calculated before the instant of its decomposition into drops.

4. Decomposition of a paraffin film into drops

The time of the decomposition of a film into drops was determined by the solving the problem of the Rayleigh – Taylor instability of the accelerated layer of heavy liquid placed between two layers of light liquid. By neglecting the liquid viscosity, the increment and scale of most unstable perturbations can be determined from the dispersion equation for capillary waves in a paraffin film

$$\omega^4-2\omega^2\frac{\sigma k^3}{\rho}\frac{\cosh(kH)}{\sinh(kH)}+\left(\frac{\sigma k^3}{\rho}\right)^2-(ak)^2=0, \tag{6}$$

where a is the acceleration of a paraffin layer. A real laser pulse was simulated taking into account that the acceleration of the paraffin film changes with time. The time of the film destruction was estimated by considering the integral characteristic of the Rayleigh – Taylor instability, which depends on the wave vector

$$I_k=\int_{\omega_k^2<0}\text{Im}(\omega_k)dt. \tag{7}$$

The characteristic time of the instability development can be estimated as a minimum time when the integral I_k becomes of the order of unity for some wave number.

5. Results of calculations

Let us compare the results of calculations performed for two limiting laser-pulse durations, 20 ms and 20 μs. The thickness of a paraffin film was varied in calculations from 10 to 100 μm and the laser energy density was varied from 2 to 20 J cm^{-2}. In the case of a long pulse, the absorbing water layer was weakly overheated by 10 – 20 °C. The excess pressure under the film becomes rapidly (for $10^{-7} - 10^{-6}$ s) low compared to the atmospheric pressure. In this case, the acceleration of the film proves to be small; for the time $10^{-4} - 10^{-3}$ s required for the film decomposition into drops, the velocity of 0.2 – 1 m s^{-1} is achieved and the height of the drop ejection is only 0.1 – 5 cm.

In the case of a short pulse, the overheating of water in the absorbing layer achieves 100 – 150 °C. Pressure under the film exceeds the atmospheric pressure by several times for the time 1 – 10 μs (Fig. 5). For characteristic times 0.5 – 5 μs of the film rupture, the calculated velocity of its lift is 5 – 50 m s^{-1}.

The results of these calculations confirm the conclusion that short laser pulses remove the film more efficiently. For the pulse duration $\tau_p = 20$ ms, the ratio of the time required for the film rupture to the pulse duration is $\tau_{br}/\tau_p \approx (0.5-5)\times10^{-2}$. After the decomposition of the film into drops, the pressure from both sides of the paraffin film becomes the same and the film is no longer subjected to any forces. Therefore, a greater part of energy in a long pulse is wasted. For $\tau_p = 20$ μs, the ratio τ_{br}/τ_p increases approximately by a factor of five and the pulse energy is more efficiently used for the destruction of the paraffin film.

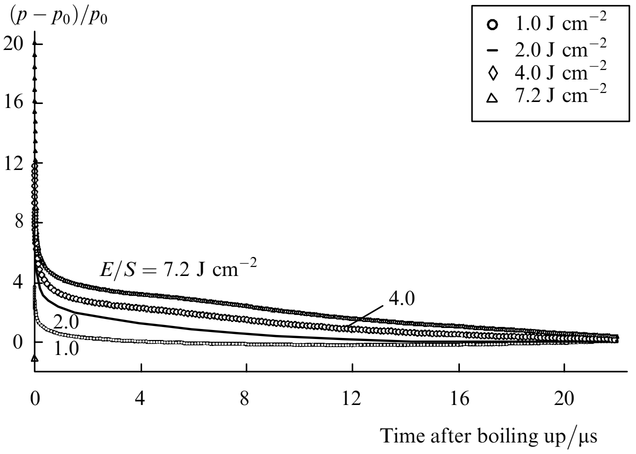

Figure 5. Dynamics of the vapour pressure under the film calculated for different energy densities of the laser pulse for $\tau_p = 20$ μs and $H = 30$ μm.

6. Qualitative analysis of the film removal from a water surface

Experiments with short pulses showed that the mass of removed paraffin can exceed the mass of paraffin irradiated by the laser pulse. One of the possible explanations of this effect is the spread of a vapour interlayer between the paraffin film and the water surface.

Consider qualitatively the dynamics of growth of a vapour bubble under the film once the bubble size at its base has exceeded the laser-beam diameter. We assume that the shape of the bubble does not change upon its expansion and represents a segment of a sphere with the dome height $h(t)$ and the radius $L(t)$ of a circle on the water surface. In this case, the bubble volume is $V_0 = \pi L^2 h/2$ and the radius of curvature is $R_0 \approx L^2/2h$ (we assume that $h/L \ll 1$). Let $V_f = \dot{h}$ be the velocity of the paraffin film, $V_{fr} = (L/2h)V_f$ be the propagation velocity of the front of the film detachment from the water surface, and the difference δp of pressures inside and outside the bubble exceeds the capillary pressure $4\sigma_f/R_0$.

When the bubble expands during the time δt, vapour performs the work $\delta W_v \approx \delta p\, \delta V_0 = \delta p V_0 (2V_{fr}/L + V_f/h)\delta t$. This work is spent for increasing the kinetic energy of the film $\delta W_{kin} \approx \delta(m V_f^2/2) \approx 2\pi L V_{fr} \delta t \rho H \times (V_f^2/2 + h\dot{V}_f)$ and the surface energy $\delta W_s \approx 2\pi L V_{fr} \delta t \sigma$, where $\sigma = \sigma_w + \sigma_f - \sigma_{wf}$. From the energy balance, we find the equation for the bubble growth

$$\frac{\dot{h}^2}{2} + h\ddot{h} = \frac{\delta p h - \sigma}{\rho H}. \tag{8}$$

Our calculations showed that in the case of short pulses, the pressure inside the bubble considerably exceeds the atmospheric pressure up to the instant of the film rupture. Therefore, we can write for the laser pulse $e(t) = E_0 t$

$$\delta p \approx \rho_v \frac{RT}{\mu_w} \approx E_0 e^{-H/A} \frac{RT}{r\mu_w} \frac{St}{\pi R_0 h^2}. \tag{9}$$

The solution of equations (8) and (9) is the constant growth velocity of the bubble

$$\dot{h} = V_f \approx \left[\frac{2h}{\rho H}\left(\delta p - \frac{\sigma}{h}\right)\right]^{1/2} = \text{const.} \tag{10}$$

In this case, the kinetic energy of the film increases due to the involvement of the addition paraffin mass in the uniform motion. One can see from (10) that to remove the film from the water surface, the pressure difference should be $\delta p > \sigma/h$.

By substituting the values of the surface tension coefficients, we obtain for $h \sim 10^{-2} - 10^{-1}$ cm a low critical pressure excess of the order of $10^{-3} - 10^{-2}$ atm. As the laser pulse duration decreases, the vapour pressure under the film increases. Simultaneously, the velocities of the bubble expansion and of the detachment front increase. As a result, the ratio m_e/m_{ei} should be higher for shorter pulses, provided the energy density is the same, which was observed experimentally (Fig. 2). Let us estimate the velocities of motion of the film and the front of the interface rupture. If the pressure drop is 1 atm, the laser spot diameter is 0.5 cm, the height of the film lift is $h = 10^{-2}$ cm, and the film thickness is $H = 50$ μm, then we have $V_f \approx 20$ m s^{-1} and $V_{fr} \approx 260$ m s^{-1}.

Therefore, a paraffin film is removed from the water surface not only in the regions where water boils up. It can be also removed in regions where the interface is ruptured under the vapour pressure when a paraffin bubble is expanded. Such a mechanism operates when the vapour pressure exceeds a critical value and it ceases when the film is ruptured and is decomposed into drops.

7. Conclusions

We have studied for the first time experimentally and theoretically the process of removal of a liquid paraffin film from the water surface irradiated by 40 – 270-μs pulses from a CO_2 laser. As the time of the local irradiation of the water surface decreases, the threshold energy density, at which water starts to boil and the removal of the paraffin film begins, decreases, the specific expenditure of energy also being decreased. When the laser beam is fixed, the interaction time is determined by the laser pulse duration. The removed paraffin mass, beginning from a certain energy density of the laser beam, exceeds the mass of paraffin directly irradiated by the laser beam and increases with increasing the energy density, without saturation. The theoretical model proposed in the paper explains these results.

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