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WAVE PARAMETERISATION IN MODELLING OF OIL EMULSIFICATION
PARAMETRIZACIJA VALOVANJA PRI MODELIRANJU EMULZIFIKACIJE NAFTE

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Abstract

We describe the upgrade of a simple numerical model (EMU) for predicting the time of oil emulsification and the type of emulsion, based on the Fingas (2010) method. The input parameters are the oil properties and wave characteristics. We rely on empirical prediction of wave parameters. In the original model only the Bretschneider's (1952) empirical wave model suitable for predictions in deep water was used. In the upgraded model we use four additional wave parameterisation methods: CEM, Seck-Hong and SMB method for both shallow and deep water. Three types of oil with significantly different properties were used to demonstrate the behaviour of oil. We compare the results of different wave parameterisation methods for computation of initial time of emulsification, for the emulsion formation time and for the total time of emulsification. In chosen conditions, the selection of adequate empirical wave model is important for low wind and short fetch. Comparison to the wave measurements and observations are needed in order to choose the most appropriate wave parameterisation.

Keywords: oil spill, water-in-oil emulsification, emulsification time, emulsion stability, wave parameterisation, EMU model.

Izvleček

Opisujemo nadgradnjo preprostega numeričnega modela za račun emulzifikacije (EMU), zasnovanega na metodi Fingas (2010), s katerim predvidimo čas emulzifikacije in stabilnost emulzije. Vhodni podatki so lastnosti nafte in valovanja na območju razlitja. V modelu uporabljamo empirične metode napovedovanja parametrov valovanja. V izvornem modelu je bila uporabljena zgolj metoda Bretschneider (1952), primerna za napovedi v globoki vodi. V dopolnjenem modelu uporabimo štiri dodatne metode: CEM, Seck – Hong ter metodi SMB za plitvo in globoko vodo ter tri tipe nafte z značilno različnimi lastnostmi. Rezultate (čas do začetka emulzifikacije, čas emulzifikacije in skupni čas emulzifikacije), dobljene po vseh metodah, primerjamo med seboj. Ugotovimo, da je v izbranih razmerah izbira ustreznega empiričnega modela valovanja pomembna pri šibkem vetru in kratkih privetriščih. Za določitev najprimernejše empirične metode parametrizacije valov je potrebna nadaljnja primerjava z meritvami in opazovanji valov.

Ključne besede: nafta, emulzifikacija vode v nafti, čas emulzifikacije, stabilnost emulzije, parametrizacija valovanja, model EMU.

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1. Introduction

Oil spills at sea usually cause severe ecological damage to marine and coastal ecosystems, and impact the economy in coastal regions. Even oil-spills of a few hundred tons cause high ecological and economic damage in small enclosed coastal environments. The consequences and the cost of remediation are very difficult to estimate due to numerous processes that change the properties of released oil. Among the physical and chemical processes that occur in the timescale of a few days after the spill in the open sea, emulsification is the most important for cleanup and remediation processes. At the sea surface oil can be gathered using skimmers, sorbents or manually. Furthermore, oil can be burnt or dispersed by the use of chemical dispersants (Fingas and Charles, 2001). However, none of the mentioned techniques can be adopted after the occurrence of emulsification. When formed, the volume of emulsion is up to three-fold the volume of parent oil and the increase in viscosity can reach even three orders of magnitude. Therefore, cleanup of emulsified oil is extremely difficult; it cannot be recovered by skimmers, dispersed or burned (Fingas and Charles, 2001).

Weathering processes depend strongly on the physical and chemical characteristics of released oil and the environmental parameters at the spill location. These processes and parameters have been studied intensively for the last few decades and described in numerous studies (Yetilmezsoy, et al., 2011 and the references therein). For a large number of oils and derivatives the connection between their physico-chemical properties (initial density, viscosity and surface tension) and behaviour at the sea has been evaluated (Fingas, 2010; Wang et al., 2003).

The mechanism of the water-in-oil emulsion formation is not yet completely understood. In the process, water droplets are dispersed in oil due to turbulent energy of the sea. Beforehand the lighter fractions of oil are removed due to evaporation (and to a lesser extent due to dissolution) and the viscosity is increased. Depending on the sea energy and the ratio between resins, waxes and asphaltenes, four types of emulsions may form: stable, meso-stable, entrained and unstable emulsions (Fingas, 2010). Unstable emulsions break down when sea energy decreases, while meso-stable and stable are very difficult to decompose and need special chemical treatment (Fingas, 2010). Moreover, due to significantly different properties, emulsion formation slows down the transport and weathering processes of oil: evaporation, biodegradation and oxidation (Fingas, 2010).

In order to support decision-making systems, different types of numerical models are used. Most take into account the processes occurring immediately after the spill: mechanical spreading, evaporation, advection and diffusion, as well as dispersion of oil droplets into the water column and emulsification. The latter is, however, usually simulated by Mackay's approach (Mackay, 1980), which takes into account the calculation of water uptake based on wind speed, and several empirical constants that need to be calibrated for each case study, and coefficients that are difficult to obtain without in-situ sampling and laboratory analyses. Despite these drawbacks, the Mackay's model in its original or slightly changed form is still included in the vast majority of oil-spill models, e.g. OSCAR (Aamo et al., 1997), GULFSPILL (Al-Rabeh et al., 2000), ADIOS (Lehr et al., 2002), PISCES (Delgado et al., 2006), MEDSLIK (http://medslikii.bo.ingv.it/), NAFTA3D (Ramšak et al., 2013) and similar.

Different numerical models are being developed solely for simulation of emulsification. In the early stages of determining remediation measures even a simplified model that provides information on the possibility of emulsion formation, stability of emulsion and the time of formation is sufficient. Fingas and Fieldhouse (Fingas and Fieldhouse, 2009a; Fingas, 2010) performed numerous measurements and published data on characteristics of more than 300 oils and petroleum products. They also proposed multi-regression models for determination of emulsion stability (Fingas and Fieldhouse, 2009b; Fingas, 2010). Recent development of emulsification models has employed fuzzy-logic in order to improve the relatively low reliability of formerly used regression models (Yetilmezsoy et al., 2011, 2012). We developed another simple model based on the equations proposed by Fingas and Fieldhuse (2009b). In the EMU model (Kvočka, 2013) the equation for stability (Fingas, 2010) and data on numerous oil and oil product characteristics (Fingas and Fieldhouse, 2009b; Fingas, 2010) are pre-included. Another option of the model enables the end-user to input any type of oil or oil product by giving its basic physical and chemical parameters. The model calculates stability index and time of emulsion formation for the selected type of oil or oil product within a few seconds. Wave-turbulence in this model is, however, either estimated or calculated by approximate equations of Bretschneider (1952). The use of Bretschneider’s method to determine wave height is limited to deep water and fully developed sea. As indicated by Tofil (2013), this method overestimates predicted wave height in comparison to other wave parameterisations. In order to compare the influence of wave model on the emulsification and to adapt the model for coastal areas with different wind-induced wave conditions, we upgraded the model with four additional wave parameterisations: Seck – Hong method (Seck-Hong, 1977), CEM method (Etemad-Shahidi et al., 2009), Sverdrup-Munk-Bretschneider (SMB) for deep water (Hasselmann et al., 1976) and SMB for shallow water (CERC, 1984).

The common parameters of all empirical methods are fetch and wind speed; therefore, we investigated the impact of these two parameters on emulsification time using all four methods and the values typical for costal area. Although the reliability of all approximate empirical models is low in the coastal area, they can be used either as the first approximation or in absence of wave forecasts or analyses obtained using the third generation wave models, such as SWAN (http://swanmodel.sourceforge.net/) or WAM (http://en.wikipedia.org/wiki/Wind_wave_model). Such forecasts and analyses are not always available. We expected different wave parameterisations to yield different results. A comparison of results could lead to a decision on which empirical wave models to abandon or to further investigate.

Furthermore, we compared the emulsification time for three types of oil that form differently stable emulsions. In the early stages of deciding on remediation measures the knowledge on the emulsification time and the ratio between the initial time and the formation time of emulsion may be crucial for adequate clean-up activities.

2. Methods and the EMU model

2.1 Stability of emulsion

The EMU model has approximately 150 types of oil preinstalled. The following properties are included: density (g/cm^3), dynamic viscosity (mPa.s), saturated hydrocarbons (%), resins (%), asphaltenes (%), and resins to asphaltens ratio. From these properties the parameters used in Eq. 1 are determined for calculating the stability of emulsion (Kvočka, 2013, Fingas, 2010; Yetilmezsoy, et al., 2012):

$$\begin{aligned} Stability\ C = {} & 12.3 + 0.259\, St - 1.601\, Rt - \\ & 17.2\, \frac{A}{Rt} - 0.50\, Vt^3 + 0.002\, Rt^3 + 0.001\, At^3 + \\ & 8.51 \left(\frac{A}{Rt}\right)^3 - 1.12 \ln(Vt) + 0.700 \ln(Rt) + \\ & 2.97 \ln\left(\frac{A}{R}\right) + 6 \cdot 10^{-8} \exp(\ln(Vt)^2) - \\ & 1.96 \exp\left(\frac{A}{Rt}\right)^2 - 4 \cdot 10^{-6}\, \frac{\log(\exp(Dt))}{Dt^2} - 1.5 \cdot \\ & 10^{-4}\, \frac{\log\left(\frac{A}{Rt}\right)}{\left(\frac{A}{Rt}\right)^2}, \end{aligned} \tag{1}$$

where *St* is the transformed content of saturates, *Rt* the transformed resin content, *A/Rt* and *A/R* the transformed asphaltene/resin ratio, *Vt* the transformed viscosity, *At* the transformed asphaltene content, and *Dt* the transformed density. The equations to calculate individual parameters are described in detail elsewhere (Fingas, 2010). The state of emulsion is determined from the calculated (dimensionless) *Stability C,* as

- Stable emulsion: *Stability C* is between 4 and 29.
- Mesostable emulsion: *Stability C* is between -10 and 5.

- Entrained water: *Stability C* is between -20 and 3, density is higher than 0,94 g/cm^{3}and viscosity is higher than 600 mPa.s.

Unstable emulsion: *Stability C* is between -18 and -4, viscosity is lower than 100 mPa.s or higher than 800,000 mPa.s, contents of both waxes and asphaltenes are lower than 1%

2.2 Formation of emulsion

The time needed for emulsion to form consists of two parts (Fingas and Fieldhouse, 2004, 2005; Kvočka, 2013): the initial time of emulsification and the formation time. The initial time of emulsification is defined as a time interval between the moment of oil spill and the beginning of emulsion formation. For most of the oils a certain quantity of light fractions needs to evaporate before emulsification can begin. Data on the initial fraction of evaporation and the stability of emulsion formed for a large number of oils is given in Fingas and Fieldhouse (2004). In the EMU model, the Fingas (2004) approach is used to calculate evaporation. Fingas proposed either a logarithmic or a square-root relationship between percentage of evaporation and time for most of the oils and oil products and further accounted for temperature variation. For oils that follow a logarithmic relationship:

$$F = [0.165\,\%D + 0.045\,(T - 15)]\ln(t_1), \tag{2}$$

and for oils following the square root relationship:

$$F = [0.0254\,\%D + 0.01(T - 15)] \cdot \sqrt{t_1}\,, \tag{3}$$

where F denotes percentage of evaporation, $\%D$ is the percentage by weight distilled at 180 °C, T is the ambient temperature in °C, and t_1 denotes time. Explicit equations for more than 300 oils and oil products are given in Fingas (2010). The heavier the oil, the longer it takes for enough oil to evaporate to start the emulsification process.

The formation time of the emulsion is described with Eq. 4 (Kvočka, 2013; Fingas and Fieldhouse, 2005):

$$y = \ a + b/x^{1,5}, \tag{4}$$

where y is the formation time of the emulsion [min], a and b are constants depending on the emulsion stability and x is wave height [cm]. Eq. 4 takes into account steady state condtions in wave motion, which are extremely rare in field conditions on longer time scales. Furthermore, it does not consider either wave period or steepness. Moreover, it is not clear whether the wave height under the slick or in the area not covered with oil should be considered (Kvočka, 2013).

Wave height is the only non-constant and nonlinear term in the Eq. 4; it can be determined in different ways. It can be estimated from field measurements, obtained by using wave models (such as SWAN or WAM), or determined from approximate empirical equations that were used before the development of accurate wave models. The original EMU model had two options for determining the wave height: estimation or Bretscheider's (1952) equation:

$$H_w = 0.0555 \cdot \sqrt{U^2\,F}, \tag{5}$$

where H_w is the wave height [ft], U is the wind speed 10 m above sea level [kn] and F is the fetch length [mi]. Tofil (2013) demonstrated that Bretschneider's equation overestimates wave height, as the method was originally intended for use in fully developed deep sea. In the performed comparison (Tofil, 2013) between Bretscneider's and four other methods (Seck-Hong, CEM, SMB for deep water and SMB for shallow water) the differences were significant, but not regular. Therefore, we suspected that different approximate methods used to determine wave height may result in significantly different formation time of the emulsion.

2.3 Wave parameterisation

2.3.1 Method Seck – Hong

The method is a modified version of Wilson's (Etemad-Shahidi et al., 2009; Goda, 2003) equation, used for calculating significant wave height in deep water (Seck-Hong, 1977; Tofil, 2013):

$$\frac{g \cdot H_S}{U^2} = 0.30 \cdot \left\{ 1 - \frac{1}{\left[1.0009 + 0.0045 \cdot \sqrt{\frac{g \cdot F \cdot (1 - e^{-U \cdot t/2.48 \cdot F}}{U^2}} \right]^2} \right\}, \tag{6}$$

where H_s denotes significant wave height [ft], F is the fetch [ft], g is gravitational acceleration [ft s^{-2}], U is wind speed [ft s^{-1}], and t is duration of wind [s]. The original Seck-Hong equation takes into account the parameter of wind duration. Since all the other equations take into account fully developed sea, we applied infinite time and simplified the equation into:

$$H_s \quad = \frac{U^2}{g} \cdot 0.30 \cdot \left\{ 1 - \frac{1}{\left[1.0009 + 0.0045 \cdot \sqrt{\frac{g \cdot F}{U^2}}\right]^2} \right\}. \tag{7}$$

Moreover, wave height is defined as a steady state parameter in the Eq. 4 and emulsification time cannot be calculated using time-variable wave height, as calculated with the original Seck-Hong equation.

2.32 CEM method

This method is also used for calculating wave height in deep water (Tofil, 2013; Etemad-Shahidi et al., 2009):

$$H_s = \frac{4.13 \cdot 10^{-2} \cdot \left(\sqrt{\frac{g \cdot F}{u_*{}^2}}\right) \cdot u_*{}^2}{g}, \tag{8}$$

where H_s is significant wave height [cm], F is fetch length [km], U is wind speed [m s^{-1}], u_* is shear wind speed [m s^{-1}] and C_D is the shear coefficient. The last two parameters are calculated as follows:

$$u_* = U \cdot \sqrt{C_D}, \tag{9}$$

$$C_D = 0.001 \cdot (1.1 + 0.035 \cdot U). \tag{10}$$

2.3.3 SMB method – deep water

The equation describing significant wave height in the SMB for deep water is (Tofil, 2013; CERC, 1984):

$$H_s = \frac{U_A{}^2 \cdot 0.0016 \cdot \sqrt{\frac{g \cdot F}{U_A{}^2}}}{g}, \tag{11}$$

$$U_A = 0.71 \ \cdot \ U^{1.23}, \tag{12}$$

where H_S is significant wave height [cm], U_A is effective wind speed [m s^{-1}] F is the fetch [m], g is gravitational acceleration [m s^{-2}] and U is wind speed [m s^{-1}].

In this equation we operate with the effective wind speed, which is calculated from actual wind speed.

2.3.4 SMB method – shallow water

Significant wave height is calculated using equations (Tofil, 2013; CERC, 1984):

$$H_s = 0.283 \cdot \frac{U_A{}^2}{g} \cdot tanh[0.530 \cdot (h')^{0.75}] \cdot$$

$$tanh \frac{0.00565 \cdot (F')^{0.5}}{tanh[0.530 \cdot (h')^{0.75}]}, \tag{13}$$

$$h' = \frac{g \cdot h}{U_A{}^2}, \tag{14}$$

$$F' = \frac{g \cdot F}{U_A{}^2}, \tag{15}$$

$$U_A = 0.71 \ \cdot \ U^{1.23}, \tag{16}$$

where H_S is wave height [cm], U_A is effective wind speed [m s^{-1}] g is gravitational acceleration [m s^{-2}], h' is dimensionless water depth, F' is dimensionless fetch, h is water depth [m], F is the fetch [m], U – wind speed [m s^{-1}].

2.4 EMU model

EMU is a simple and user-friendly model with pre-included physical and chemical characteristics of about 150 types of oil. It enables the end-user to either choose among the pre-encoded options in menus or to input physical and chemical data for oil types not yet included into the model (Figure 1).

When the model is run, the user can choose among the oil types and the model automatically finds and fills the form with the oil properties, including the percentage of evaporation (%) and percentage by weight distilled at 180° (%). With the properties written, the button “Asphaltene/resin ratio” should be clicked in order to calculate the parameter and to further transform the oil properties into parameters needed for computation of oil stability. When the button “Transform” is clicked, the form fills with further data: Stability-C and the stability class. For the calculation of the initial time (until the beginning of emulsification) one needs to enter the water temperature and click the button “Initial time of emulsification”. Finally, the wind/wave parameters (either wind speed and fetch or the estimated wave height) are entered and by pressing the buttons “Wave height” and “Time to formation the emulsion” the computation is finished and the form filled with all results, including wave height used in computation and the full time from the spill to formation of the emulsion.

2.5 Upgrade of the EMU model

We included the described methods (equations) of wave parameterisation into the model. As the four methods require different input parameters for computation, we developed four new interfaces for the model in order to test and compare the results for different wave parameterisations. When new observations and measurements become available, we will be able to decide on the most appropriate version, which will be further upgraded.

The interface is slightly different in each version of the model in order to enable input of required wind/wave parameters and to show the intermediate results. Interfaces for the Seck-Hong and CEM parameterisation are shown in figures 2 and 3, respectively. The changed part of the interface on both figures is shown in a yellow frame.

2.6 Case studies

2.6.1 Case study A: Emulsification time computed using constant wind speed

In computations the wind speed 18 m/s was used as a constant parameter and fetch as a variable (values between 1 and 20 km). Calculations with two water depths (10 and 20 m) were performed with the SMB shallow water method. In order to avoid either extremely long or short emulsification time, we used the Cook Inlet – Granite Point oil (Table 1) with two-day evaporation time before the beginning of emulsification.

2.6.2 Case study B: Emulsification time computed using constant fetch

The following parameters were used: constant fetch 15 km, two depths 10 m and 20 m with the SMB method and variable wind speed (1 – 20 m/s). The same type of oil as in Case study A was used in computations.

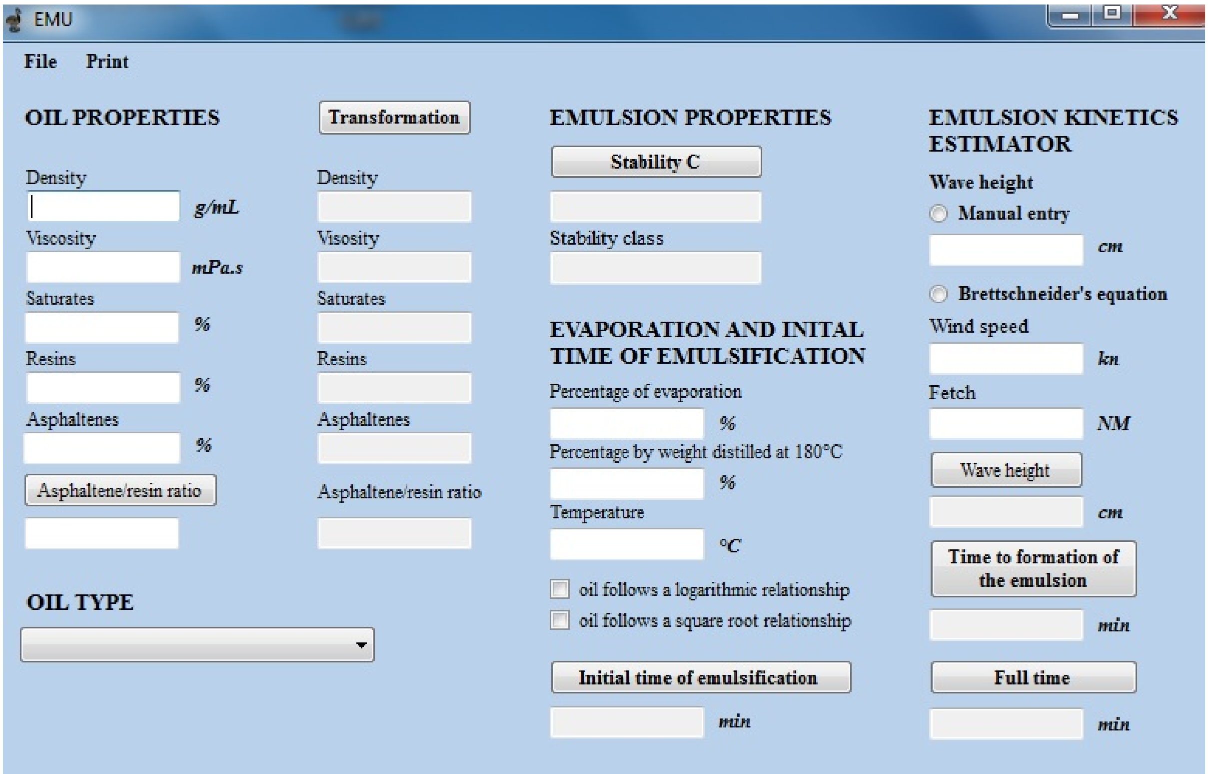
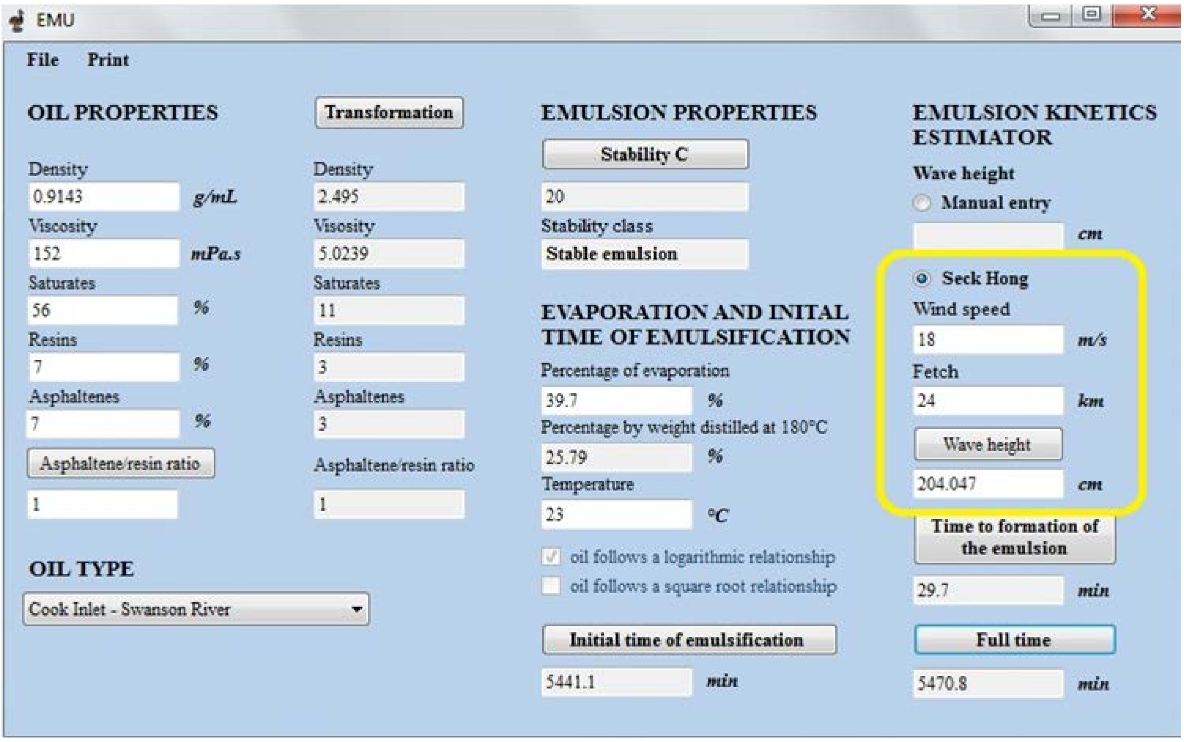


Figure 1*: User interface of the original EMU model.*

Slika 1: *Uporabniški vmesnik prvotnega modela EMU.*



OIL PROPERTIES
Density: 0.9143 g/mL
Viscosity: 152 mPa.s
Saturates: 56 %
Resins: 7 %
Asphaltenes: 7 %
Asphaltene/resin ratio: 1

Transformation
Density: 2.495
Visosity: 5.0239
Saturates: 11
Resins: 3
Asphaltenes: 3
Asphaltene/resin ratio: 1

OIL TYPE: Cook Inlet - Swanson River

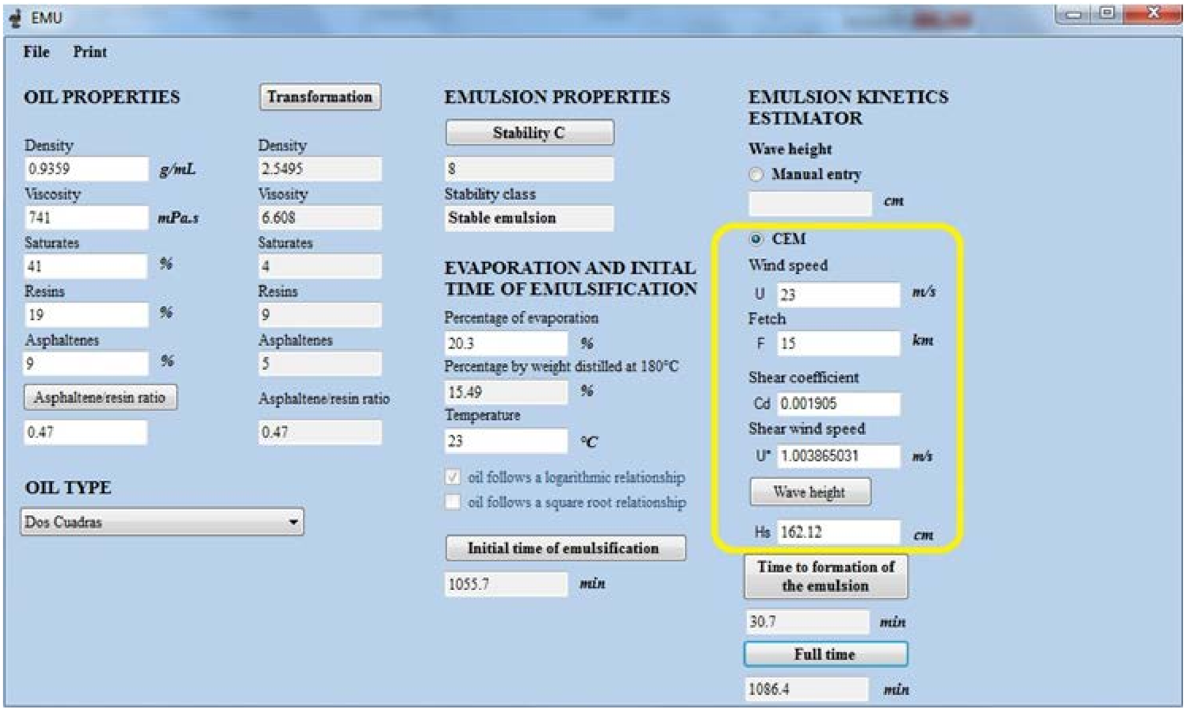
EMULSION PROPERTIES
Stability C: 20
Stability class: Stable emulsion

EVAPORATION AND INITAL TIME OF EMULSIFICATION
Percentage of evaporation: 39.7 %
Percentage by weight distilled at 180°C: 25.79 %
Temperature: 23 °C
☑ oil follows a logarithmic relationship
☐ oil follows a square root relationship
Initial time of emulsification: 5441.1 min

EMULSION KINETICS ESTIMATOR
Wave height
○ Manual entry
cm
● Seck Hong
Wind speed: 18 m/s
Fetch: 24 km
Wave height: 204.047 cm
Time to formation of the emulsion: 29.7 min
Full time: 5470.8 min

***Figure 2**: User interface of the EMU model adapted for the Seck-Hong method. New entry fields in the yellow rectangle.*

***Slika 2:** Uporabniški vmesnik modela EMU prirejenega metodi Seck-Hong. Nova polja so v rumenem pravokotniku.*



OIL PROPERTIES
Density: 0.9359 g/mL
Viscosity: 741 mPa.s
Saturates: 41 %
Resins: 19 %
Asphaltenes: 9 %
Asphaltene/resin ratio: 0.47

Transformation
Density: 2.5495
Visosity: 6.608
Saturates: 4
Resins: 9
Asphaltenes: 5
Asphaltene/resin ratio: 0.47

OIL TYPE: Dos Cuadras

EMULSION PROPERTIES
Stability C: 8
Stability class: Stable emulsion

EVAPORATION AND INITAL TIME OF EMULSIFICATION
Percentage of evaporation: 20.3 %
Percentage by weight distilled at 180°C: 15.49 %
Temperature: 23 °C
☑ oil follows a logarithmic relationship
☐ oil follows a square root relationship
Initial time of emulsification: 1055.7 min

EMULSION KINETICS ESTIMATOR
Wave height
○ Manual entry
cm
● CEM
Wind speed: U 23 m/s
Fetch: F 15 km
Shear coefficient: Cd 0.001905
Shear wind speed: U* 1.003865031 m/s
Wave height: Hs 162.12 cm
Time to formation of the emulsion: 30.7 min
Full time: 1086.4 min

***Figure 3**: User interface of the EMU model adapted for the CEM method. New entry fields in the yellow rectangle.*

***Slika 3:** Uporabniški vmesnik modela EMU prirejenega metodi CEM. Nova polja so v rumenem pravokotniku.*

Table 1*: Oil types and their properties (Fingas, 2010).*

Preglednica 1: *Uporabljene vrste nafte in njihove lastnosti (Fingas, 2010).*

	OIL PROPERTIES					
Oil type	**Density [g/mL]**	**Viscosity [mPa.s]**	**Saturates [%]**	**Resins [%]**	**Asphaltenes [%]**	**Asphaltene/resin ratio**
Cook Inlet – Granite Point	0.9028	75	62	7	3	0.43
BCF 24	0.9342	557	41	14	8	0.57
Catalytic Cracking Feed	0.9144	938	53	8	1	0.12
IFO 300	0.9859	14470	26	12	10	0.83

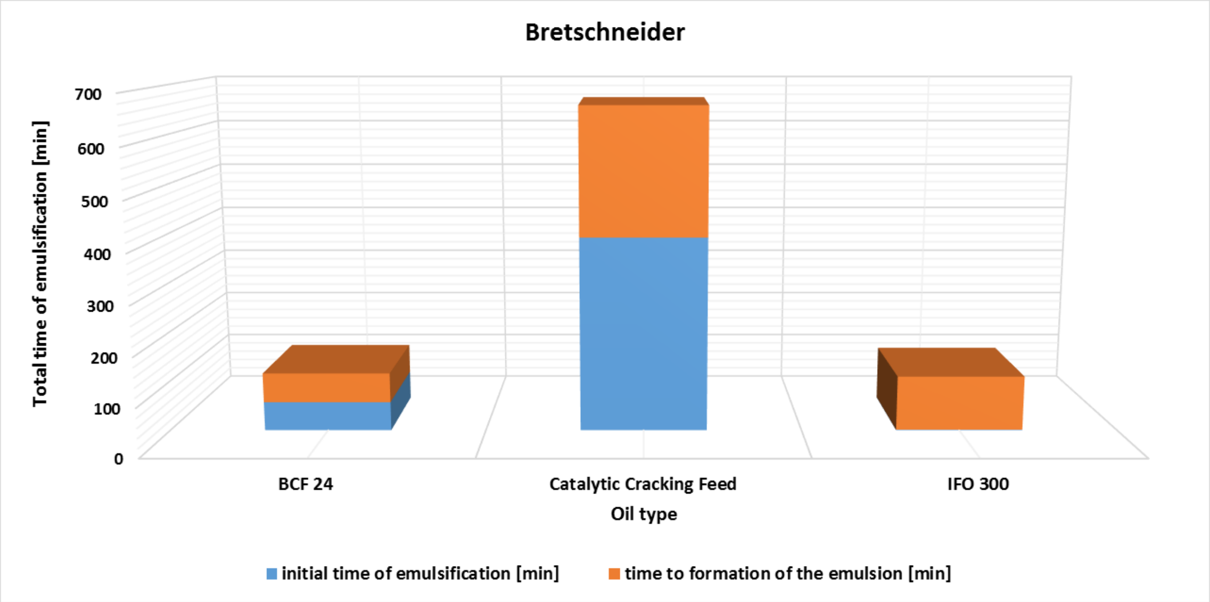


Figure 4*: The initial time of emulsification and the time to formation of emulsion for three oil types, using Bretschneider wave parameterisation (U=4 m/s, F=15 km, h=20 m and T=25˚C***).**

Slika 4: *Čas do začetka emulzifikacije in čas emulzifikacije za tri vrste nafte izračunan s parametrizacijo valov po metodi Bretschneider (U=4 m/s, F=15 km, h=20 m in T=25˚C).*

2.6.3 Case study B: Emulsification time computed using constant fetch

This case study was performed using constant environmental parameters: wind speed 4 m/s, fetch 15 km, depth 20 m and ambient temperature 25˚C. We compared the initial time, the formation time and the overall emulsification time for three oil types (Table 1): BCF 24, Catalytic Cracking Feed and IFO 300 using all wave parameterisations. The ratio between the initial time and the formation time for the three oils is evident from Figure 4. Oils with equal stability class have equal emulsification time in the same wave conditions, even though their initial viscosity, density and other properties may be significantly different. Therefore, the case studies were performed on oils with different stability class: BCF 24 forms a stable emulsion, Catalytic Cracking Feed forms a mesostable emulsion and IFO 300 converts into entrained water.

3. Results and discussion

3.1 Case study A – constant wind speed and variable fetch (Table 2 and Figure 5)

The highest waves were calculated using the Seck-Hong method (fetch below 13 km) and the Bretschneider method (fetch above 13 km). The CEM method gave the lowest waves in the entire range. The difference between the three SMB methods increases with fetch; it reaches up to 10% at a 20-km fetch. The opposite is valid for the minimum and maximum wave height: it exceeds 50% at 1-km fetch and decreases to approximately 30% at longer fetch lengths. Similarly, the difference between the emulsification time decreases with fetch: from 40% at 1 km to less than 10% at 15 km. It is evident that in high-wave conditions the emulsification time does not differ significantly regardless of the wave parameterisation method.

3.2 Case study B – constant fetch and variable wind speed (Table 3 and Figure 6)

Here, the highest waves were obtained with the Bretschneider parameterisation (except for U = 20 m/s, where the Seck-Hong method predicted higher waves). The lowest waves were calculated using the SMB – shallow equation for 10 m depth (up to 4 m/s) and the CEM method (5 m/s and above). The difference between the minimum and the maximum wave height decreases with wind speed, from 8 fold at 1 m/s to approximately 35% at 20 m/s. The differences in emulsification time also decrease with increasing wind, from an order of magnitude at 1 m/s to less than 10% at 14 m/s. Similarly to case study A, in high-wave conditions (above 1.5 m) the emulsification time is approximately equal regardless of the wave parameterisation.

3.3 Case study C – emulsification time for oils forming differently stable emulsions

Table 4 depicts the variability of emulsification time for three different oils with all described wave parameterisations. All environmental parameters in calculations were kept constant. We deliberately chose oil types with different characteristics, with regard to both the initial time and the formation time of emulsion. The initial time depends solely on oil properties and the ambient temperature, while the wave parameterisation has no impact (Eq. 2 and Eq. 3). The chosen oil types vary significantly with regard to the initial time: IFO 300 (light oil) evaporates extremely fast and begins to form the emulsion after 1 minute; BCF 24 (medium heavy) requires about one hour, while Catalytic Cracking Feed (heavy oil) begins to emulsify after more than 6 hours. Furthermore, the three chosen oil types form emulsions of different stabilities, which impacts the formation time of the emulsion through the parameters *a* and *b* in Eq. 4. None of the other oil properties is connected to the formation time. Wave energy, which depends on wave parameterisation, is the only additional parameter. Hence, oils forming emulsions of equal stability and exposed to the same wave energy have equal formation time of the emulsion.

The results in Table 4 reveal that the formation time is within the range of about 90% using all parameterisations, and the ratio between the initial time and the formation time is approximately equal for all chosen oils. Furthermore, one can determine the ratio between the initial time and the formation time for the chosen types of oil. It is evident that the wave parameterisation method is much more important with (very) light oils and fuels, which evaporate fast. The range of the total emulsification time is about 80% using different wave parameterisations. The medium and heavy oils have an approximately equal ratio between the initial time and the formation time. Therefore, the range of the total emulsification time using different parameterisations is also lower (within 30 – 40%).

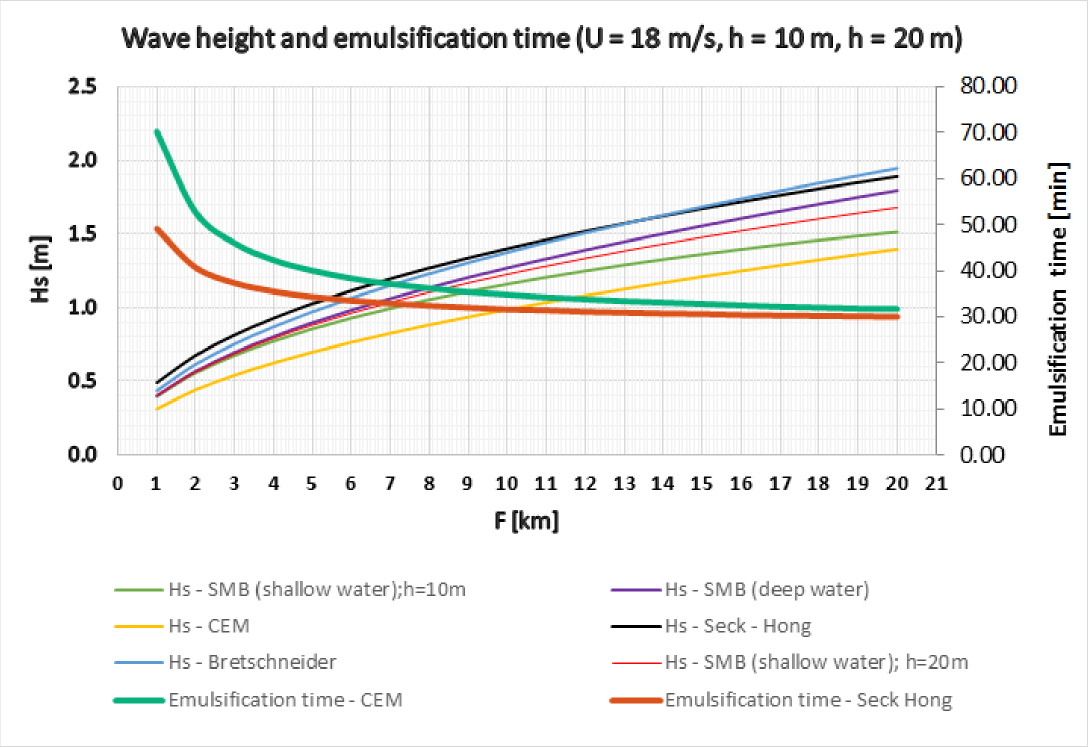


***Figure 5**: Wave height and emulsification time at constant wind speed (U=18 m/s) and variable fetch.*

***Slika 5:** Višina valovanja in čas emulzifikacije pri stalni hitrosti vetra (U=18 m/s) in spremenljivem privetrišču.*

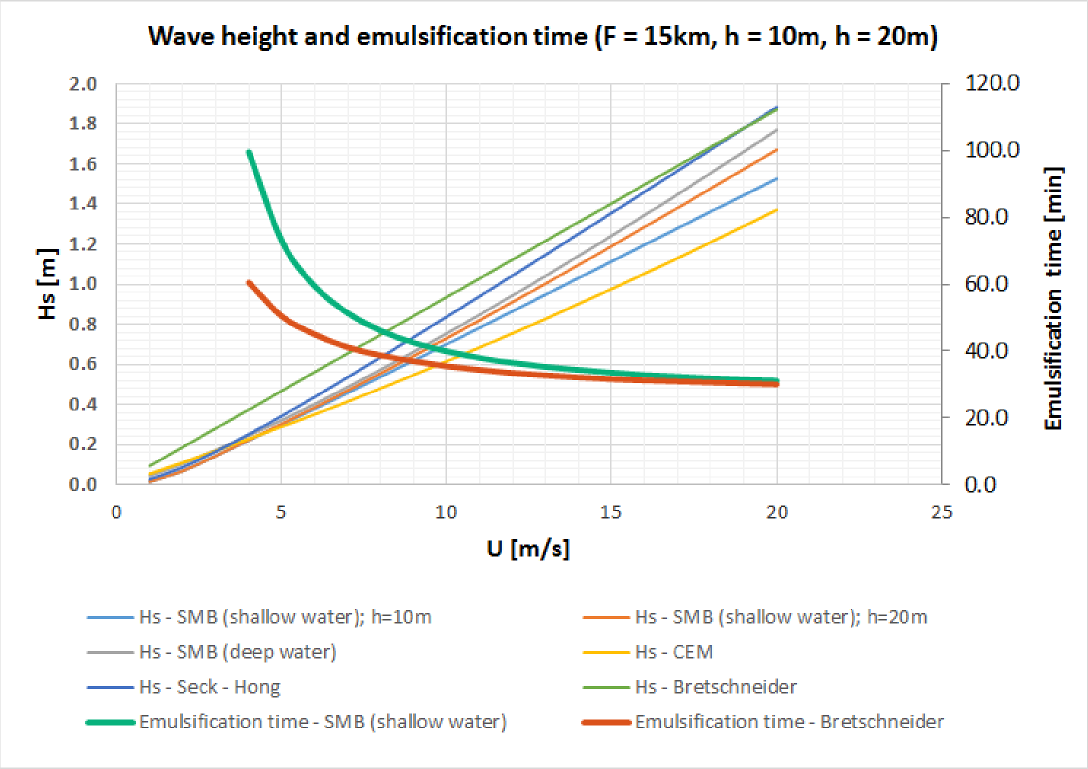


***Figure 6:** Wave height and emulsification time at constant fetch (F=15 km) and variable wind speed.*

***Slika 6:** Višina valovanja in čas emulzifikacije pri stalnem privetrišču (F=15 km) in spremenljivi hitrosti vetra.*

***Table 2**: Wave height using different wave parameterisations, and the emulsification time for the highest and lowest waves. Cook Inlet – Granite Point oil, constant wind speed 18 m/s, variable fetch.*

***Preglednica 2:** Višina valov pri različnih parametrizacijah valovanja in čas emulzifikacije za najnižje in najvišje valove. Nafta Cook Inlet – Granite Point, stalna hitrost vetra 18 m/s, spremenljivo privetrišče.*

U = 18 m/s	**Wave height**						**Time of emulsification [min]**	
	h = 10 m	**h = 20 m**	**/**	**/**	**/**	**/**		
Fetch [km]	**SMB (shallow water) [m]**	**SMB (shallow water) [m]**	**SMB (deep water) [m]**	**CEM [m]**	**Seck Hong [m]**	**Bretschneider [m]**	**minimum wave**	**maximum wave**
1	0.3973	0.3997	0.4014	**0.3122**	**0.4896**	0.4350	70.20	49.10
2	0.5566	0.5633	0.5676	**0.4415**	**0.6752**	0.6151	52.70	40.70
3	0.6753	0.6876	0.6952	**0.5407**	**0.8139**	0.7534	46.00	37.30
4	0.7727	0.7912	0.8027	**0.6244**	**0.9284**	0.8699	42.30	35.50
5	0.8561	0.8816	0.8975	**0.6981**	**1.0275**	0.9726	40.00	34.30
6	0.9295	0.9625	0.9831	**0.7647**	**1.1157**	1.0654	38.30	33.50
7	0.9951	1.0361	1.0619	**0.8260**	**1.1957**	1.1508	37.10	32.90
8	1.0546	1.1040	1.1352	**0.8830**	**1.2691**	1.2302	36.20	32.40
9	1.1089	1.1670	1.2041	**0.9366**	**1.3373**	1.3048	35.40	32.00
10	1.1590	1.2261	1.2692	**0.9872**	**1.4010**	1.3754	34.80	31.60
11	1.2054	1.2817	1.3311	**1.0354**	**1.4609**	1.4426	34.20	31.40
12	1.2486	1.3343	1.3903	**1.0814**	**1.5176**	1.5066	33.80	31.10
13	1.2889	1.3842	1.4471	**1.1256**	**1.5714**	1.5681	33.40	30.90
14	1.3268	1.4318	1.5017	**1.1681**	1.6227	**1.6273**	33.10	30.70
15	1.3624	1.4773	1.5544	**1.2091**	1.6718	**1.6844**	32.80	30.60
16	1.3959	1.5208	1.6054	**1.2487**	1.7188	**1.7397**	32.50	30.40
17	1.4277	1.5626	1.6548	**1.2872**	1.7640	**1.7932**	32.20	30.20
18	1.4577	1.6027	1.7028	**1.3245**	1.8075	**1.8452**	32.00	30.10
19	1.4862	1.6414	1.7495	**1.3608**	1.8496	**1.8958**	31.80	30.00
20	1.5133	1.6787	1.7949	**1.3961**	1.8902	**1.9451**	31.70	29.90

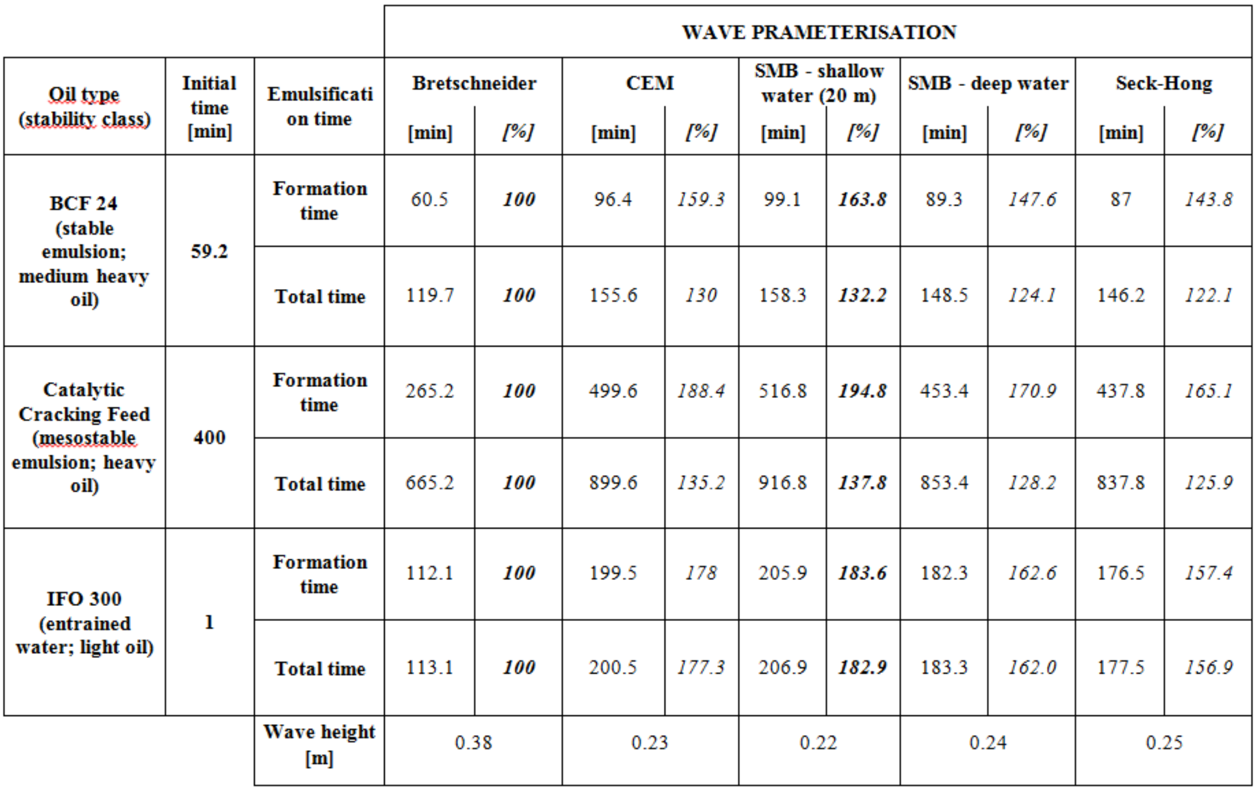
***Table 3**: Wave height using different wave parameterisations, and the emulsification time for the highest and lowest waves. Cook Inlet – Granite Point oil, constant fetch 15 km, variable wind speed.*

***Preglednica 3:** Višina valov pri različnih parametrizacijah valovanja in čas emulzifikacije za najnižje in najvišje valove. Nafta Cook Inlet – Granite Point, stalno privetrišče 15 km, spremenljiva hitrost vetra.*

F = 15 km	**Wave height**						**Time of emulsification [min]**	
	h = 10 m	**h = 20 m**	/	/	/	/		
Speed [m/s]	**SMB (shallow water) [m]**	**SMB (shallow water) [m]**	**SMB (deep water) [m]**	**CEM [m]**	**Seck Hong [m]**	**Bretschneider [m]**	**minimum wave**	**maximum wave**
1	**0.014**	0.014	0.044	0.054	0.026	**0.094**	4342.90	305.60
2	**0.069**	0.069	0.104	0.110	0.087	**0.187**	442.20	117.90
3	**0.143**	0.143	0.172	0.168	0.164	**0.281**	166.40	77.90
4	**0.221**	0.222	0.244	0.227	0.251	**0.374**	99.60	60.50
5	0.299	0.303	0.322	**0.289**	0.343	**0.468**	75.70	50.40
6	0.378	0.386	0.402	**0.351**	0.438	**0.561**	63.30	45.00
7	0.458	0.470	0.486	**0.415**	0.536	**0.655**	55.30	41.10
8	0.538	0.555	0.573	**0.480**	0.635	**0.749**	49.70	38.70
9	0.619	0.642	0.663	**0.547**	0.736	**0.842**	45.70	36.90
10	0.701	0.731	0.754	**0.615**	0.838	**0.936**	42.70	35.40
11	0.783	0.820	0.848	**0.685**	0.940	**1.029**	40.40	34.30
12	0.866	0.911	0.944	**0.756**	1.043	**1.123**	38.60	33.40
13	0.949	1.004	1.042	**0.828**	1.147	**1.217**	37.10	32.70
14	1.032	1.097	1.141	**0.902**	1.251	**1.310**	35.90	32.10
15	1.114	1.191	1.242	**0.977**	1.356	**1.404**	34.90	31.60
16	1.197	1.285	1.345	**1.053**	1.461	**1.497**	34.10	31.20
17	1.280	1.381	1.449	**1.130**	1.566	**1.591**	33.40	30.90
18	1.362	1.477	1.554	**1.209**	1.672	**1.684**	32.80	30.60
19	1.445	1.574	1.661	**1.289**	1.778	**1.778**	32.20	30.30
20	1.526	1.671	1.770	**1.370**	**1.884**	1.872	31.70	30.00

***Table 4**: Calculation and comparison of the emulsification times of 3 oil types, using all wave parameterisations (U = 4 m/s; F=15 km; T = 25°C).*

***Preglednica 4:** Račun in primerjava časov emulzifikacije za 3 vrste nafte z vsemi parametrizacijami vetra (U = 4 m/s; F = 15 km; T = 25°C).*



			WAVE PRAMETERISATION									
Oil type (stability class)	**Initial time [min]**	**Emulsification time**	**Bretschneider**		**CEM**		**SMB - shallow water (20 m)**		**SMB - deep water**		**Seck-Hong**	
			[min]	***[%]***	**[min]**	***[%]***	**[min]**	***[%]***	**[min]**	***[%]***	**[min]**	***[%]***
BCF 24 (stable emulsion; medium heavy oil)	**59.2**	**Formation time**	60.5	***100***	96.4	*159.3*	99.1	***163.8***	89.3	*147.6*	87	*143.8*
		Total time	119.7	***100***	155.6	*130*	158.3	***132.2***	148.5	*124.1*	146.2	*122.1*
Catalytic Cracking Feed (mesostable emulsion; heavy oil)	**400**	**Formation time**	265.2	***100***	499.6	*188.4*	516.8	***194.8***	453.4	*170.9*	437.8	*165.1*
		Total time	665.2	***100***	899.6	*135.2*	916.8	***137.8***	853.4	*128.2*	837.8	*125.9*
IFO 300 (entrained water; light oil)	**1**	**Formation time**	112.1	***100***	199.5	*178*	205.9	***183.6***	182.3	*162.6*	176.5	*157.4*
		Total time	113.1	***100***	200.5	*177.3*	206.9	***182.9***	183.3	*162.0*	177.5	*156.9*
		Wave height [m]	0.38		0.23		0.22		0.24		0.25	

4. Conclusions

Apart from oil type and its properties, correct prediction of wave height is crucial for defining the emulsification time. The differences between the parameterisation methods are undoubtedly important. It is evident from Tables 2 and 3 that particularly in low-wave conditions the emulsification time calculated using various approximate wave parameterisations differs even by an order of magnitude. The disagreement decreases with wave height and is below 10% at waves higher than 1.5 m. A similar conclusion can be reached for different oil types, where the discrepancies between emulsification time reach 30% to 80% and are higher with light oils.

The empirical equations presented in this paper are not accurate; therefore, the presented results must be thoroughly compared to the results of wave measurements (e.g. at the existing buoys in the Gulf of Trieste: Vida, Zora and Zarja), as well as to the results of the state-of-the-art wave models (SWAN for the coastal area and WAM for the open sea). Only in this way will it be possible to determine which parameterisation should be used in such simple emulsification models. Furthermore, it is very likely that different parameterisations need to be used in different areas; e.g., the equation that best fits in the Gulf of Trieste or even in a certain part of it is not necessarily the most appropriate for other areas in the Adriatic Sea.

Despite the use of empirical equations and the demonstrated drawbacks in calculation of the formation time, the EMU model can already serve to predict the approximate emulsification time and as such to help in the oil-spill clean-up and remediation processes. Furthermore, it can serve as a valuable tool for quick determination of the emulsion stability and the initial time before the emulsification begins, when removal of oil from the water surface is relatively easy to perform.

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