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Separation Of Water-In-Oil Emulsions By Freeze/Thaw Method And Microwave Radiation

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ABSTRACT

In this paper, the demulsification has been achieved with the use of freeze/thaw (F/T) method and microwave radiation (MWR). The object of investigation were emulsion samples prepared by mixing the metal-working-oil, FESOL 09, produced by FAM, Krusevac, Serbia, and deionized water. F/T method has been successfully applied for the removal of oil from emulsions in our previous work. In this work, MWR has been additionally used for separation and enhanced heating of emulsion samples. The efficiency of oil removal has been improved with the assistance of MWR, up to 90%.

Keywords : freeze/thaw, emulsion, Freezing , deionized, demulsification

1. Introduction

Demulsification is a process of oil and water (o/w) separation from emulsions .Typical demulsification techniques include thermal, electrical, chemical, acoustic, or mechanical methods. Recently, in the work of Chen and He, freeze/thaw method (F/T) forwater removal from water -in-oil emulsionswastested and introduced as effective demulsification method, with nearly 90% of water removal from w/o emulsion. They have used oily sludges as emulsion samples that were treated with F/T method. According to their experimental results the optimal freezing temperature was around −40 ◦C and demulsificationis achieved due to expelling of surfactant molecules from ice lattice during freezing and forming of surfactant micells during thawing. In procedure proposed in this work, emulsion samples have been separated with the combined use of F/T and MWR. MWR has also been exploited for demulsification as an alternative method for the separation, with promising results, obtained by Xia et al. They have proved that MWR is a very effective method for demulsification of o/w emulsion. They compared the results performed in an oil-bath or microwave oven and samples treated with MWR have improved the demulsification rateby an order of magnitude .MWR destabilizes emulsions in several ways: with high temperature and by selective absorption of MW energy by surfactant and oil molecules, rather thenice, which is known as having low loss factor for MW. Higher temperature reduces the continuous phase viscosity and breaks the outer film of the drops, thus allowing the coalescence If absorption of MW by surfactants results in faster thawing, it also continues with surfactant molecules that take some oil molecules with them, too. It may be assumed that all mentioned effects from MWR enhance separation and result in emulsion breaking. In this paper combination of both, F/T and MWR, has been used for separation of oil from o/w emulsions. This combination of alternative demulsification methods has proved to be more effective then F/T method alone . F/T and MWR, are both non-destructive, physical methods, that don't demand addition of chemical agents, which implies that there is no further waste water treament. In other words, the methods used are in accordance with "green chemistry" demands.

2. Experimental

2.1. Sample preparation

The object of investigation in this paper were emulsion samples that have been prepared by mixing the commercially available metal-working-oils FESOL 09 produced by FAM, Kruˇsevac, and deionized water. The demulsification has been investigated on the samples with the following oil content: 0.1, 1.0, 3.0, 5.0, 10.0 and 30.0%. For all the emulsion samples the preparation procedure was the same: the volume of oil has been measured with the pipette (±0.1 cm3) and put in a normal flask 100.0 cm3 (±0.1 cm3). Samples with low oil concentration have been prepared by measuring oil on analytical balance, with the precision of±0.1 mg. The concentration of all samples has been labelled with %; it signifies (v/v) percentage. The experiments have been repeated five times and the results are a mean value of each result obtained, for all the procedures and steps.

2.2. Demulsification procedure

The demulsification experiments were performed by the use of an ultrafreezer, at three chosen temperatures (−20, −40 or −60 ◦C) for 30 h (in total, 10 h +10 h +10 h, each sample three times) before thawed in air (20 ◦C), water-bath (40 ◦C) or microwave oven (at 95 ◦C and 800W at 2450 MHz). For the determination of oil concentration, before and after the treatment, several methods have been used: gravimetric, volumetric (COD, BOD), optic (FTIR and measurement of the refraction index), electroanalitical methods (pH and conductivity measurements). In Table 1 the list of all the methods used for the determination of quality parameters of emulsions is presentedm. For the low oil concentrations, less then 1%, FTIR method has been applied (with the precision of ±0.1%). For the oil concentrations from 1.0 to 30.0% the DIN 51368 method has been applied. This method is being performed with the use of special graduated flask for the oil content determination (up to 30.0%) in emulsions (with the precision from ±0.1% when the oil content is from 0 to 5.0% and with\ the precision of ±0.5% when the oil content is from 5.0 to 30.0%) [8]. The oil concentration in each sample, before and after the treatment and separation, has been determined according to the sensitivity range of each, which has been described in previous work [6]. One of the diagrams obtained for examined oil, for determination of oil in water is shown in Fig. 1. Although COD belongs to classicmethods, the relation between oil concentration obtained for low oil concentrations (below 5%, the percentage typical for waste water emulsions in nature) is directly proportional and can be applied for oil determination in water, since the coefficient of linear correlation is 2393, as shown in Fig. 1.

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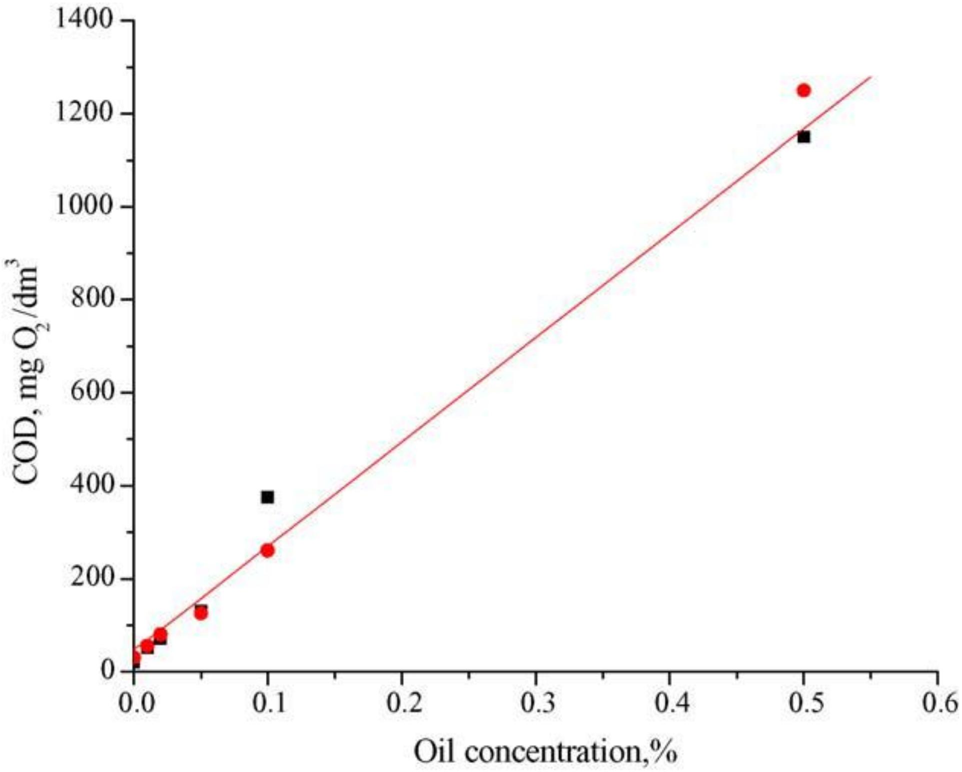

3. Results and discussion

3.1. Optimal F/T parameters

The optimal freezing temperature, as one of the keyparameteres, has been determined and it has been found that the optimal demulsification has been achieved at −40 ◦C. The optimal temperature for the separation is not the lowest temperature (−60 ◦C) tested, as expected, but it is the temperature that enhances all the processes that happen during the demulsification
(−40 ◦C) process. Beside temperature, the parameter that needs to be optimized is freezing time. It takes 20 h for all samples to freeze and reach the constant value of oil removal,
after this period of freezing. This long time is necessary because the inner part of emulsion has to be completely frozen andsurfactants expelled from the ice lattices, parallely with new
micelles forming

3.2. Effect of thawing procedure and rate

The efficiency of oil removal, from 3.0% emulsion samples, compared on thawing procedure, is shown in Table 2. The efficiency of the oil removal for the oil concentration from 1.0
to 30.0% can be expressed as: _*V* (%) = [(*V*in −*V*ter)/*V*in]100 where: *V*in is the inital volume of oil, before the treatment, *V*ter the volume of oil, after the treatment, and *V*in–Vterthe volume of oil left after the treatment. For the oil concentration less then 1.0%

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the concentration, *c*, is expressed in mg/dm3 and it was used instead of the (v/v) percent. The experiments have been repeated five times and the results are a mean value of each result obtained, for all the procedures and steps. All the samples were placed in an ultrafreezer at −40 ◦C temperature, for 10 h, repeating the process three times. The first set of emulsion
samples have been left at 20 ◦C for 5 h in ambient air. The second set of emulsions, was left for 5 h in water bath at 40 ◦C. The third set of emulsions, was placed in microwave oven, for
3.5 minutes. Freezing and thawing was repeated three times, as shown in Table 2. Comparing thawing procedure the efficiency of oil removal has an unexpected order. The highest efficiency is reached when MWR is applied, as expected, but the efficiency of water bath is lower then thawing in air. When thawing rate is slow, the time allowing the surfactant to form new hydrophobic micelles in oil phase and to migrate away from the water-oil interface is longer. In that way, more water can be removed. If thawing rate is fast, less surfactant can move from the interface, less hydrophobic micells that tahke oil with them can form.. With MWR the demulsification is the most effective. The key advantage of non-classical energy input by MWR over classical heating methods is the way in which the energy is introduced via radiation instead of heat transfer and convection. By means of MWR, more molecules become energized, resulting in superheating and higher reaction rates [9]. It is also assumed that exceptional MWR performance may derive from absorption of MW energy by surfactant and oil molecules rather then the ice,which is known to have low loss factor for MW. Even if surfactant molecules are more lossy, thawing will occur first with surfactant molecules, that take some oil molecules with them, and form hydrophobic micells of surfactant, that enhance separation. The microwave radiation process increases both the speed
and efficiency of the demulsification. It is the most efficient thawing procedure. In Fig. 2, the experimental scheme for F/T and MWR assisted demulsification process is shown.

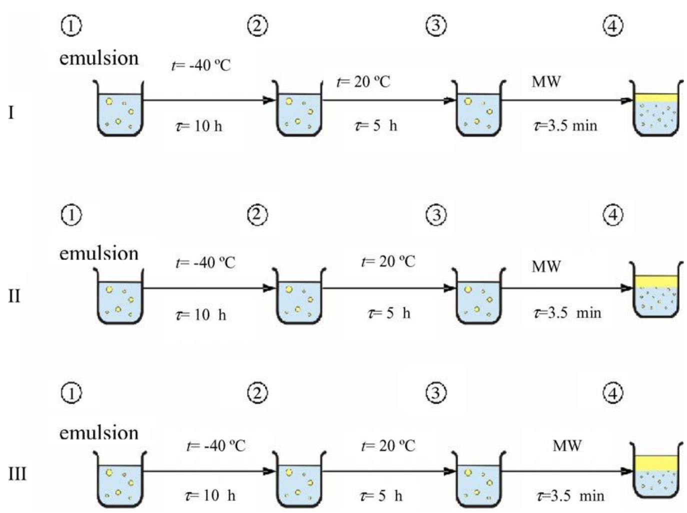

Fig. 2. The scheme of experimental procedure for F/T and MWR assisted demulsification process.

3.3. Oil and water quality after the demulsification

As mentioned before, there are some small water droplets in the separated oil, as well as there are some organics present in the removed water after F/T and MW assisted demulsification Process . After the removal of oil from emulsions the content of oil in treated water samples has been detected with different Fig. 2.instrumental techniques. For the 3.0% emulsions, before and after the demulsification, the refractive index measurements has been the most suitable analysing tool.

4. Conclusion

The efficiency of demulsification based on F/T and MWR assisted process depends on the initial oil content, freezing temperature, freezing time and thawing procedure. When MWR is applied molecules become energized, resulting in superheating and higher reaction rates. The microwave radiation process increases both the speed and efficiency of the demulsification. It is the most efficient procedure, considering the thawing procedure used in our experimental set-up. The water collected contains some organic materials. The content of oil left out demulsification process can be successfully determined with several methods, such as classic: chemical oxygen demand determination, and instrumental: refractive index measurements and FTIR measurements. For o/w emulsions up to 30% the efficiency of oil removal was above 90%.

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