Destabilization and Recuperability of Oil Used in the Formulation of Concentrated Emulsions and Cutting Fluids

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Lubricants known as cutting fluids are used in the metal-mechanic industry with the function of cooling and lubricating the cutting zone. These lubricants normally have a water phase, an oil phase, emulsifying agents and additives. Once the operational capacity of these fluids has ceased, either due to biological deterioration or to overabundance of contaminants, the emulsions being used must be treated in order to adequate their effluents for discharge. This study aims to evaluate the destabilization process and recuperability of the oil used in the formulation of concentrated emulsions and cutting fluids. For this purpose, the following destabilizing factors were tested: temperature, centrifugation speed, and concentration of inorganic salts. The optimization of the process with concentrated emulsion allowed for the following most adequate condition of demulsification: temperature of $\vartheta = 70$ °C, centrifugation of 2000 rpm, and salt concentration of $\gamma = 2000$ g L^{-1}. As for the cutting fluids, the conditions were less severe, with salt concentration around $\gamma = 50$ g L^{-1}, and temperature of $\vartheta = 50$ °C. FTIR technique was used to determine the concentration of emulsifying agents used in the preparation of concentrated emulsions. This procedure was not carried out for the cutting fluid due to the diversity of substances present in its composition derived from the additives that either make it difficult or prevent the identification of the peaks shown in the FTIR spectra.

Key words:
O/W emulsion, cutting fluids, demulsification, recuperability, turbidity

Introduction

Cutting fluids, also known as cutting oils (or metalworking fluids), are a class of lubricants used in metal cutting operations, such as: turning, drilling, tapping, reaming, milling, sawing.[1] Besides the primary functions of cooling and lubricating the parts-tools system, cutting fluids are important to improve the finish of the milled surface, reduce the efforts in cutting, and remove the scrap through washing. Being of an emulsive type, these fluids are composed of an oil phase, a water phase, an emulsifying agent and additives.[2] Anticorrosive, antioxidant and bactericide additives are used more often.

The final discharge of cutting fluids raises great environmental concerns,[3,4] mainly because inadequate discharge may cause serious problems due to the richness of oxygenate products and polyaromatics formed during heating to which the fluids are submitted while being used. The most environmentally adequate solution consists of the recovery of the basic oil that was used.[5] For this purpose, the cutting fluid (emulsion) needs to be treated for recycling its components through a process called demulsification.[6,7]

The classic demulsification operations cause destruction of the emulsifying film and the coalescence of the oil drops. Chemical and physical methods can be found in the literature and may be used either individually or in combination.[8,9,10] The chemical methods involve the addition of demulsifiers (salts and acids) that affect the interfacial properties of the adsorbed surface and increase the coalescence rate of the dispersed drops.[11] The physical methods, on the other hand, use temperature or electric field and act to increase the frequency of contact between the dispersed drops, and then cause the separation of the phases.[12]

In this context, the main objective of this study was to evaluate viable ways of demulsification of concentrated emulsions and of cutting fluids aiming at a later recovery of the oil used.

Turbidimetric technique has very often been used to follow up the destabilization of emulsions, mainly because the turbidity of a solution can be related to the concentration of particles dispersed in it. Following the destabilization of the emulsion,

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the number of oil drops tends to decrease. Consequently, the value of turbidity will also decrease with time.[13] Deluhery and Rajagopalan[14] have recently published a study about the applicability of a turbidimetric method, using a spectrophotometer, to evaluate the stability of a metalworking fluid emulsion. In that study, the reading of turbidity in the samples was carried out after the addition of calcium chloride solution (29 to $200 \cdot 10^{-6}$), in wavelength ranging between $\lambda = 400$ and 500 nm for a period of $t = 10$ min. Based on the variation of the exponent of the wavelength with time, the results showed that below $\gamma = 72.5$ mg L^{-1} of calcium chloride the emulsion is stable. In the same context, Coca *et al.*[15] proposed the study of destabilization of three types of cutting fluids using as demulsifying agent calcium chloride and aluminum chloride salts in concentrations between $\gamma = 5-40$ g L^{-1}, and temperatures of $\vartheta = 40$, 50 and 60 °C. The variation of turbidity with time indicates that there is no difference in the behavior observed with $CaCl_2$ and $AlCl_3$. Measurement of turbidity has also been used to evaluate the stability of the W/O type of emulsions (water in oil) through a method known as the *turbidity ratio method*, based on the turbidity ratio (R) in two wavelengths ($\lambda = 850$ and 450 nm) for $t = 50$ min. The inclination of the R curve with time is used as an indication of emulsion stability.[16]

Experimental

Materials and equipments

Naphthenic mineral oil, kindly supplied by Lubrificantes e Derivados de Petróleo do Nordeste (LUBNOR/PETROBRAS), was used as the oil phase for the preparation of concentrated emulsions and cutting fluids. The main properties of the sample we used are listed in Table 1. The non-ionic surfactants sorbitan monolaurate (Span 20), sorbitan monooleate (Span 80), polyoxyethylene (20) sorbitan monolaurate (Tween 20), and polyoxyethylene (20) sorbitan monooleate (Tween 80) from Sigma Aldrich were used to prepare the blends studied. All materials were used as received. The combinations of surfactants in each of the selected emulsions were as follows: A. Tween 20/Span 20 (T20/S20, HLB = 12 blend) emulsifying blend; B. Tween 40/Span 80 (T40/S80, HLB = 10 blend) emulsifying blend. The concentrated emulsions, as previously formulated by De Lima,[17] were composed of $w = 56.3$ % water, $w = 38.6$ % oil, and $w = 5.1$ % emulsifying blend. The emulsions were prepared by incorporating the emulsifying agent into the oil phase, followed by the addition of the resulting mixture to the water phase in the following preparation conditions: temperature of $\vartheta = 70$ °C, mixing

Table 1 – *Physicochemical characterization of the naphtenic mineral oil*

Characteristic	Method	Result	Unit
aspect	VISOOO	Clear and bright	
color	ASTM D1500	L0.5	
kinematic viscosity at 40 °C	ASTM D445	21.14	mm^2 s^{-1}
kinematic viscosity at 100 °C	ASTM D445	3.61	mm^2 s^{-1}
total acidity	ASTM D974	0.01	mg g^{-1} KOH
ash fraction	ASTM D482	< 0.001	w/%
Ramsbotton carbon	ASTM D524	0.05	w/%
copper corrosion 3H 100°C	ASTM D130	1b	
relative density	ASTM D4052	0.9023	
sulfur fraction	ASTM D4294	0.0580	w/%
aniline temperature point	ASTM D611	71.0	ϑ/°C
water fraction	ASTM D1744	71	w/%
refractive index at 20 °C	ASTM D1218	1.4974	
aromatic carbon	ASTM D3238	14.1	w/%
naphtenic carbon	ASTM D3238	40.1	w/%
paraffinic carbon	ASTM D3238	45.9	w/%
cloud point	ASTM D97	−45	ϑ/°C
pour point	ASTM D92	164	ϑ/°C

rate of 800 rpm for a period of $t = 5$ min. The cutting fluid was formulated with commercial products supplied by Clariant® Brasil – Funtional Chemicals Division, being one of them of the emulsifying agent type (ethoxyl fatty acid with 7 moles of ethylene oxide), another composed of the mixture of emulsifying agent and corrosion inhibitor (combination of sodium sulfonate and an alkanolamine of a fatty acid), and finally a bactericide product (mixture of benzothiazolinone and hexahydrotriazine). In its concentrated form (oil and additives), this fluid was composed of 17 % mixture of emulsifying agent and corrosion inhibitor, $w = 2$ % biocide, and $w = 81$ % oil. The ratio of preparation of this fluid was of $\Psi = 25 : 1$ (water/additive oil). Commercial sodium chloride supplied by Marlin was used as demulsifying agent.

The measurements of turbidity of the water phase were carried out using a micro processed turbidimeter model DLM-2000B required for turbidity measurement up to 1000 NTU.

The oil phase (initial and recuperated) was characterized with the infrared spectroscopy technique with Fourier technique using a BIO-RAD FAX–3000 FTIR (fourier transform infrared spectroscopy) spectrophotometer, equipped with a DTGS detector. The sweeping band used was $\nu = 400$ and 4000 cm^{-1} with spectral resolution of $\nu = 4.0$ cm^{-1}.

The tests of physical-chemical characterization of the oils were carried out following the *American Society for Test Materials* – ASTM standard procedures.

The characterization of the size and dispersion of the emulsion drops was carried out in an Olympus optical microscope model CH30 with automatic exposition system for micrography model PM-10AK3 (400x). The photomicrography analyses were carried out both at 1 h and at 24 h after the formulation.

Experimental procedure

In this work, evaluated were the emulsion destabilization processes and divided into two different parts. In the first one, the parameters that can cause phase separation of emulsionable systems containing naphtenic mineral oil were investigated in concentrated emulsions. In the second part, the same thing was done but using cutting fluids instead of the emulsions.

It should be noticed that the composition is an important difference between the emulsions concentrated and cutting fluids studied. In general, emulsions contain a water phase, an oil phase and emulsifying agents. On the other hand, cutting fluid also contains surfactants and a diversity of substances like anticorrosive and biocide compounds that make its composition more complex. This means, the processes of destabilization of concentrated emulsion were the scientific basis for studies of recuperability of the oil used on the formulation of cutting fluids.

Demulsification process of emulsions and cutting fluids was carried out in the presence of destabilizing factors of temperature, centrifugation, and the presence of electrolyte (salt solution). The typical procedure involves the addition of salt solution to the emulsion phase in which the separation is to occur, followed by heating for five minutes at investigated temperature. Following centrifugation the water phase was analyzed by turbidometry.

Results and discussions

Destabilization methodology of concentrate emulsions

The influence of temperature on destabilizing the emulsions was tested by heating at $\vartheta = 40$, 50 and 60 °C for a period of $t = 30$ min. No modification in the system was observed. Likewise, it was possible to verify the effect of centrifugation on the studied emulsions, submitted to three rotation speeds (1000, 2000 and 3000 rpm). Once more, no phase separation was observed. A third test of destabilization was performed by the addition of salt solution at room temperature, as follows. The experiments were carried out for a fixed volumetric proportion of emulsion/salt solution of $\Psi = 1 : 1$, and the influence of adding different concentrations of salt could then be noticed. The option was for using commercial sodium chloride because it could easily be found and was more economically viable. The initial tests, at low concentrations ($\gamma = 0.05$ to 0.8 g L^{-1}), showed to be very inefficient. Higher concentrations of NaCl ($\gamma = 50$, 100, 150 and 200 g L^{-1}) were then tested. The obtained results show that only in the case when the emulsion in contact with 200 g L^{-1} NaCl solution present in the oil phase separate in 24 h after mixing. The amount of oil separated from the emulsion was much lower than the initial volume of oil added to the formulation (< 5 %).

In view of these results, the destabilizing parameters of salt concentration, temperature and centrifugation were studied simultaneously, aiming to obtain the most adequate demulsifying condition.

The evaluation of the influence of operational parameters of demulsification was initially carried out by fixing a concentration of NaCl at $\gamma = 200$ g L^{-1} and by varying the levels of temperature ($\vartheta = 50$ and 70 °C), and centrifugation (500, 1000, 2000 and 3000 rpm). Figs. 1 and 2 show the variation of

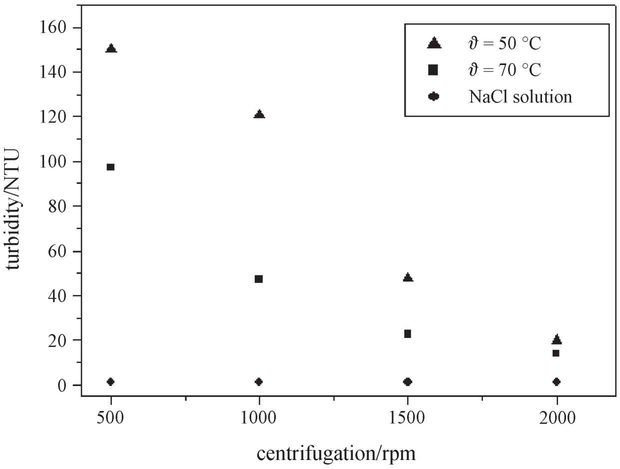


Fig. 1 – *Demulsification of concentrate emulsion prepared with blend T20/S20 (emulsion A). Sodium chloride concentration of* $\gamma = 200$ *g* L^{-1}.

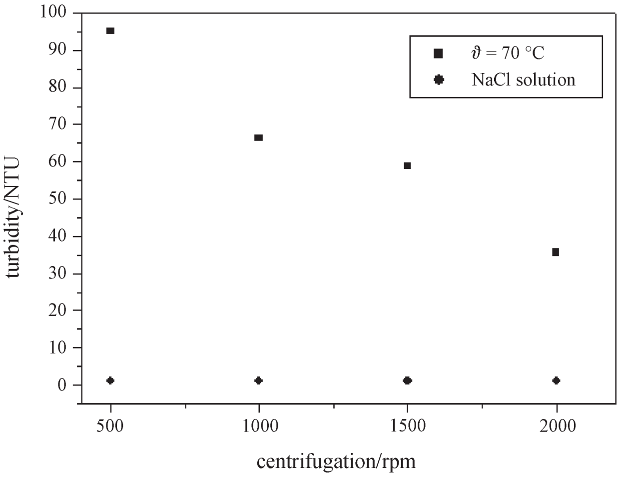


Fig. 2 – *Demulsification of concentrate emulsion prepared with blend T40/S80 (emulsion B). Sodium chloride concentration of* $\gamma = 200$ *g* L^{-1}.

turbidity of the bottom water phase with the centrifugation of the emulsions A and B, respectively, in the different selected temperatures.

As observed in the previous figures, the increase in the mixing rate causes a decrease in the turbidity of the analyzed systems. For emulsion A it is clear that at the temperature of 70 °C the values of turbidity are lower than those observed at 50 °C under the same centrifugation conditions. As for the process of destabilization of emulsion B at 50 °C, it was not possible to identify a variation of turbidity of the bottom water phase, mainly due to the emulsive aspect of the system, which characterized the absence of complete separation of the mixed phases.

Using the optimized conditions of rotation and temperature (2000 rpm and $\vartheta = 70$ °C), concentrations lower than $\gamma = 200$ g L^{-1} still capable of producing good results for destabilization of the emulsion were investigated. This is important due to economic aspects and mainly because of the environmental impact related to the demulsifying process. Fig. 3 shows the variation of turbidity with concentration of NaCl for emulsions A and B destabilized according to the operational conditions at $\vartheta = 70$ °C and 2000 rpm. According to the results presented on Fig. 3 that the most adequate concentration of salt solution for the destabilization and recovery of the used oil needed to reach the lowest turbidity is $\gamma = 200$ g L^{-1}.

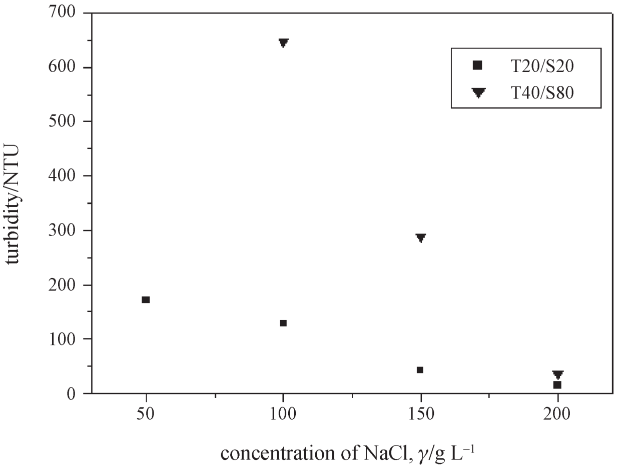


Fig. 3 – *Demulsification of concentrated emulsions A and B at* $\vartheta = 70$ *°C and mixing rate of 2000 rpm*

Fig. 4 shows the general profile of recovery of the mineral oil from the initially formulated emulsions, clearly indicating a bigger recovery for the demulsified oils from the blend composed by the Tween 40 and Span 80 (T40/S80) surfactants. This is mainly due to the greater stability determined by the Tween 20 and Span 20 emulsifying blend, in which it is more difficult to break the emulsifying film that is formed around the drops. The results obtained are considered very promising for this type of application.

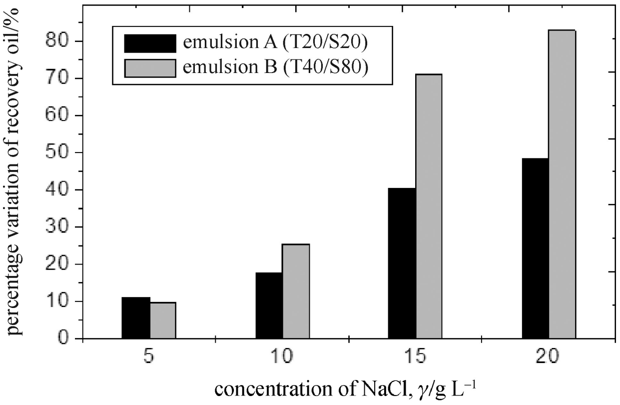


Fig. 4 – *Percentage variation of recovery oil with sodium chloride concentration*

Physico-chemical characterization of initial and recovery oil samples

The results of the physical-chemical characterization of the recovered oil were compared to the properties of the starting oil (Table 2).

The results show that the oil recovered with the optimized operational conditions (70 ° C, 2000 rpm and 200 g L^{-1} of NaCl) presents characteristics very similar to those of the initial oil. This is very interesting from the viewpoint of the industrial applications of these emulsive systems. Infrared spectra of the recovered samples of naphthenic oil were also checked (Fig. 5). In each spectrum the highlighted values refer to integrated area of the carbonyl band (functional group with the chemical structure of the surfactants used).

FTIR spectra indicate the presence of surfactants in the recovered oil. Tables 3 and 4 show the values of the carbonyl band area and of the percentage of blend quantified from the samples of recovered oil with concentrations of tested NaCl (γ = 50, 100, 150 and 200 g L^{-1}). The results of blend percentage were obtained through curves of calibration for each emulsifying blend used.

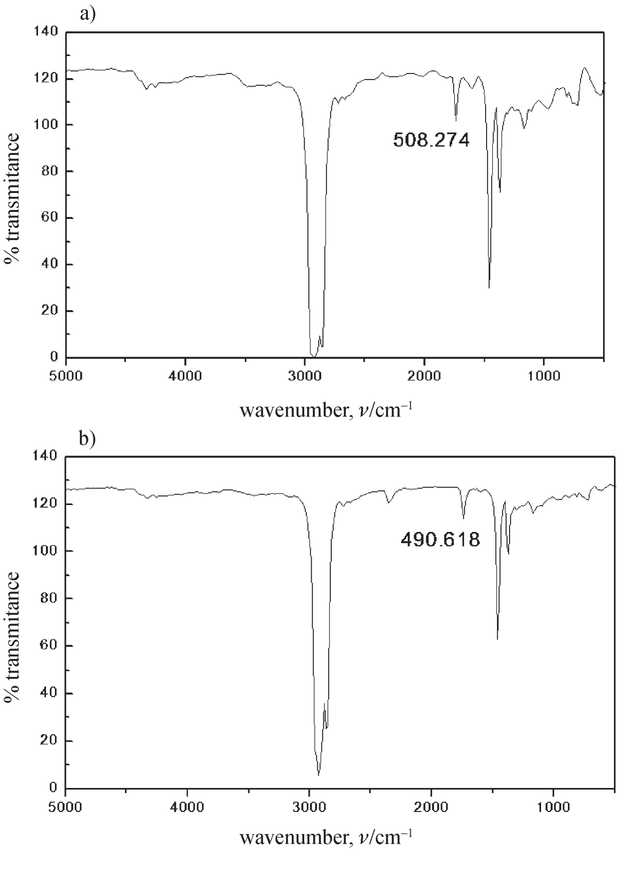


Fig. 5 – *FTIR spectrum of samples of recovery oil of concentrate emulsions A and B. Destabilization conditions: ϑ = 70 °C, 2000 rpm, and γ = 200 g L^{-1} of sodium chloride.*

Table 2 – *Physicochemical characterization of recovery and initial oil*

Characteristic	Recovery oil (emulsion A – T20/S20)	Recovery oil (emulsion B – T40/S80)	Initial mineral oil
kinematic viscosity 40 °C/mm^2 s^{-1}	22.404	22.467	20.736
kinematic viscosity 100 °C/mm^2 s^{-1}	4.490	4.507	4.300
relative density 20 °C	0.907	0.906	0.901
refraction index	1.491	1.490	1.493

Table 3 – *Integrated area of carbonyl band of the samples of recovery oil and of the emulsions A and B in different concentrations of sodium chloride*

Sodium chloride concentration γ/g L^{-1}	Integrated area of carbonyl band (C = O)	
	recovery oil (emulsion A – T20/S20)	recovery oil (emulsion B – T40/S80)
50	244.606	217.893
100	392.187	535.160
150	375.319	409.501
200	508.274	490.618

Table 4 – *Percentage of blend surfactants present in the recovery oil*

Sodium chloride concentration γ/g L^{-1}	Percentage of blend surfactants, %	
	recovery oil (emulsion A – T20/S20)	recovery oil (emulsion B – T40/S80)
50	2.54	0.74
100	4.04	2.78
150	3.86	1.98
200	5.22	2.50

The percentage of blend present in the original emulsion sample in relation to the quantity of oil was w = 13.2 %. However, as the re-utilization of oil was one of the main objectives of the study on recoverability, the presence of surfactants did not present problems regarding the formulation of emulsion with recovered oil.

O/W emulsion formulation with used mineral oil

According to the optimal conditions described previously (70 °C, 2000 rpm and 200 g L^{-1}), the recovered oil was used to re-formulate the emulsion. The stability of the emulsions was evaluated through optical microscopy. These tests were carried out after 1 h and 24 h, beginning at the moment of formulation of the emulsions. Fig. 6 shows the photomicrography of the emulsions prepared with recovered oil. It should be noted that the emulsion prepared with T20/S20 blend presents uniform aspect regarding the distribution of the drops, while the emulsion with T40/S80 presents an increase in the size of the drops after 24 h, causing physical-chemical changes in the system. Phase separation in the form of oil on the surface of the emulsions was macroscopically observed in a period of 48 hours after the formulation.

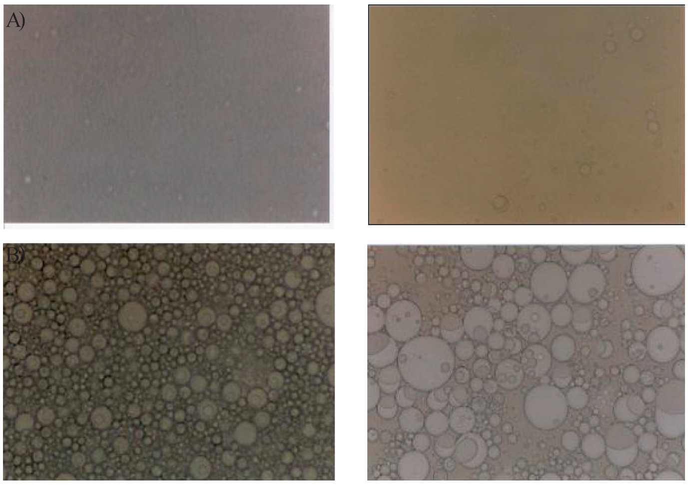


Fig. 6 – *Photomicrography of emulsions A and B prepared with recovery oil*

Recuperability of used oil in the formulation of cutting fluids

The study of the cutting fluids demulsification was carried out through the following destabilizing factors: temperature and presence of electrolyte (salt solution). It should be noted that in this case, unlike concentrated emulsion, the use of mixing rate was not necessary, due to the rapid evolution of the demulsification process. Therefore, the concentrations of electrolyte (sodium chloride) tested were γ = 15, 25, 35 and 50 g L^{-1}, at temperatures of ϑ = 25 and 50 °C at a constant level of centrifugation at 1500 rpm.

The variation of turbidity with relation to the concentration of salt at the temperatures of 25 and 50 °C is shown in Fig. 7. It can be seen that the turbidity at 50 °C presents values lower than those obtained at 25 °C, indicating a better profile of phase separation. During the reading of turbidity, it was not possible to analyze the sample with addition of γ = 15 g L^{-1} of NaCl at 25 °C, since the bottom phase presented an emulsion aspect with turbidity value above 1000 NTU, which is the limit of the equipment being used.

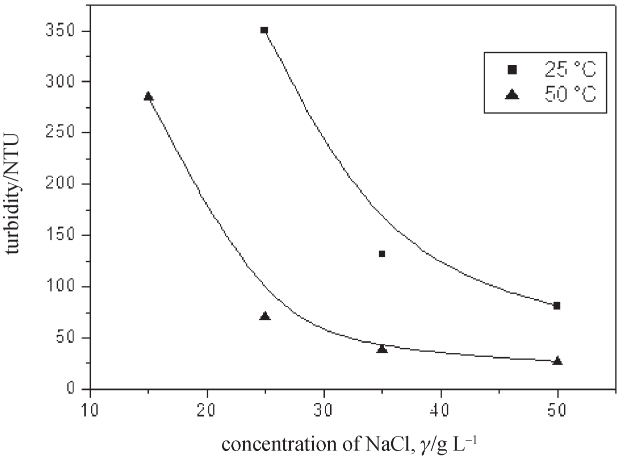


Fig. 7 – *Effect of salt concentration and temperature on the demulsification process of cutting fluids*

The percentages of oil recovery for different salt concentrations are shown in Fig. 8. The results indicate greater yield of recovery when the temperature of 50 °C and salt concentration of 50 g L^{-1} are used.

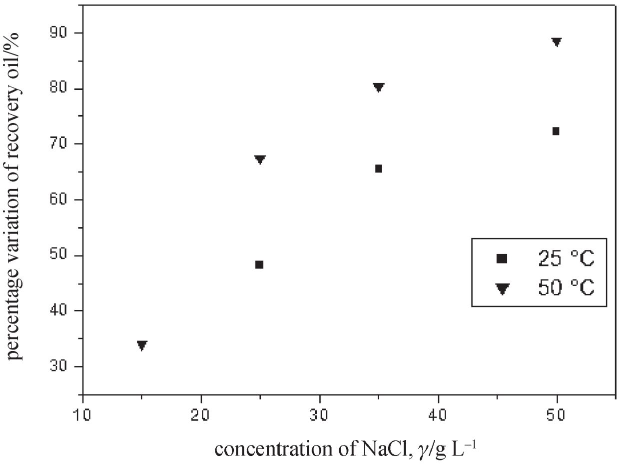
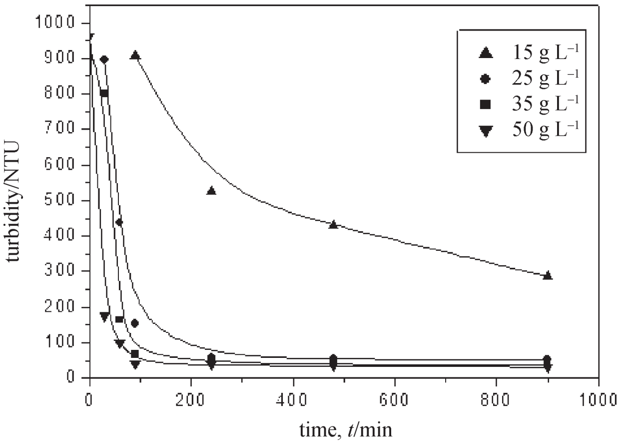


Fig. 8 – *Percentage variation of recovery oil in two level of temperature (ϑ = 25 and 50 °C) and sodium chloride concentration*

Additionally, the recovery of the used oil was developed by the determination of the kinetic profile of the demulsifying phenomenon. Curves of turbidity vs. time were made, since the variation of turbidity in the sample, when submitted to destabilizing agents, expresses the rate of coalescence of the dispersed drops in the oil until it reaches the complete separation of phases. In this



F i g . 9 – *Demulsification of cutting fluid at four level of concentration of NaCl (γ = 15, 25, 35 and 50 g L^{-1}) at ϑ = 25 °C*

context, Fig. 9 shows the kinetic follow-up at room temperature for the fluid being studied.

Fig. 9 shows kinetic curves for highest concentrations. In the first 100 min, a fast demulsification rate was observed for concentrations of $\gamma = 25$, 35 and 50 g L^{-1} of the demulsifying agent (NaCl). For concentration 15 g L^{-1}, high values of turbidity at long separation times were observed, different from the others. This way, unlike the behavior observed, a large band of salt concentrations (NaCl) can be adopted to accomplish the crack and separation phenomenon, and besides that, the required values of salt present themselves in relatively low concentrations.

Conclusions

Based on the results shown, it may be concluded that:

1) The conditions obtained as the most adequate for destabilizing and recovering the oil being used from concentrated emulsions are: temperature of $\vartheta = 70$ °C, mixing rate of 2000 rpm and sodium chloride concentration of $\gamma = 200$ g L^{-1}. The oil recovered in these conditions presents physical-chemical characteristics very similar to those of the original oil. FTIR analyses indicated the presence of surfactant in the recovered oil.

2) For the destabilization and recovery of the oil used in the compositions of the studied cutting fluid, 50 g L^{-1} of NaCl showed to be the most adequate concentration of salt solution, which enables lower turbidity in the water phase, and consequently greater yield of recovered oil.

3) The concentration of salt solution necessary to cause the separation of the phases for the cutting fluids is lower than the one necessary for the same procedure carried out with concentrated emulsions.

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List of symbols

R – turbidity ratio, –
t – time, h, min
w – mass fraction, %
γ – mass concentration, g L^{-1}
ϑ – temperature, °C
λ – wavelength, nm
ν – wavenumber, cm^{-1}
ψ – volume ratio, –

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