

A NEW TECHNIQUE FOR THE MECHANICAL DEMULSIFICATION OF O/W EMULSIONS

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The development of a demulsification technique seems to be the key step for the industrial practice of hydrocarbon separation by liquid membrane permeation. This paper describes an experimental study of a new mechanical demulsification technique, in which strong agitation of an O/W emulsion with a coexisting oil phase caused instantaneous and efficient demulsification. The yields in the demulsification were as high as 80 % in batch runs. Continuous demulsification was also achieved successfully.

Introduction

Emulsion breaking or demulsification is one of the important operations in industrial emulsion treatment. Dehydration of crude petroleum is a typical example of large-scale demulsification of W/O emulsions, in which several basic methods such as settling, heating, electrical dehydration, use of chemicals and centrifuging or combinations of these methods are used extensively.²⁾ To the contrary, breaking of O/W emulsion is much less used in industrial treatment because its importance is limited to the demulsification of unwanted emulsions. Recent developments in liquid membrane permeation (LMP), however, necessitate a highly efficient demulsification technique because LMP processes for hydrocarbon separation must treat a large amount of O/W emulsion to be demulsified. If LMP processes are used in the petroleum refinery industry, heating or distillation may be available as a breaking method because petroleum refinery plants abound with low-pressure steam. But, in general, heating is an energy-consuming method and high temperature may cause the degradation of surfactants. Although a chemical method can be another candidate, recovery processes for the chemicals are required in this method.

Emulsions, particularly these in LMP, are not stable and they often change their types from O/W to W/O and vice versa. Phase inversion is sensitive to many factors²⁾ such as agitation strength, oil-to-water ratio, temperature, concentration and properties of surfactants. Since inversion is one of the resultant phenomena of emulsion instability, it might be used

as the basic idea for emulsion breaking. For example, if an O/W emulsion is changed to a W/O type or to an (O/W)/O type by an increase in the volume of dispersed oil and also by strong agitation, the resultant emulsion may be unstable and be quickly settled because the hydrophilic surfactant added originally in aqueous phase serves to keep the emulsion in an O/W type.

The purpose of this paper is to show the usefulness of a new mechanical demulsification technique by which an O/W emulsion is strongly agitated with a coexisting oil phase.

1. Experimental Apparatus and Procedures

Isooctane was used for both dispersed oil in O/W emulsions and the coexisting oil added to the emulsions to be demulsified. Aqueous solutions consisted of water and saponin, which is a hydrophilic surfactant. In some runs, glycerin was added to the aqueous solutions because it is commonly used as a membrane-strengthening agent in LMP.

Three different emulsifiers were used. **Figures 1a to 1c** show simple sketches of them: a) a turbine-type impeller with six flat blades and a stirring vessel (S.V.) of 80 mm diameter with four baffles; b) a high-speed homogenizer (H.S.H.) made by Nichion Irikakiki Co. with a standard generator shaft A (NS-20TP type); and c) a H.S.H. with a generator shaft B (NS-35UG type) specially modified to obtain better agitation. These three emulsifiers were also used as demulsifiers.

In the preparation of feed emulsions, oil-soluble dye (Oil Red) was added to isooctane as a tracer and the oil phase was agitated with an aqueous solution. Emulsification periods were 5 minutes for S.V. and 0.25 minutes for H.S.H. In demulsification experiments, pure isooctane was added as a coexisting oil

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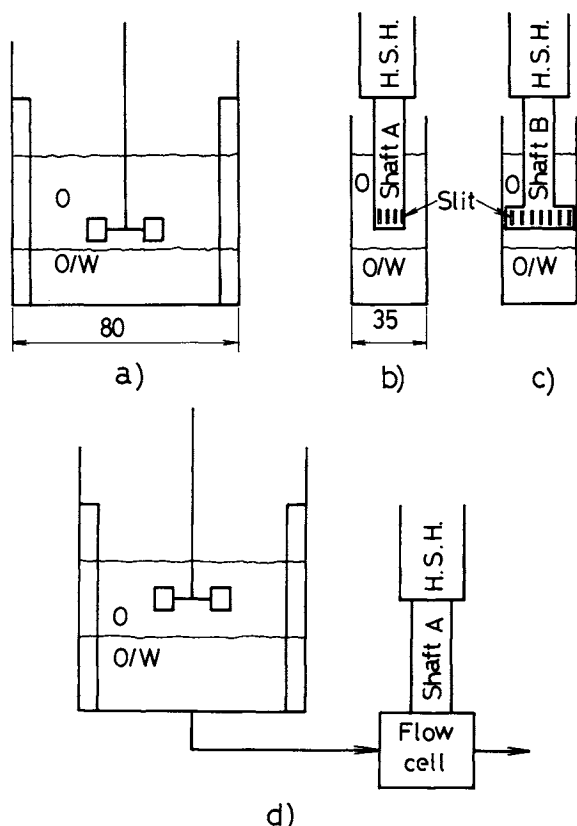


Fig. 1. Simple sketch of agitation devices: a) stirring vessel; b) high-speed homogenizer (H.S.H.) with generator shaft A; c) H.S.H. with generator shaft B; and d) combination of S.V. and H.S.H. with generator shaft A.

phase to the O/W emulsion. Then the oil and the O/W emulsion were strongly agitated. After the agitation, the resultant multiple emulsion was settled to form an O/W emulsion phase and a coexisting oil phase. The decrease in volume of the O/W emulsion was then measured, and the dye concentration in the coexisting oil phase was determined by a spectrophotometer.

Figure 1d shows a schematic diagram for continuous emulsification and breaking. Both a S.V. and a H.S.H. were used as emulsifier: the S.V. served as a premixer and the H.S.H. with generator shaft A pumped and agitated the premixed O/W emulsion through a flow cell (FO-20 type). The volume of the cell was 9 cm³ and the flow rate by self-pumping was about 80 cm³/s, but fluctuations in the flow rate were observed. The residence time in the cell seems to be about 0.1 seconds. In continuous demulsification, the O/W emulsion and coexisting oil of pure isooctane were premixed in the S.V. and were pumped out by the H.S.H. to another container. The dye concentration in the continuous oil phase was measured to determine yields in the demulsification. Fluctuations in flow rate were observed in the continuous demulsification as well, but no special modifications to stabilize the flow rate were applied to the apparatus because the operations were preliminarily conducted

to show that O/W emulsions can readily be broken by continuous operations.

Table 1 summarizes operation parameters. One of the parameters tabulated was varied to examine its relation with the amount demulsified, while the others were kept constant.

2. Results and Discussion

2.1 Definition of yield in demulsification

Equation (1) defines the yield in demulsification obtained from the volume decrease of the O/W emulsion as illustrated in Fig. 2.

$$Y_v = (V_{ow} - V) / (V_{ow} - V_w) \quad (1)$$

The emulsion after the breaking, in general, consists of the aqueous membrane phase, the original-oil droplets which were not demulsified and the coexisting-oil droplets remaining after the breaking. The mass balance for dye before and after the breaking gives information about the amount of coexisting oil remaining in the emulsion:

$$(V_{ow} - V_w)C_{d0} = (V_t - V)C_d + (V - V_w)C_{d1} \quad (2)$$

If it is assumed that the coexisting oil does not remain in the O/W emulsion after the breaking, the average dye concentration for the oil droplets after the breaking, C_{d1} , is equal to the initial concentration, C_{d0} . Then,

$$(V_{ow} - V)C_{d0} = (V_t - V)C_d \quad (3)$$

Substituting Eq. (3) into Eq. (1) and changing the notation of Y_v to Y_d , one gets

$$Y_d = (C_d / C_{d0}) (V_t - V) / (V_{ow} - V_w) \quad (4)$$

Eliminating V in Eq. (4) by use of Eq. (3), one gets another expression for yield:

$$Y_d = C_d (V_t - V_{ow}) / (C_{d0} - C_d) (V_{ow} - V_w) \quad (5)$$

Measurement errors of about 10% must be allowed for the values of Y_v , while those for Y_d in Eq. (5) were within about 3%. Therefore, in the calculation of Y_d , Eq. (5) was used. It should be noted that the coexisting oil does not remain in the emulsion after the breaking, if Y_d calculated from Eq. (5) is equal to Y_v .

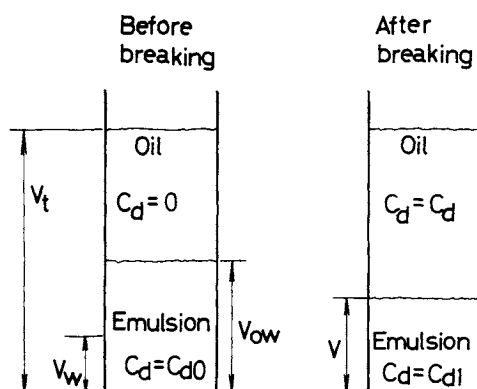
2.2 Observation of batch demulsification by H.S.H.

As soon as the O/W emulsion and the transparent coexisting oil were agitated by generator shaft A or B, the O/W emulsion phase quickly prevailed in the coexisting oil phase, which corresponded to the propagation of new emulsification in an O/W type. In most cases, in particular without glycerin, agitation for 2 seconds was enough to cause phase inversion. At the moment of the inversion, two distinct phenomena could be observed: the glass container was pulled with much force and large oil lumps and O/W emulsion lumps appeared in the agitated region. Not all the

Table 1. Operation parameters in demulsification

Saponin concentration:	$C_s = 0.1 \text{ wt}\%$
Glycerin concentration:	$\phi_G = 0$
Volume fraction of aqueous phase:	$\phi_w = 0.5$
Volume fraction of coexisting oil:	$\phi_c = 0.5$
Agitation speed	$N = 20,000 \text{ min}^{-1}$ for H.S.H. 1200 min^{-1} for S.V.
Total volume*	$V_t = 100 \text{ cm}^3$ for H.S.H. $= 400 \text{ cm}^3$ for S.V.

* Total volume after breaking was equal to that before breaking

**Fig. 2.** Decrease in volume of O/W emulsion by breaking.

parts of the original O/W emulsion were demulsified because a part of the O/W emulsion remained below the oil phase after the settling of the lumps. But a remarkable decrease in emulsion volume and clear coloring in red of oil phase were observed when the demulsification was successfully accomplished. The dispersion in the multiple emulsion after the phase inversion seemed to be an (O/W)/O type, because the oil-emulsion interface moved downward during the setting, which means that the O/W emulsion drops settled down and aggregated.

When the generator head was located in the coexisting oil phase, the demulsification proceeded more efficiently. It is empirically recognized^{2,8)} that the phase in which the impeller is located is liable to become a continuous phase. Therefore, the generator head location in oil phase seems to have helped the dispersed oil droplets in the original O/W emulsion to become a continuous oil phase.

2.3 Selection of a surfactant

Surfactants have great importance in the breaking phenomena of emulsions. They must also satisfy some requirements in LMP performance. Thus experiments on liquid membrane separation were conducted first to examine if the surfactants chosen can work satisfactorily in LMP. Experimental apparatus and procedures for LMP runs were the same as those in a previous report.⁵⁾ A five-component mixture was used as hydrocarbon feed. **Table 2** shows the rates

Table 2. Rates of increase in yield in hydrocarbon permeation through liquid emulsion membranes

Surfactant	C_s wt%	x_s [—]	dY_i/dt [l/min]				
			Ben.	Tol.	Xyl.	Hex.	Non.
Triton-X100	0.04	0.18	3.6	2.1	1.0	0.34	0.29
	0.1	0.20	3.7	1.6	1.1	0.45	0.38
	0.4	0.05	4.2	3.0	1.6	0.42	0.06
Saponin	0.1	0.01	4.4	3.2	2.1	0.56	0
	0.4	0	3.7	2.5	1.6	0.45	0

Hydrocarbon feed: benzene (10 wt%) + toluene (10 wt%) + *m*-xylene (10 wt%) + *n*-hexane (66 wt%) + *n*-nonane (4 wt%); solvent: isooctane;

$\phi_G = 0$, $\phi_w = 0.5$, $\phi_{ow} = 0.25$, $N = 600 \text{ min}^{-1}$, $C_{sp} = 0.3 \text{ wt}\%$

of increase in yield at $t=0$, dY_i/dt , and they were obtained from the permeation data at 10 seconds in the presence of Span 20 of 0.3 wt% in solvent (isooctane) phase. Two surfactants, Triton-X100 and saponin, were examined because these were relatively efficient surfactants in LMP.^{1,3,6)} Although emulsions prepared with Triton-X100 showed almost the same permeation rates as those prepared with saponin, stability of liquid membrane was not satisfactory in the former case because dY_i/dt of nonane, which represents membrane breakup, and concentration of isooctane in inner oil phase, which represents mechanical entrainment of solvent, were large. Thus, in the demulsification runs saponin was used as the hydrophilic surfactant, and a concentration of 0.1 wt% was mainly employed because liquid membranes with saponin at this concentration can work satisfactorily as shown in **Table 2**.

2.4 Batch demulsification

1) **Effects of the volume of coexisting oil** **Figure 3** shows the relation between the volume fraction of coexisting oil, ϕ_c , and yields, in which generator shaft A was used. O/W emulsions were also prepared by shaft A. The yields increased with volume fraction of oil, which means that a large amount of coexisting oil is favorable to help phase inversion which results in the demulsification. Meanwhile, more than a limited amount of coexisting oil must be used to promote the inversion, since the entire amount of the coexisting oil was dispersed in the aqueous phase and formed a stable O/W emulsion at $\phi_c = 0.3$. **Figure 3** shows that more than 50% of O/W emulsion was demulsified by shaft A.

Two yields, Y_o and Y_d , showed fairly good agreement, which implies that the coexisting oil did not remain in the O/W emulsions after the breaking. In fact, the dye concentration in oil droplets in the O/W emulsion after breaking was equal to that before breaking, as ascertained experimentally for the emulsion of $\phi_c = 0.5$ in **Fig. 3** by use of thermal

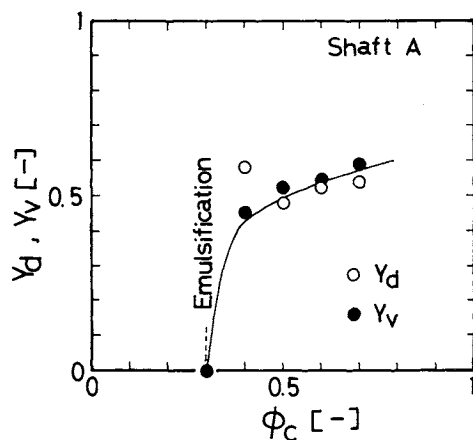


Fig. 3. Relation between volume fraction of coexisting oil and yield.

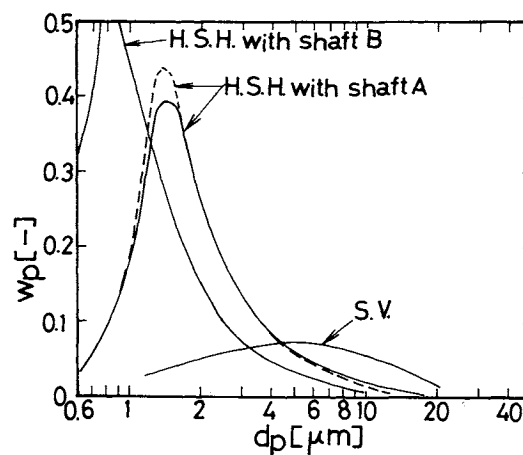


Fig. 4. Size distribution of oil droplets in O/W emulsion: solid lines, before breaking; dashed line, after breaking.

demulsification technique.

Figure 4 shows size distributions of oil droplets in the O/W emulsions before and after demulsification, as measured by a centrifugal particle-size analyzer. The solid lines represent the size distributions of oil droplets in the emulsions prepared by the S.V. and the H.S.H. with shafts A and B. The dashed line represents the distribution after breaking, in which shaft A was used for both emulsification and demulsification. The conditions of emulsification and demulsification corresponded to those in Table 1. Comparison of the two distributions before and after the breaking conducted with shaft A shows that, although large oil droplets were demulsified preferentially to some extent, the size distribution was barely changed on the whole.

2) Effects of stirring speed **Figure 5** shows the effects of stirring speed on yield with generator shaft A. An O/W emulsion is liable to change its type to a W/O type if agitation speed is elevated.⁷⁾ The pattern appearing in Fig. 5 seems to have resulted from the same connection: the elevation in the agitation speed helped the oil phase to be continuous. It must also be noted that the agitation speed must exceed a lower limit, 7000 rpm, to realize efficient breaking.

The type of demulsifier can have great effects as well. Demulsifiers must be able to exert enough power to agitate all the liquid in the system strongly. Although the S.V. was used at 1200 rpm to break the emulsion prepared by generator shaft A, agitation merely resulted in the formation of a new stable O/W emulsion. To the contrary, an emulsion prepared by the S.V. was quite successfully demulsified by generator shaft A as shown in Fig. 5. This is probably because emulsions prepared by the S.V. included relatively large oil droplets as shown in Fig. 4.

3) Effects of surfactant concentration **Figure 6** shows the relation between saponin concentration in the aqueous phase and the yield obtained by gener-

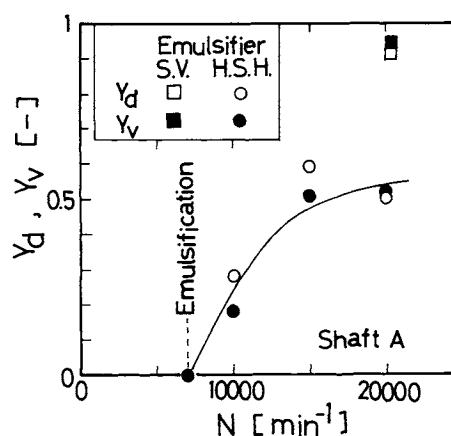


Fig. 5. Effects of agitation speed on yield.

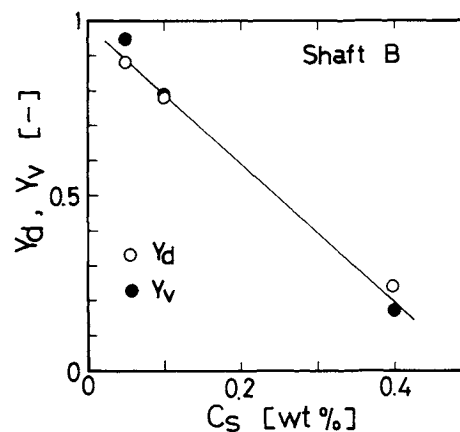


Fig. 6. Effects of saponin concentration on yield.

ator shaft B. O/W emulsions were prepared by shaft B. The yield at $C_s = 0.1$ wt%, which can be reasonably employed in LMP as shown in Table 2, was as high as 80%. The highly efficient agitation by shaft B is characterized by the existence of smaller droplets in the prepared emulsions as shown in Fig. 4. Yields decreased with increasing saponin concentration. This is probably because O/W emulsions become more

stable when the aqueous phase is concentrated with hydrophilic surfactants.⁷⁾

4) Effects of water content in O/W emulsions
Figure 7 shows the relation between the volume fraction of water in O/W emulsions and the yield obtained by generator shaft B. With increasing water content, the yield decreased because the phase of which the volume is increased is liable to become the continuous phase.²⁾ The pattern appearing in Fig. 7 is closely related to that in Fig. 3.

In Figs. 5 to 7, the values of Y_d and Y_v are nearly equal as well. Then, the relation of $C_{d1} = C_{d0}$ seems to have been closely satisfied, which means that the coexisting oil did not remain in the emulsions after breaking.

5) Effects of glycerin content in aqueous phase
Glycerin is used in LMP as a membrane-strengthening agent. Figure 8 shows the effects of the volume fraction of glycerin in aqueous phase on the yield obtained by generator shaft B. Addition of glycerin is expected, in general, to help inversion from O/W to W/O because more viscous phase is liable to become dispersed phase.^{2,8)} But the yield calculated from Eq. (1), Y_v , decreased with increasing glycerin concentration, which means that addition of glycerin in aqueous phase is not favorable for the demulsification. This is probably because the agitation of the mixture of O/W emulsion and coexisting oil was weakened by the increase in viscosity owing to the existence of glycerin. In fact, agitation periods of more than 10 seconds for breaking were required in the cases with glycerin.

The yields determined from dye concentration, Y_d , were larger than Y_v and were close to unity. If C_{d1} is equal to C_d , the following relation can be obtained from Eq. (2):

$$(V_{ow} - V_w)C_{d0} = (V_t - V_w)C_d \quad (6)$$

Substituting the expression of C_{d0}/C_d obtained from Eq. (6) into Eq. (5), one gets the relation, $Y_d = 1$. Therefore, in the case with glycerin, the average dye concentration for the oil droplets in the emulsion after the breaking seems to have been equal to that in coexisting oil phase. Furthermore, because the coexisting oil remained in the emulsions after the breaking and because Eq. (3) did not hold for this case, there existed large differences between the values of Y_d and Y_v .

In LMP, O/W emulsions prepared by a H.S.H. were stable even in the case without glycerin,⁴⁾ and glycerin seems to be required for the emulsification by a S.V. Although the use of glycerin caused a decrease in yield in demulsification, it may cancel out with the increase resulting from the use of a S.V. as shown in Fig. 5. However, both the emulsification by a S.V. and the demulsification by a H.S.H. along with per-

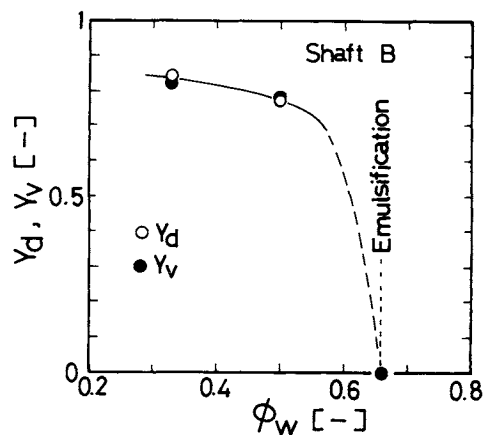


Fig. 7. Relation between volume fraction of water in O/W emulsion and yield.

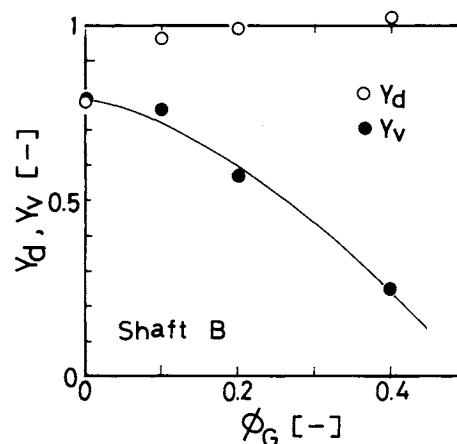


Fig. 8. Relation between volume fraction of glycerin in aqueous phase and yield.

meation should be extensively studied further.

2.5 Continuous demulsification

Figure 9 shows the relation between the yield determined from Eq. (5) and the volume fraction of coexisting oil for the data obtained from the continuous demulsification by use of the S.V. and the H.S.H. with generator shaft A. Although the yields were about 0.5 and almost the same as those obtained in batch runs shown in Fig. 3, yield decreased with ϕ_c . Clear reasons for this interesting result are not yet obvious, and more detailed studies of continuous demulsification are required.

Figure 10 illustrates a schematic diagram for a continuous demulsification process. The settled oil is recycled to be used as the coexisting oil. Hence, although Y_d and Y_v may be different from each other, the value of Y_v is important for the efficiency of the process in Fig. 10.

The technique developed in this study does not realize the complete demulsification of O/W emulsions, and hence combinations with other techniques such as filtration, thermal or chemical demulsification are required for complete demulsifi-

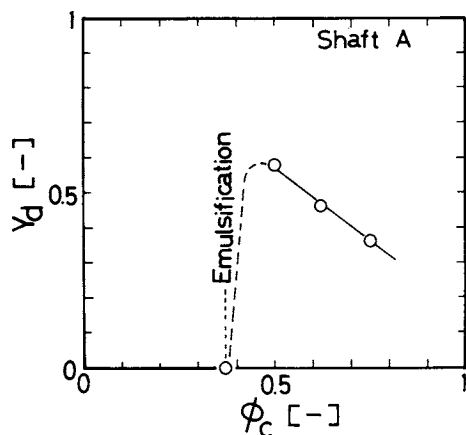


Fig. 9. Relation between volume fraction of coexisting oil and yield obtained from continuous demulsification.

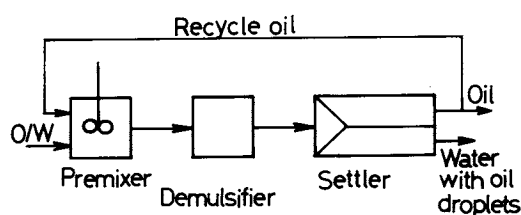


Fig. 10. Flowdiagram for a continuous demulsification process.

cation. However, in an LMP process, complete demulsification is not necessarily required because the aqueous membrane phase which includes a slight amount of residual oil droplets is recycled to form a new O/W emulsion with feed oil at the first stage in the process. The existence of the residual oil droplets may cause a decrease in the selectivity of separation of the process, and hence the technique developed in this study should be further pursued for higher efficiency.

Conclusion

A new technique to demulsify O/W emulsions was proposed. The strong agitation of the O/W emulsion with some amount of coexisting oil caused almost instantaneous demulsification in both batch and continuous runs. Yields of more than 80% were obtained by this technique. Many factors which promote phase inversion from O/W to W/O promoted demulsification: increase in both agitation speed and amount of coexisting oil and decrease in surfactant concentration.

The development of this new technique may facilitate the processing of liquid emulsion membrane separation in industrial practice.

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Nomenclature

C_d	= dye concentration in oil phase	[wt%]
C_{d0}	= dye concentration in oil droplets in O/W emulsion before breaking	[wt%]
C_{d1}	= average dye concentration for oil droplets in O/W emulsion after breaking	[wt%]
C_s	= weight percent of surfactant in aqueous phase	[wt%]
C_{sp}	= weight percent of Span 20 in solvent	[wt%]
d_p	= diameter of oil droplet	[μm]
N	= stirring speed	[min^{-1}]
t	= agitation or contact time	[min]
V	= volume of O/W emulsion after breaking	[cm^3]
V_{ow}	= volume of O/W emulsion before breaking	[cm^3]
V_t	= total volume	[cm^3]
V_w	= volume of aqueous phase	[cm^3]
w_p	= weight fraction of oil droplet	[—]
x_s	= weight fraction of isooctane in inner oil phase in LMP after 10 seconds	[—]
Y_d	= yield in demulsification defined by Eq. (5)	[—]
Y_i	= yield of permeate i in LMP	[—]
Y_v	= yield in demulsification defined by Eq. (1)	[—]

ϕ_c	= volume fraction of coexisting oil at $t=0$	[—]
ϕ_G	= volume fraction of glycerin in aqueous phase	[—]
ϕ_w	= volume fraction of water in O/W emulsion	[—]

<Subscripts>

c	= coexisting oil
d	= dye
G	= glycerin
i	= component i
ow	= O/W emulsion
s	= surfactant or solvent in LMP
t	= total
v	= volume
w	= aqueous phase

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