

## **Batch Separation of Styrene/Ethyl Benzene/Water Dispersions**

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### **Abstract**

*The separation of immiscible liquids is an important process in oil and petrochemical industries. In the outlet stream of a catalytic reactor of dehydrogenation of ethyl benzene to styrene monomer, water is present because it is used as a high pressure steam to provide reaction heat. Therefore, aqueous and immiscible organic phases should be separated in a horizontal separator before fractionation. The aim of this work is to study the batch separation of ethyl benzene and styrene from water. Different mixtures of water, styrene and ethyl benzene were prepared using different amounts of organic compounds and various mixing rates. The experiments show that the separation time of ethyl benzene and water mixtures are more than that for styrene and water mixtures. Furthermore, increasing the mixing rate increases the separation time because the dispersity of the system increases, but it has more effects on water/ethyl benzene mixtures.*

**Keywords:** *Styrene-Ethyl Benzene-Water Dispersion, Batch Separation, Immiscible Phases, Separation Time*

### **1- Introduction**

Phase separation is an important operation in the oil and petrochemical industries. But, most works have been concerned with gas-liquid separation. Nevertheless, the separation of immiscible liquid phases is also of great importance. The first step of the separation of the crude oil produced from wells which is accompanied by water and gas, is traditionally performed in a horizontal cylindrical gravity settling vessel in which water and gas are separated from oil [1]. Furthermore, in those petrochemical

processes that steam is used to provide the required heat of reactions, like catalytic dehydrogenation of ethyl benzene (EB) to styrene monomer (SM), water vapor (W) is present in the outlet stream of the reactor. After condensation, this mixture is indeed a hydrocarbons-in-water emulsion or dispersion because these compounds (SM, EB and other byproducts of reaction) are almost immiscible with water. Thus, before fractionation or distillation of the stream obtained from the dehydrogenation reactor, it is necessary to separate hydrocarbons from

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water in a horizontal gravity separator [2-3]. These separators are usually large in size because the volume flow rates of streams in oil and petrochemical industries are usually high and therefore they are costly to purchase and install. Reducing their size without losing separation effectiveness would reduce capital cost [1]. In addition, depending on the process, the separated water may then be recycled and reused or discharged. In both cases, it is essential that the amount of hydrocarbons in water should not exceed certain limits. Therefore, the operational problems of these vessels should be investigated.

In recent years attention has been directed towards understanding the vessel hydrodynamics using residence time distribution (RTD). Further, computational fluid dynamics (CFD) has been applied to these separators in order to understand where dead zones are likely to occur. In addition, many efforts have been focused upon the modification of the vessel internals by introducing structured packing [4-7]. However, these investigations are almost restricted to oil-in-water dispersions and there is no data for the separation of SM/EB in water dispersion in the literature. In order to improve the efficiency of horizontal separators used in SM plants, it is essential to have an insight into the immiscibility and required time of the separation of SM/EB and water mixtures before carrying out the experiments in the separator. In these plants, horizontal separators are subject to self-polymerization of styrene causing blockages and consequently, increasing the water height in the separator. So far, high cross-entrainments have been observed.

The objective of the present work is to study the batch separation of SM/EB and water mixtures. Experiments have been carried out using a mixing tank designed for a pilot-scale horizontal separator and measuring the time required for complete separation of organic and aqueous phases. The mixing rate and the volume fraction of EB and SM were changed to figure out the effect of dispersity and the ratio of organic to aqueous phase on the separation time.

## **2- Theory**

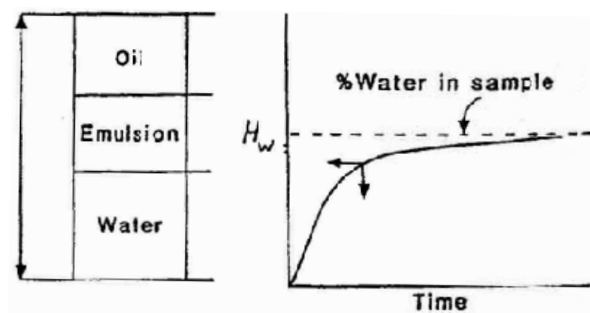
Batch separation or bottle test is a common method of determining relative emulsion stability. A batch separation test involves agitating a mixture of oil and water to form a uniform dispersion, then stopping the agitation to allow the dispersion to settle naturally. It is an attractive method to study the separation behavior of water in oil and oil in water emulsions because the experiments are simple and inexpensive to perform [6]. The major factors controlling separation of immiscible phases are settling and coalescence of drops [2]. Batch separation is performed to take into account the specific coalescence properties of the dispersions. Furthermore, it provides the basis of the engineering design of horizontal gravity separators [7].

EB and SM are of those hydrocarbons that are almost insoluble in water and can be called hydrophobic. Hydrophobic effect is mainly an entropic phenomenon and arises from the strong attractive forces (hydrogen bonds) between water molecules. When a solute is dissolved in water, these attractive forces must be disrupted or distorted. Upon solubilization of a solute, hydrogen bonds in

water are often not broken, but are maintained in distorted form. They rearrange themselves such that they can participate in hydrogen bond formation, *more or less* as in bulk pure liquid water. In doing so, they create a higher degree of local order than that in pure water, thereby producing a *decrease in entropy*. It is this loss of entropy that leads to an unfavorable Gibbs energy change for solubilization of insoluble hydrocarbons in water [8]. Thus, the higher the positive Gibbs energy, the poorer the solubility in water. We can, therefore, expect that EB and SM have a highly unfavorable (or positive) Gibbs energy of solubilization in water because they are almost insoluble. On the other hand, the solubility of SM is much less than that of EB, that is, the amount of Gibbs energy for the transfer of SM from its pure liquid to water is more than that of EB. Consequently, the time required for separation of SM is much less than that of EB. Therefore, increasing the amount of EB in the mixture of SM/EB will increase the time required for separation of organic and aqueous phases. It means that, if the conversion of the dehydrogenation reaction of EB decreases, the amount of EB will increase and the efficiency of separation in an operational horizontal separator will decrease.

When a mixture of immiscible liquids, e.g. a mixture of water and styrene or water and oil, is allowed to stand without agitation, separation into layers of water, emulsion, and hydrocarbon occurs as illustrated in Fig. 1. The height of the water and emulsion interface increases, whereas the height of emulsion and hydrocarbon decreases. The time at which two curves meet each other depends on the interaction of the molecules

of the mixture. If the solubility of hydrocarbon in water decreases, two curves reach each other after a few minutes and complete separation takes place.



**Figure 1.** Separation of oil (hydrocarbon) and water [9]

### 3- Experimental

#### 3.1- Equipment

The mixing tank used in this work was part of a pilot scale model of a horizontal separator used in the Styrene Monomer Plant at the Tabriz Petrochemical Complex. The mixing tank was manufactured from carbon steel and has a diameter of 66 cm and height of 90 cm. A shaft with two marine impellers was used to mix pure SM, EB and water. An electromotor (Deg, 0.55 kW, Germany) controlled by an inverter (LS600, Taiwan) was used to vary mixer speed. The prepared mixture is then taken by a pump having an outlet split into two streams; the main stream (to feed pilot scale separator) and a bypass stream (to control the flow rate of the main stream). Samples were taken by filling a glass cylinder of 250 mm height and 50 mm inner diameter (ISOLAB, Germany) put in the bypass stream.

### 3.2- Overall consideration

In the following, there are two types of interface, Upper Height of Interface (UHI) which indicates the interface between the organic and dispersion phases, and the Lower Height of Interface (LHI), which indicates interface between aqueous and dispersion phases. In all experiments, UHI and LHI are dependent variables. The volume fraction of any species in the mixture is defined as

$$\alpha_i = \frac{V_i}{\sum V_i} \quad i = SM, EB \text{ and } W \quad (1)$$

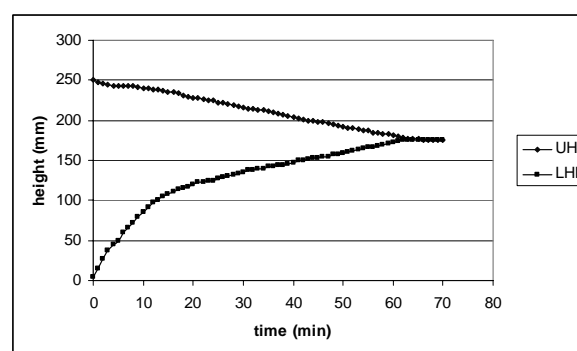
Where,  $V_i$  indicates volume of species  $i$  used to prepare a mixture. Three types of mixtures were prepared in this work; W and EB, W and SM, and finally, W, SM and EB. Table 1 shows different types of experiments and their conditions. By mixing rate, we mean the rotation rate of the mixer and mixing time refers to the time spent to prepare the mixture. All experiments were performed at a constant temperature of 20°C.

## 4- Results and discussion

In order to understand the effect of mixing rate and composition on the separation time, three types of mixture were considered, as mentioned before. Notice that the separation time is defined as the time required to separate organic and aqueous phases completely so that the upper and lower heights of the interface (UHI and LHI) reach each other.

### 4.1- Mixtures involving W and EB

Fig. 2 shows the UHI and LHI curves for experiment No. 1. It can be seen that a dispersion of W/EB is completely separated after 65 minutes.

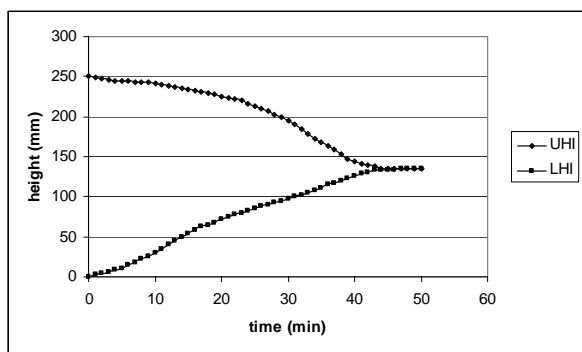


**Figure 2.** Upper and Lower Heights of Interface of EB/W Mixture, Vol. Frac. of EB = 0.33, Mixing Rate = 100 RPM, Mixing Time = 4 min

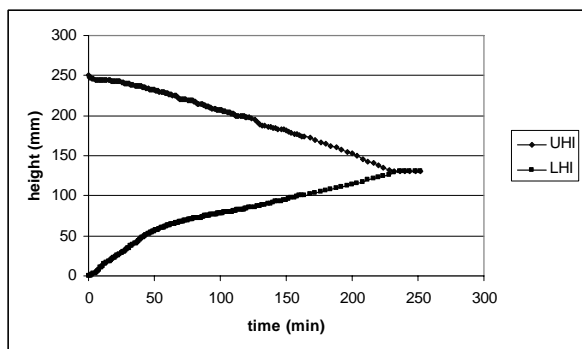
**Table 1.** Different types of experiments and their conditions

No. of Expt.	Mixture	Mixing Rate (RPM)	Mixing Time (min)	$\alpha_w$	$\alpha_{SM}$	$\alpha_{EB}$
1	W/EB	100	4	0.67	0	0.33
2	W/EB	100	4	0.50	0	0.50
3	W/EB	132	4	0.50	0	0.50
4	W/SM	100	5	0.67	0.33	0
5	W/SM	100	10	0.67	0.33	0
6	W/SM	100	5	0.50	0.50	0
7	W/SM	132	5	0.50	0.50	0
8	W/SM/EB	100	5	0.67	0.165	0.165
9	W/SM/EB	132	5	0.67	0.165	0.165
10	W/SM/EB	132	5	0.67	0.11	0.22

Fig. 3 shows the UHI and LHI curves for experiments No. 2 and 3. As might be expected, the separation time increases by increasing the mixing rate, because the dispersity of the system increases and allows the EB molecules to have a greater hydrogen bond with the water molecules so that the time required to separate them increases.



(a) 100 RPM



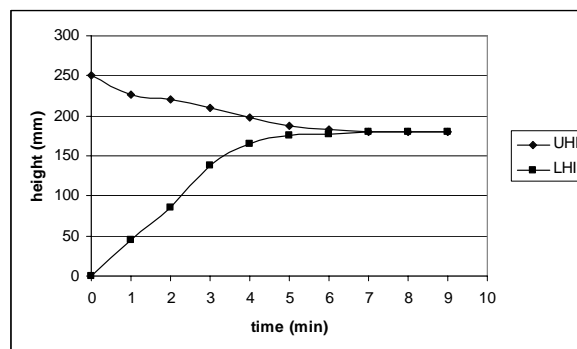
(b) 132 RPM

**Figure 3.** Upper and Lower Heights of Interface of EB/W Mixture, Vol. Frac. of EB = 0.50, Mixing Time = 4 min

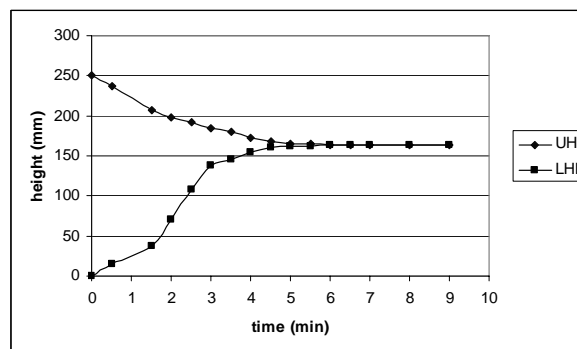
#### 4.2- Mixtures involving W and SM

The UHI and LHI curves for experiments No. 4 and No. 5 are shown in Fig. 4. Comparison between Fig. 4(a) and Fig. 4 (b) shows that increasing the mixing time does not affect the separation time and both mixtures are almost separated after 7 minutes. Fig. 5 shows that by increasing the

volume fraction of SM from 0.33 up to 0.50, the separation time decreased from 7 minutes to 2.5 minutes (compare Fig. 4(a) with Fig. 5(a)). However, the separation time increased about 0.5 minutes when the mixing rate increased from 100 RPM up to 132 RPM (Fig. 5).



(a) 5 minutes

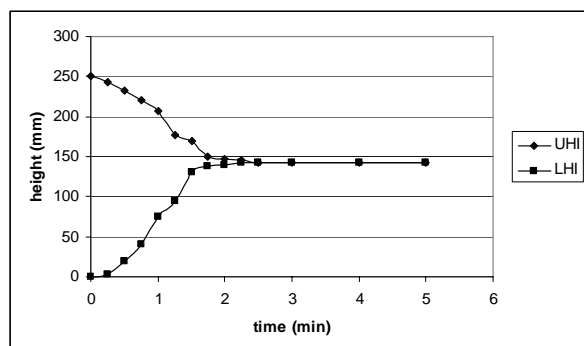


(b) 10 minutes

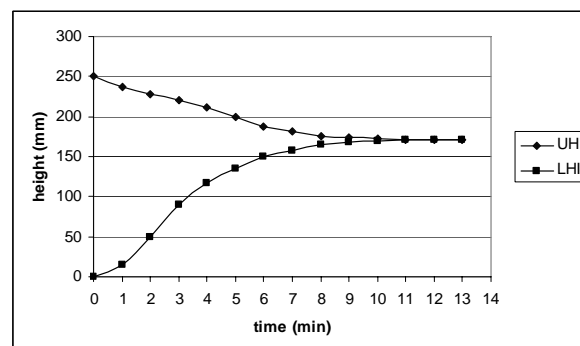
**Figure 4.** Upper and Lower Heights of Interface of SM/W Mixture, Vol. Frac. of SM = 0.33, Mixing Rate = 100 RPM

It can be seen that the separation time for mixtures involving W and EB is dramatically more than that for mixtures involving W and SM, as expected. For instance, at the same conditions, (e. g. mixing rate of 100 RPM, mixing time of 5 minutes, and volume fraction of 0.33) the separation time of W and EB is more than 9 times of that for W

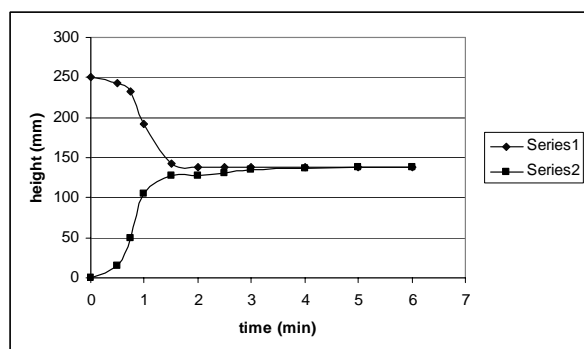
and SM. This difference is more than 50 times at a mixing rate of 132 RPM. (compare Fig. 3 (b) with Fig. 5. (b))



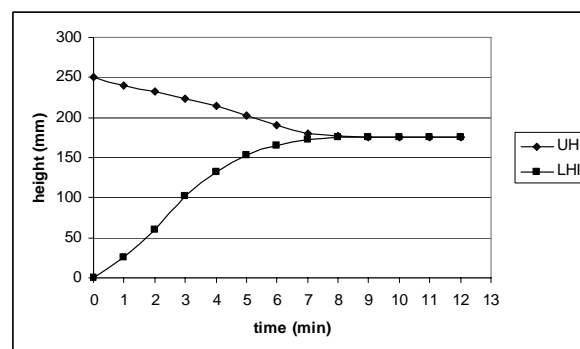
(a) Mixing Rate = 100 RPM



(a) Mixing Rate = 100 RPM



(b) Mixing Rate = 132 RPM



(b) Mixing Rate = 132 RPM

**Figure 5.** Upper and Lower Heights of Interface of SM-Water Mixture, Vol. Frac. of SM = 0.50, Mixing Time = 5 min

**Figure 6.** Upper and Lower Heights of Interface of SM-EB and Water Mixture, Vol. Frac. of SM = 0.165, Vol. Frac. of EB = 0.165, , Mixing Time = 5 min

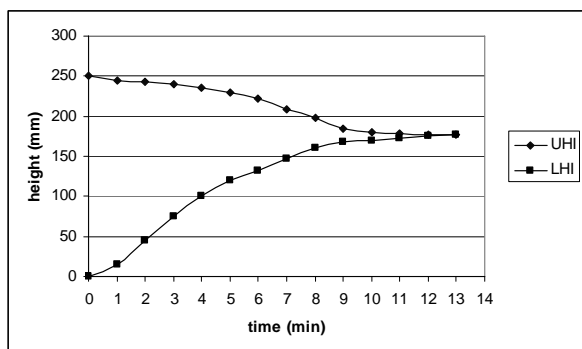
#### 4.3- Mixtures involving W, EB and SM

Since the outlet stream of a dehydrogenation of an EB reactor contains all the components W, EB, SM, and other byproducts of reaction, these series of experiments are much closer to a real situation than the other experiment mentioned previously. However, the former experiments can be considered as limits of time required for separation in a horizontal separator. Here, we expect that the time required for separation of the organic phase (SM and EB) and the aqueous phase should be less than that of the EB/W mixture

and more than that of the SM/W mixture. Figure 6 shows the UHI and LHI curves for experiments No. 8 and 9. It can be seen that the presence of both SM and EB would increase the separation time even though it is not remarkable (see Figs. 3, 5 or 6). It may be related to interactions between SM and EB molecules; when both EB and SM are present in the mixture, their molecules may tend to attract each other and make a homogenous phase, thereby immediately separating from the aqueous phase.

The UHI and LHI curves for experiment No. 10 are shown in Fig. 7. In these experiments the amount of EB was increased to figure out

its effect on the separation time. As might be expected, the required time increased when the volume fraction of EB increased from 0.11 up to 0.22. (Figs. 6 (b) and 7).



**Figure 7.** Upper and Lower Heights of Interface of SM-EB and Water Mixture, Vol. Frac. of SM = 0.11, Vol. Frac. of EB = 0.22, Mixing Rate = 132 RPM, Mixing Time = 5 min

## 5- Conclusions

The objective of this work was to study the batch separation of SM/EB and water mixtures. Several experiments were performed using different amounts of EB, SM, and water. It was shown that the required time for separation of EB and water was dramatically increased when the mixing rate was increased from 100 RPM up to 132 RPM. Further, experiments showed that the separation time of SM/W mixtures is much less than that for EB/W mixtures. It may be related to the molecular structures of EB and SM. EB has two more hydrogen than SM and it probably increases the hydrogen bond between EB and water and therefore, its solubility in water is more than that of SM. However, it was shown that the separation time of EB/SM/W mixtures were just a few minutes more than that of SM/W mixtures.

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