Title: PROCESSES FOR SEPARATION OF OIL/WATER EMULSIONS

Abstract: The present invention relates to a process for the separation of emulsions, such as oil/water emulsions. More particularly, the present invention is a process for separating oil/water emulsions that does not require the use of high temperatures or chemicals, such as demulsifiers. Somewhat more particularly, the invention comprises a continuous or batch process for separating oil/water emulsions which comprises the following general steps. An oil/water emulsion is mixed with an excess of water such that a water continuous phase is formed and maintained. The water and emulsion mixture is then allowed to settle, and the oil phase is recovered.
PROCESSES FOR SEPARATION OF OIL/WATER EMULSIONS

FIELD OF THE INVENTION

The invention relates generally to processes for the separation of emulsions, such as oil/water emulsions. More specifically, the invention relates to processes for the separation of oil/water emulsions from waste oils for the recovery of "clean" oil.

BACKGROUND OF THE INVENTION

Conventional techniques for separating emulsions include the use of high temperatures, pressure, gravity, chemicals, high shear, and sonic energy. For example, U.S. Patents No. 4,971,703 and 5,100,559 to Sealock, Jr. et al. disclose a method for separating petroleum oil and water emulsions by heating the emulsion to temperatures above about 200°C (360°F) under a pressure that is greater than the vapor pressure of water. The emulsion is maintained in this state for the period of time necessary to effect separation of the oil and water into three distinct phases. These phases are individually extracted from the container while maintaining the high temperature and pressure conditions employed in the separation process.

U.S. Patent No. 4,316,805 also uses heat to separate oil from an oil and water mixture. This process uses heat and gravity to effect separation. The process is enhanced by using
a hydrophobic wick to remove the oil as it separates from the emulsion.

Chemicals, such as extractants and demulsifiers, have also been used to separate oil from oil/water emulsions. U.S. Patent No. 4,895,641 to Briceno et al. discloses the use of a surfactant or alkali to desalt and separate oil from oil-in-water emulsions. U.S. Patent No. 4,292,277 to Bonny et al. and U.S. Patent No. 4,824,555 to Paspek et al. each disclose the use of an organic compound as an extractant. The Bonney et al. patent contacts an organic/water emulsion with an organic extractant in a multi-stage, co- or counter-current liquid-liquid extraction apparatus. The organic extractant pulls the organic compound from the emulsion into the extractant. The Paspek et al. patent discloses contacting an oil/water emulsion with a volatile solvent liquefied under pressure to form a two-phase system between the emulsion and the volatile solvent. The oil and liquefied solvent exchange places in the emulsion, resulting in a solvent/water emulsion and a separate oil layer. Some of the oil layer is then drawn from the container while it is still under pressure. The hydrocarbon solvent dissolved in the emulsion is vaporized by decreasing the system pressure, leaving separate water and oil layers.

Another method which has been used to separate oil/water emulsions is the use of high shear or turbulence to drive the oil from the mixture. For example, U.S. Patent No. 4,481,130 to Robertson uses a venturi tube or similar restriction-containing pipe in conjunction with a demulsifier to
separate the oil and water. The emulsion and demulsifier are mixed by the turbulence of the mixture created by the restriction in the tubes. This turbulent mixing enhances the action of the demulsifier to separate the oil and water in the emulsion. U.S. Patent No. 5,093,006 to Kalnins discloses the use of a hydrocyclone to separate the oil and water components. This device creates a vortex which separates the two components. The oil layer is drawn from an overflow valve in the hydrocyclone, and the water is withdrawn from an underflow valve for further processing, such as filtering to remove residual oil. U.S. Patent No. 4,816,165 to Carroll et al. also discloses the use of a cyclone for the separation of liquid-liquid mixtures. However, the Carroll et al. method traps a gas in the liquid-liquid mixture under pressure prior to passing the mixture into the cyclone. The pressure of the mixture is reduced during the vortexing process causing the gas to bubble from the mixture. This bubbling action aids in the separation of the two liquid components which are drawn from the cyclone at separate points based on their relative densities.

U.S. Patent No. 5,334,317 to Bannach Sichtermann et al. discloses a multiple step method for separating the organic component from organic/water emulsions. The emulsion is first washed in an aqueous solution to remove solid particles. The resulting organic-in-water mixture is then treated with an organic phase. The organic phase is miscible with the organic phase in the emulsion and immiscible with the aqueous phase of the emulsion. The organic phase is added in an amount that creates a phase inversion to produce a
water-in-organic emulsion. This mixture is then agitated to mechanically break the emulsion, followed by decanting to recover the separated organic and water phases.

U.S. Patent No. 5,538,628 to Logan discloses a device for the separation of components in an emulsion. This device provides intermittent sonic energy to a continuous flow of the emulsion. The device uses a flat plate oriented in the direction of flow that creates pressure fronts in the liquid to produce separation. U.S. Patent No. 4,483,695 to Covey, Jr. discloses an elongated vibrator for separating oil/water emulsions in large tanks. The process requires the introduction of gas into the emulsion. The vibrator is then used to agitate the emulsion and gas, resulting in a stratifying of the oil and water phases and the driving off of the gas from the mixture in the tank which aids separation.

Therefore, there is a need in the art for a simple process for the separation of oil/water emulsions which does not require the use of high temperatures or pressure to the emulsion. There is also a need in the art for a process for separating oil/water emulsions that does not require the addition of chemicals, such as demulsifiers, or the addition of gas to the emulsion. Further, there is a need for a separation process that does not require a high shear mechanism. Thus, there is a need in the art for a simple and efficient process for commercial scale separation of water from various waste oils in oil/water emulsions.
SUMMARY OF THE INVENTION

Stated generally, the present invention comprises a process for separating emulsions, such as oil/water emulsions. In one aspect, the present invention comprises a process for separating oil/water emulsions that does not require the use of high temperatures or pressure. In another aspect the invention comprises a process for separating oil/water emulsions that does not require the addition of gas or chemicals, such as demulsifiers, to the emulsion. In yet another aspect, the process of the present invention comprises mixing an oil/water emulsion with an amount of water that establishes and maintains a water continuous phase.

Stated somewhat more specifically, the invention comprises a process for separating oil/water emulsions which comprises the following general steps. An oil/water emulsion is mixed with an excess of water such that a water continuous phase is formed and maintained. The water and emulsion mixture is then allowed to settle, and the oil phase is recovered.

In one disclosed embodiment the process is performed in a continuous manner, while in another disclosed embodiment the process is performed as a batch process. When the process of the invention is performed in a continuous manner, it is advantageous to maintain the water continuous phase by adding water to the mixing apparatus during the mixing process. In a preferred embodiment, the additional water that is added to the mixing apparatus is provided by recycling the water phase recovered from the
settler. Although the process is advantageously performed without the addition of chemicals, it is possible to add chemicals, such as demulsifiers, to enhance separation of the water and oil.

5 BRIEF DESCRIPTION OF THE FIGURES

Figure 1 is a continuous phase schematic of one embodiment of the present invention.

DETAILED DESCRIPTION OF THE PREFERRED EMBODIMENTS

It should be understood to those well versed in the art of emulsion separation that the process of the present invention may have many variations, and that the disclosure of the preferred embodiments herein does not limit the scope of the invention.

The present invention comprises a process for the separation of emulsions. The process may be used to separate any emulsion in which the emulsion phase is water and the continuous or holding phase is an organic liquid that is not soluble in water. For convenience, the invention will be described in terms of separating oil/water emulsions. However, it should be understood that this is a preferred embodiment and that the invention is not limited to such emulsions.

The invention comprises a process for the separation of oil and water in oil/water emulsions. The oil/water emulsion may be from any source and is typically
some type of waste oil. For example, oils such as bunker oils, fuel oils, and other industrial oils may be used in the process of the present invention. Generally, the oil may contain from about 5 to about 60 volume percent water in the form of a water-in-oil emulsion. Preferably, the oil contains about 30 to about 50 volume percent water.

The process of the invention generally comprises the following steps. An oil/water emulsion is mixed with an excess of water such that a water continuous phase is formed and maintained. The water and emulsion mixture is then allowed to settle, and the oil phase is recovered.

More particularly, the process can be described as follows. Water is added to a mixing apparatus, and the mixing process is begun. An oil/water emulsion or both water and an oil/water emulsion are then added to the mixing apparatus in amounts that form and maintain a water continuous phase. The water continuous phase can be maintained by controlling the mixing conditions or by adding additional water to the mixing apparatus. The water and emulsion mixture is then allowed to settle, and the oil phase is recovered.

An important feature of the present process is the establishment and maintenance of a water continuous phase. It is possible to form the water and emulsion mixture, having a water continuous phase, by adding the reactants to the mixing apparatus in any order. However, it is easier and more advantageous to add the water to the mixing apparatus prior to addition of the oil/water emulsion. Also, while not
necessary, it is advantageous to start the mixing process before the oil/water emulsion is added to the water.

The water continuous phase can be created by mixing copious amounts of water with the oil/water emulsion. The exact amount of water needed to create and maintain the water continuous phase depends upon the particular type of oil contained in the emulsion and the water content of the emulsion. In general, amounts of water that are about two to four times the volume of the emulsion are sufficient to establish and maintain a water continuous phase throughout the mixing stage of the process.

The presence of a water continuous phase can be monitored in any conventional manner. In one embodiment of the present invention, the presence of a water continuous phase is monitored by monitoring the conductivity of the water and emulsion mixture in the mixing apparatus. The conductivity of the mixture can be monitored, for example, by placing an electrode in the mixture.

Water is a conductive liquid, while oil is generally nonconductive. Therefore, when the electrode indicates that the mixture in the mixing apparatus is conducting, a water continuous phase is present. When the electrode indicates that the mixture is nonconductive, a water continuous phase is no longer present.
The water and emulsion mixture is mixed for a period of approximately 90 seconds to approximately 1 hour. The preferred mixing duration is about 15 minutes.

After the water and emulsion are thoroughly mixed, the mixture is allowed to settle until a substantial layer of dry oil is present in the settler. In general, settling periods of between approximately 15 minutes and approximately 1 hour are sufficient to separate the oil from the water and emulsion mixture. After settling, at least two phases will be discernible: a water phase and an oil phase. The water phase may contain a portion of the solids originally present in the oil/water emulsion and small amounts of residual oil. The oil phase will contain “clean” oil. “Clean” oil is oil from which the majority of water has been removed.

The “clean” oil is then recovered. The “clean” oil may be recovered from the settler by any conventional method, such as overflow, skimming, or decanting. Optionally, the “clean” oil may be subjected to further purification processes. Such processing may include, for example, distillation.

The water phase may be discarded or may be recycled to the mixing apparatus to form the water continuous phase. When the water phase is recycled to the mixing apparatus, it may preferably be processed prior to recycle to remove suspended solids and residual oil. Residual oil can be removed by subjecting the water phase to a conventional oil/water separator. Other components can be removed by any conventional means, for example, by filtration,
ultrafiltration, or cartridge filtration. It is preferable to subject the water phase to a conventional oil/water separator prior to filtration to remove the other suspended components. The water phase may also be heated prior to recycling it to the mixing apparatus to increase the fluidity of the oil and thereby enhance the mixing process. Preferred heating temperatures are those below 150°F, for example, temperatures from about 120°F to about 150°F.

The process of the present invention may be performed as either a continuous process or a batch process. In one embodiment, the process of the present invention may be performed as a continuous process. For example, water may be fed into the mixing apparatus through an inlet tube. The water is optionally heated to increase the fluidity of the oil and thereby enhance the mixing process. Preferred heating temperatures are those below 150°F, for example, temperatures from about 120°F to about 150°F. The mixing process is begun, and then water and the oil/water emulsion are both fed into the mixing apparatus. The water and the emulsion are fed into the mixing apparatus at rates which form and maintain a water continuous phase. In general, flow rates which provide a 2:1 or higher ratio of water:emulsion in the mixing apparatus will be sufficient to maintain a water continuous phase. The mixing chamber is designed to provide a residence time of about 90 seconds to 1 hour, preferably 15 minutes.

The water and emulsion mixture are then passed from the mixing apparatus to the settler. Although the mixture
can be passed by any means, it is advantageous to allow the mixture to overflow the mixing apparatus and flow into the settler through an inlet tube. Any container may be used for settling of the mixture. The particular design of the settling container will depend upon the desired settling time for the water and emulsion mixture. For example, containers having a large surface area will result in more expedient separation of the mixture, while containers having a smaller surface area will result in a slower rate of separation. Preferred settling times are between about 15 minutes and 1 hour.

The “clean” oil which is separated from the mixture may be recovered by any method. Preferably, the “clean” oil is recovered by allowing it to overflow the settler and be collected through an outlet tube. The separated water phase may also be collected from the settler by any means. Preferably the water phase is drawn from the settler by means of an outlet tube. The water phase may be passed directly from the settler to the mixing apparatus to provide water for the water continuous phase in the mixing process. Alternatively, the water phase may be passed through an oil/water separator and filters to remove residual oil and solids before it is recycled to the mixing apparatus. While recycle of the water phase is preferred, the water phase may also be discarded.

Figure 1 is a schematic of one possible continuous system for the practice of the present invention. In this embodiment, wet oil is fed into a mixing tank (1) that contains
a mixer. The mixer can be positioned either at the side of the mixing tank, as indicated in the Figure, or overhead. Water is initially added to the mixer at a rate that forms and maintains a water continuous phase and is mixed with the wet oil via the mixer. This mixture is then passed to a settling zone or tank (2) and allowed to settle. The good or "clean" oil is then collected in a recovery tank (3). The water separated from settling tank (2) is recirculated to mixer (1) via a water recirculation pump (4).

In another embodiment, the process of the present invention may be performed as a batch process. For example, water is added to the mixing chamber of the mixing apparatus and optionally heated to increase the fluidity of the oil and thereby enhance the mixing process. Preferred heating temperatures are those below 150°F, for example, temperatures from about 120°F to about 150°F. Then, the mixing process is begun, and the oil/water emulsion is added to the mixing chamber in an amount which forms and maintains a water continuous phase. Amounts which result in about a 2:1 ratio of water:emulsion are sufficient to maintain the water continuous phase. The emulsion may be added to the mixing chamber by any means. The water and emulsion are mixed for a period sufficient to form droplets of the emulsion in the water. In general, mixing times of between about 90 seconds and 1 hour are sufficient, with a mixing time of 15 minutes being preferred.
Once the water and emulsion are mixed, the mixture is allowed to settle. In one embodiment, the mixer may simply be stopped, and the water and emulsion mixture allowed to settle in the mixing apparatus. In another embodiment, the mixture may be transferred to a separate settling container. The mixture can be transferred by any means, but is preferably transferred by means of an outlet on the mixing apparatus which is connected to an inlet on the settler. Use of a separate settling container is preferred so that additional emulsion may be mixed with water in the mixing apparatus while the mixture is settled.

After settling, the oil may be recovered by any method. For example, if the oil phase separates on top of the water phase, the oil may be decanted, skimmed, or allowed to overflow from the top of the water phase. Alternatively, the water phase may be removed from the settler via an outlet valve, leaving the “clean” oil in the settler tank for recovery. Where the water phase separates on top of the oil phase, the oil phase may be removed from the settler via an outlet valve.

While the process of the present invention can advantageously be performed in the absence of additional chemicals, such as demulsifiers, the present invention encompasses the optional use of such additional chemicals. For example, demulsifiers can be used in the present invention to reduce the viscosity of the oil, which enhances the mixing process. Any demulsifier can be used in the present invention,
including conventional demulsifiers or those which may be developed in the future.

Another important feature of the present invention is the nature of the mixing process. The mixing apparatus should be designed to provide a low speed, low shear mixing. Low shear mixing provides the ability to control and maintain a water continuous phase during the mixing process. Mixing methods which produce high shear mixing, such as venturi tubes and hydrocyclones, are not suitable for the present invention because they create continuous turbulence. While the turbulence allows for mixing of the oil/water emulsion with other components, the turbulence hinders control of the continuous phase. Mixers that use a high shear to mix the oil/water emulsion, thus, make it difficult if not impossible to maintain a water continuous phase during the mixing process.

The design of the mixing apparatus should be such that it imparts enough energy to allow the dropwise formation of the emulsion in the water continuous phase. This can be accomplished, for example, by varying the type of mixing blade and the speed of the mixer. Where the oil/water emulsion has a low viscosity, a blade type and speed are selected to provide a low shear rate. Where the oil/water emulsion has a high viscosity, the blade type and speed are selected to create a higher shear rate. However, in any case, the shear rate is not so high as to produce turbulence in the mixture which would be detrimental to the formation and maintenance of a water continuous phase.
This invention is further illustrated by the following examples, which are not to be construed in any way as imposing limitations upon the scope thereof. To the contrary, it is to be clearly understood that resort may be had to various other embodiments, modifications, and equivalents thereof which, after reading the description herein, may suggest themselves to those skilled in the art without departing from the spirit of the present invention and/or the scope of the appended claims.

EXAMPLES

Example 1

Water (2 L) was placed in a mixing chamber and heated to 150°F. Water and an emulsion of #6 bunker oil, containing 50% oil, 48% water, and 2% solids, were then fed into the mixing chamber. The water was passed into the mixer at a rate of 12 L/h, while the emulsion was passed into the mixer at a rate of 6 L/h. The mixture was allowed to overflow the mixing chamber and pass into a settling tank. The water and emulsion mixture separated as it passed through the settling tank. The retention time for the mixture in the settling tank was about 1 hour. The "clean" oil was then allowed to overflow the settling tank and recovered. Samples were taken from the "clean" oil effluent at 1 hour intervals for a total time period of five hours and analyzed for water and solids content. The "clean" oil contained 3% water and 0.8% solids. As seen in Table 1, these results were stable over time.
Example 2

Water (2 L) was placed in a mixing chamber and heated to 150°F. Water and an emulsion of #6 bunker oil, containing 50% oil, 48% water, and 2% solids, were then fed into the mixing chamber. The water was passed into the mixer at a rate of 6.6 L/h, while the emulsion was passed into the mixer at a rate of 6.0 L/h. The mixture was allowed to overflow the mixing chamber and pass into a settling tank. The water and emulsion mixture separated as it passed through the settling tank. The retention time for the mixture in the settling tank was about 1 hour. The "clean" oil was then allowed to overflow the settling tank and recovered. Samples were taken from the "clean" oil effluent at 1 hour intervals for a total time period of five hours and analyzed for water and solids content. The "clean" oil contained 2.4% water and 0.2% solids.

The above examples are intended to be demonstrative, rather than limiting, of the embodiments contemplated by the invention and encompassed within the scope of the claims.
We Claim:

1. A process for the separation of oil and water in an oil/water emulsion comprising the steps of
   (1) adding water to a mixing apparatus;
   (2) adding an oil/water emulsion or both water and an oil/water emulsion to the mixing apparatus, wherein the water and oil/water emulsion are present in amounts that form a water continuous phase containing the emulsion;
   (3) mixing the water and emulsion while maintaining a water continuous phase;
   (4) allowing the water and oil/water emulsion to settle to form "clean" oil and a water phase;
   (5) recovering the "clean" oil; and
   (6) optionally recycling the water phase to the mixing apparatus.

2. The process of Claim 1 wherein the process is performed in a continuous manner.

3. The process of Claim 1 wherein the process is performed as a batch process.

4. The process of Claim 3 wherein the water and emulsion mixture is allowed to settle in the mixing apparatus.
5. The process of Claim 3 wherein the water and emulsion mixture is passed to a separate settling apparatus.

6. The process of Claim 1 wherein the water phase is recycled to the mixing apparatus.

7. The process of Claim 6 wherein the water phase is processed to remove solids prior to being recycled to the mixing apparatus.

8. The process of Claim 6 wherein the water phase is processed to remove residual oil prior to being recycled to the mixing apparatus.

9. The process of Claim 6 wherein the water phase is heated prior to being recycled to the mixing apparatus.

10. The process of Claim 9 wherein the water phase is heated to a temperature between about 120°F and about 150°F.

11. The process of Claim 1 wherein the water continuous phase is maintained by the addition of water to the mixer.

12. The process of Claim 1 wherein the water added to the mixing apparatus in (1) is heated.
13. The process of Claim 12 wherein the water is heated to a temperature between 120°F and 150°F.

14. The process of Claim 1 wherein a demulsifier is added to the water and emulsion mixture in the mixing apparatus.

15. The process of Claim 1 wherein the water and emulsion are mixed for a period of time between approximately 90 seconds and approximately 1 hour.

16. The process of Claim 15 wherein the water and emulsion are mixed for a approximately 15 minutes.

17. The process of Claim 1 wherein the water and emulsion mixture is allowed to settle for a period of time between approximately 15 minutes and approximately 1 hour.

18. The process of Claim 1 wherein the source of the oil/water emulsion is selected from the group consisting of bunker oils, fuel oils, and industrial oils.

19. The process of Claim 1 wherein the mixing apparatus imparts enough energy to allow dropwise formation of the emulsion in the water continuous phase.